Sublimation pressure and sublimation enthalpy of H$_2$O ice Ih between 0 and 273.16 K

Rainer Feistel a,*, Wolfgang Wagner b

a Leibniz-Institut für Ostseeforschung, D-18119 Warnemünde, Germany
b Lehrstuhl für Thermodynamik, Ruhr-Universität Bochum, D-44780 Bochum, Germany

Received 22 June 2006; accepted in revised form 28 August 2006

Abstract

The sublimation of water in the region of extremely low pressures and temperatures meets increasing interest for the exploration of icy cosmic bodies. At temperatures below 130 K, the shape of the sublimation curve of H$_2$O is not known; neither experimental data nor theoretical treatments exist for this region. Based upon theoretical upper and lower bounds for the heat capacity of water vapor in this range, a narrow region in the pressure–temperature diagram is identified which must necessarily enclose the sublimation curve down to virtually any lower pressures and temperatures. Within this region, an approximate sublimation curve is computed from the 2006 Gibbs potential of ice Ih, using available heat capacity data points of water vapor between 10 and 130 K. The theoretical zero-point limiting law of the sublimation pressure is derived. Valid between 20 and 273.16 K, correlation equations for the sublimation enthalpy and the sublimation pressure are fitted to the computed data. All quantities are expressed in the 1990 temperature scale ITS-90. Under cosmic conditions, our results suggest that the sublimation of ice is unlikely below 50 K and impossible below 23 K.

1. Introduction

In the Cosmos, water is one of the most fundamental geochemical substances. The interest in its sublimation behavior at extremely low pressures and temperatures is growing, e.g. for understanding the stability of comets, the stability of ice on planetary surfaces, and the exploration of icy bodies in the solar system with impacting probes (Whipple and Huebner, 1976; Weissman, 1980; Blake et al., 1999; Treffer et al., 2006). Even though temperatures below 130 K are certainly encountered in deep space and on the distant planets and moons, the sublimation of ice at these low temperatures is not sufficiently well known.

Several experimental (Douslin and Osborn, 1965; Jancso et al., 1970; Bryson et al., 1974; Marti and Mauersberger, 1993; Mauersberger and Krankowsky, 2003) and theoretical works (Wexler, 1977; Hyland and Wexler, 1983; Wagner et al., 1994; Murphy and Koop, 2005) were published in the past about the shape of the sublimation curve of water. Since a comprehensive Gibbs energy function for hexagonal ice has recently become available, a new, consistent and very accurate way to determine the sublimation properties became possible by equating the chemical potentials of ice (Feistel and Wagner, 2005, 2006) and of water vapor given by the IAPWS-95 formulation (Wagner and Prüß, 2002). This method is limited, however, by the range of validity of the IAPWS-95 formulation, because the IAPWS-95 heat capacity of water vapor is undefined for temperatures below 130 K. As well, experimental sublimation pressure data are only available above 130 K, or 12 nPa (Murphy and Koop, 2005), being properly described by the IAPWS-95 formulation in conjunction with the 2006 Gibbs function of ice. The latter itself was determined using only sublimation data at pressures above 100 Pa, and thus extrapolates very well over all these 10 orders of magnitude in pressure. We assume its validity down to even lower pressures, especially because of its minor pressure dependence in this region.
Quantum theory predicts (Landau and Lifschitz, 1966) the specific isobaric heat capacity \( c_p \) of an ideal gas to decrease monotonously and exponentially with falling temperature, due to the subsequent disappearance of excited molecular rotational and vibrational quantum states (i.e., degrees of freedom). Finally, in the zero-temperature limit only the three translational contributions remain, and the specific heat capacity converges to \( c_v(T = 0) = 3R/2 \), \( R \) being the specific gas constant of water. Thus, even if we do not know the exact shape of the function \( c_v(T) \) of water vapor, we do know its upper and lower bounds in the region of interest.

In Section 2, we investigate how sensitively computed sublimation temperatures for \( T < 130 \) K may depend on this uncertainty of vapor heat capacity. In Section 3, we exploit the heat capacity data of Woolley (1980) to provide even narrower limits for the sublimation pressure region, applying the method of the previous section to the intervals between subsequent data points. By linear interpolation of \( c_p \) between those points, we obtain an approximate sublimation curve, together with its uncertainty due to the interpolation method chosen, for the pressure range between 10 nPa and \( 10^{-250} \) Pa, corresponding to the sublimation temperature range from 130 and 10 K. In Section 4, we derive the theoretical limiting law of sublimation pressure close to 0 K. Using additionally the structure of the Clausius–Clapeyron law at the triple point, we fit suitable correlation equations for the sublimation enthalpy and the sublimation pressure in the range 20–273.16 K representing the data computed before. In Section 5, we estimate the uncertainties of the sublimation pressure and the sublimation enthalpy provided in this paper.

At a vapor pressure of \( P = 10^{-100} \) Pa, corresponding to about \( T = 23 \) K sublimation temperature, the ideal gas volume per water molecule is \( V/N = kT/P = 3 \times 10^{78} \) m\(^3\), which is about the volume of the entire universe with its present radius of \( 14 \times 10^9 \) light-years = \( 1.3 \times 10^{26} \) m \((k = 1.38 \times 10^{-23} \) J K\(^{-1}\) is Boltzmann’s constant). It is physically evident that only sublimation pressures much higher than \( 10^{-100} \) Pa can be observed in nature. In practice, a more realistic lowest pressure limit, e.g. for extreme interstellar vacua, may be in the order of \( 10^{-40} \) Pa, corresponding to a sublimation temperature of about 50 K. Hence, the sublimation of icy cosmic bodies, which are in thermal radiation equilibrium with the 3 K background photon gas, is practically inhibited, and rather precipitation will occur. Mathematically, the thermodynamic formulae permit the computation of physically fictitious values. In this sense, the sublimation pressure equation studied here in the lowest temperature range is mainly of theoretical interest for the construction of the correlation equations.

### 2. Sublimation temperature region

If a specific Gibbs energy function \( g(T, P) \) is known at some temperature-pressure reference point \((T_n, P_n)\), it can be extended into the surrounding \((T, P)\) space region by the path integral

\[
g(T, P) = g(T_n, P_n) + \int_{P_n}^{P} v(T_n, P') dP' - \int_{T_n}^{T} s(T', P) dT'.
\]

Expressing the specific volume \( v \) by the ideal gas equation, and the specific entropy \( s \) by a temperature integral of specific isobaric heat capacity \( c_p \), we obtain for the Gibbs function of low-density vapor after partial integration

\[
g(T, P) = g(T_n, P_n) + (T_n - T) \cdot s(T_n, P_n) + R \ln \frac{P}{P_n} + \int_{T_n}^{T} \left( 1 - \frac{T}{T'} \right) c_p(T') dT'.
\]

To derive (2.2), we have made use of the ideal gas equation e.g. in form of the identity

\[
s(T, P) - s(T_n, P_n) = \int_{P_n}^{P} \left( \frac{\partial s}{\partial P} \right)_T dP' - \int_{P_n}^{P} \left( \frac{\partial s}{\partial T} \right)_P dP' = -R \ln \frac{P}{P_n}.
\]

The specific gas constant of water is denoted here by \( R = 461.52364 \) J kg\(^{-1}\) K\(^{-1}\) (Feistel and Wagner, 2006). The isobaric heat capacity of an ideal gas is known to be independent of pressure, which is evident from the Maxwell relation \( \frac{\partial s}{\partial T} = -\frac{1}{\gamma} \left( \frac{\partial^2 p}{\partial T^2} \right)_T = \frac{(\gamma - 1)}{\gamma} \frac{\partial p}{\partial T} \).

Considering in the following only temperatures \( T \leq T_n \), and specifying for the unknown heat capacity function \( c_p(T) \) certain lower and upper bounds, \( c_A, c_B \) by

\[
0 < c_A(T) \leq c_p(T) \leq c_B(T),
\]

we infer the validity of the inequalities

\[
\int_{T_n}^{T} \left( 1 - \frac{T}{T'} \right) \left( c_p(T') - c_A(T') \right) dT' \leq 0
\]

and

\[
\int_{T_n}^{T} \left( 1 - \frac{T}{T'} \right) \left( c_B(T') - c_p(T') \right) dT' \leq 0.
\]

We now define suitable bounding Gibbs functions \( g_A, g_B \) of vapor by

\[
g_{A,B}(T, P) = g(T_n, P_n) + (T_n - T) \cdot s(T_n, P_n) + RT \ln \frac{P}{P_n} + \int_{T_n}^{T} \left( 1 - \frac{T}{T'} \right) c_{A,B}(T) dT'.
\]

Then it follows from the relations (2.2) and (2.4) that the unknown, true Gibbs function \( g \) must lie in the interval

\[
g_A(T, P) \geq g(T, P) \geq g_B(T, P),
\]

At given pressure \( P \), the intersection points of these three Gibbs functions with the Gibbs function of ice Ih, \( g_{\text{Ih}}(T, P) \), define the true and two approximate sublimation temperatures, which we denote by \( T_{\text{subl}}, T_A \) and \( T_B \):

\[
g_A(T, P) = g_{\text{Ih}}(T, P),
\]

\[
g_A(T, P) = g_{\text{Ih}}(T, P),
\]

\[
g_A(T, P) = g_{\text{Ih}}(T, P).
\]
\[ g(T_{\text{sub}}, P) = g^h(T_{\text{sub}}, P), \quad (2.8) \]
\[ g_b(T_b, P) = g^h_b(T_b, P). \quad (2.9) \]

For the intended proof that the unknown value of \( T_{\text{sub}} \) is confined to the interval \((T_A, T_B)\), we suppose the sublimation curve to exceed the ice entropy in the vicinity of the sublimation curve, i.e.

\[ s(T, P) - s^h_b(T, P) > 0. \quad (2.10) \]

Integrating this inequality between any two temperatures \( a \) and \( b \), regarding \( s = -\left(\frac{\partial g}{\partial T}\right)_P \) and \((b - a)dT \geq 0\), we find the condition

\[ (b - a) \int_a^b \left( \frac{\partial g}{\partial T} \right)_P - \left( \frac{\partial g^h_b}{\partial T} \right)_P \right) dT \leq 0. \quad (2.11) \]

We apply this integral to both the intervals \((T_A, T_{\text{sub}})\) and \((T_{\text{sub}}, T_B)\) and obtain, using the definitions (2.7)–(2.9),

\[ \begin{align*}
(T_A - T_{\text{sub}})[g_A(T, P) - g(T, P)] & \geq 0 \\
(T_{\text{sub}} - T_B)[g_B(T, P) - g(T, P)] & \geq 0.
\end{align*} \quad (2.12) \]

Together with (2.6), we can conclude now from (2.12) the desired condition for the three sublimation-related temperatures,

\[ T_A \geq T_{\text{sub}} \geq T_B. \quad (2.13) \]

Thus, we have shown that the computation of sublimation temperatures by means of the approximate Gibbs functions for vapor, \( g_A, g_B \) from Eq. (2.5), results in temperatures \( T_A \) and \( T_B \) which constitute upper and lower bounds for the true sublimation temperature, \( T_{\text{sub}} \). The situation is displayed graphically in Fig. 1 for the pressure \( P = 10^{-14} \) Pa and the bounds \( c_A = 1.5R \) and \( c_B = 4R \); it remains qualitatively the same for the entire sublimation region.

For the actual computation of the limiting Gibbs functions of vapor, Eq. (2.5), we use the specific gas constant of water, \( R = 461.52364 \) J kg\(^{-1}\) K\(^{-1}\) (Feistel and Wagner, 2006), and as the lower bound of the specific heat capacity its theoretical zero-temperature value, \( c_A = 1.5R \). We place the reference point \((T_n, P_n)\) at the ending point of the sublimation curve of Feistel and Wagner (2006) at \( T_n = 130 \) K, \( P_n = 12.00376 \) nPa. Using the IAPWS-95 formulation (Wagner and Prüß, 2002) for vapor, the reference point properties are computed as \( g(T_n, P_n) = -254588.9 \) J kg\(^{-1}\) and \( s(T_n, P_n) = 19160.636 \) J kg\(^{-1}\) K\(^{-1}\). The assumed upper bound of heat capacity is chosen as the asymptotic lower limit of \( c_P \) in the IAPWS-95 formulation, \( c_B = 4.00709R \). The Gibbs function of ice is taken from Feistel and Wagner (2006).

The computed sublimation temperature bounds \( T_A \geq T_B \) after Eqs. (2.7) and (2.9) are displayed in Fig. 2 and listed in Table 1.

For practical application as a sublimation temperature, \( T_{\text{sub}}(P) \approx T_A(P) \) may be used, since this upper bound curve for the real sublimation temperature asymptotically coincides with the true values in both limits for \( T \to 130 \) K and \( T \to 0 \) K. In the intermediate range, it slightly overestimates the real value. The corresponding figures are listed in Table 1, together with the maximum possible deviation \( \Delta T = T_A(P) - T_B(P) \) due to the physical bounds of vapor heat capacity.

In the next section, these uncertainties will be further reduced using heat capacity data points of water vapor below 130 K.

3. Sublimation curve

Woolley (1980) published heat capacity data of water vapor between 10 and 2000 K. Between 130 and 2000 K, these values are represented by an analytical expression developed by Cooper (1982) which became part of the IAPWS-95 formulation for water vapor, and was used by Feistel and Wagner (2006) for the computation of the sublimation curve, in conjunction with a new equation of state for ice Ih. Due to the lack of an accurate formula for \( c_P \) below 130 K, a corresponding continuation of the sublimation curve was not possible.

Woolley’s (1980) heat capacity data for the low-temperature range are given in Table 2. These data were theoretically derived from infrared spectra of vapor, and therefore do not require any temperature scale conversion. The more recent data from Vidler and Tennyson (2000) with an accuracy of 20 ppm are not immediately usable for the sublimation problem at very low temperatures because of their very wide spacing in \( T \). For this reason and for consistency with the IAPWS-95 formulation, we used Woolley’s data.

We consider three simple, different approximations of the unknown function \( c_p(T) \), all of them consistent with Woolley’s heat capacity data, as shown in Fig. 3. First, the lower-bound function, Fig. 4.
second, the upper-bound function,
\[ c_B(T) = c_{i+1} \quad \text{if} \quad T_i < T \leq T_{i+1}, \]

and finally, a medium-value function, obtained by linear interpolation between the table entries,
\[ c_M(T) = p_i + q_i T \quad \text{if} \quad T_i \leq T \leq T_{i+1}, \]

with the coefficients
\[
p_i = \frac{c_i \cdot T_{i+1} - c_{i+1} \cdot T_i}{T_{i+1} - T_i}, \quad q_i = \frac{c_{i+1} - c_i}{T_{i+1} - T_i}.\]

We use the medium function \( c_M(T) \) as a suitable approximation for the computation of the best sublimation pressure curve available, while the other two will provide the limits in between which all physically valid curves must lie.

The given interval \( \Delta T = T_A(P) - T_B(P) \) is the range for the true temperature, \( T_{\text{subl}}(P) \), which is located in the interval \( T_B(P) \leq T_{\text{subl}}(P) \leq T_A(P) \) with respect to the physically possible values for the heat capacity of vapor.

Below \( T_{13} = 130 \text{ K} \), the sublimation pressure is smaller than \( 10^{-8} \text{ Pa} \), which is less than the normal pressure by a factor of \( 10^{-13} \). Under these conditions, the Gibbs function of ice, \( g_{\text{Ih}}(T, P) \), is practically independent of pressure,
\[ g_{\text{Ih}}(T, P) \approx g_{\text{Ih}}(T, 0). \]

Then, we can analytically solve the phase equilibrium Eqs. (2.7)–(2.9),

<table>
<thead>
<tr>
<th>log(P/Pa)</th>
<th>( T_A ) (K)</th>
<th>( \Delta T ) (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-8</td>
<td>129.49</td>
<td>0.00</td>
</tr>
<tr>
<td>-9</td>
<td>123.42</td>
<td>0.01</td>
</tr>
<tr>
<td>-10</td>
<td>117.90</td>
<td>0.03</td>
</tr>
<tr>
<td>-11</td>
<td>112.83</td>
<td>0.06</td>
</tr>
<tr>
<td>-12</td>
<td>108.22</td>
<td>0.09</td>
</tr>
<tr>
<td>-13</td>
<td>103.96</td>
<td>0.12</td>
</tr>
<tr>
<td>-14</td>
<td>100.02</td>
<td>0.16</td>
</tr>
<tr>
<td>-15</td>
<td>96.37</td>
<td>0.19</td>
</tr>
<tr>
<td>-16</td>
<td>92.98</td>
<td>0.23</td>
</tr>
<tr>
<td>-17</td>
<td>89.81</td>
<td>0.26</td>
</tr>
<tr>
<td>-18</td>
<td>86.86</td>
<td>0.29</td>
</tr>
<tr>
<td>-19</td>
<td>84.10</td>
<td>0.33</td>
</tr>
<tr>
<td>-20</td>
<td>81.50</td>
<td>0.36</td>
</tr>
<tr>
<td>-21</td>
<td>79.06</td>
<td>0.38</td>
</tr>
<tr>
<td>-22</td>
<td>76.76</td>
<td>0.41</td>
</tr>
<tr>
<td>-23</td>
<td>74.60</td>
<td>0.44</td>
</tr>
<tr>
<td>-24</td>
<td>72.55</td>
<td>0.46</td>
</tr>
<tr>
<td>-25</td>
<td>70.61</td>
<td>0.48</td>
</tr>
<tr>
<td>-26</td>
<td>68.77</td>
<td>0.50</td>
</tr>
<tr>
<td>-27</td>
<td>67.03</td>
<td>0.52</td>
</tr>
<tr>
<td>-28</td>
<td>65.37</td>
<td>0.54</td>
</tr>
<tr>
<td>-29</td>
<td>63.79</td>
<td>0.56</td>
</tr>
<tr>
<td>-30</td>
<td>62.28</td>
<td>0.57</td>
</tr>
<tr>
<td>-40</td>
<td>50.39</td>
<td>0.67</td>
</tr>
<tr>
<td>-50</td>
<td>42.31</td>
<td>0.71</td>
</tr>
<tr>
<td>-60</td>
<td>36.46</td>
<td>0.72</td>
</tr>
<tr>
<td>-70</td>
<td>32.02</td>
<td>0.71</td>
</tr>
<tr>
<td>-80</td>
<td>28.55</td>
<td>0.70</td>
</tr>
<tr>
<td>-90</td>
<td>25.76</td>
<td>0.68</td>
</tr>
<tr>
<td>-100</td>
<td>23.46</td>
<td>0.65</td>
</tr>
<tr>
<td>-110</td>
<td>21.54</td>
<td>0.63</td>
</tr>
<tr>
<td>-120</td>
<td>19.90</td>
<td>0.61</td>
</tr>
<tr>
<td>-130</td>
<td>18.50</td>
<td>0.59</td>
</tr>
<tr>
<td>-140</td>
<td>17.28</td>
<td>0.57</td>
</tr>
<tr>
<td>-150</td>
<td>16.22</td>
<td>0.54</td>
</tr>
<tr>
<td>-160</td>
<td>15.27</td>
<td>0.53</td>
</tr>
<tr>
<td>-170</td>
<td>14.43</td>
<td>0.51</td>
</tr>
<tr>
<td>-180</td>
<td>13.68</td>
<td>0.49</td>
</tr>
<tr>
<td>-190</td>
<td>13.00</td>
<td>0.47</td>
</tr>
<tr>
<td>-200</td>
<td>12.39</td>
<td>0.46</td>
</tr>
<tr>
<td>-210</td>
<td>11.83</td>
<td>0.45</td>
</tr>
<tr>
<td>-220</td>
<td>11.32</td>
<td>0.43</td>
</tr>
<tr>
<td>-230</td>
<td>10.85</td>
<td>0.42</td>
</tr>
<tr>
<td>-240</td>
<td>10.42</td>
<td>0.41</td>
</tr>
<tr>
<td>-250</td>
<td>10.02</td>
<td>0.40</td>
</tr>
<tr>
<td>-260</td>
<td>9.65</td>
<td>0.38</td>
</tr>
</tbody>
</table>
Table 2
Specific isobaric heat capacity data \( c_i \) of water vapor at temperatures \( T_i \) from 10 to 130 K from Woolley (1980)

<table>
<thead>
<tr>
<th>( i )</th>
<th>( T_i ) (K)</th>
<th>( c_i/R )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>100</td>
<td>4.005</td>
</tr>
<tr>
<td>11</td>
<td>90</td>
<td>4.006</td>
</tr>
<tr>
<td>10</td>
<td>80</td>
<td>4.006</td>
</tr>
<tr>
<td>9</td>
<td>70</td>
<td>4.007</td>
</tr>
<tr>
<td>8</td>
<td>60</td>
<td>4.006</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>4.006</td>
</tr>
<tr>
<td>6</td>
<td>40</td>
<td>4.006</td>
</tr>
<tr>
<td>5</td>
<td>30</td>
<td>4.006</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>4.006</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>4.006</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>4.006</td>
</tr>
</tbody>
</table>

Fig. 3. Specific isobaric heat capacity of vapor between 10 and 130 K. A, lower bound \( c_\ell(T) \), Eq. (3.1); B, upper bound \( c_u(T) \), Eq. (3.2); M, interpolated \( c_\ell(T) \), Eq. (3.3). At the data points from Woolley (1980), Table 2, all three functions coincide.

Assuming \( T \) to be within the interval \( T_{k-1} < T \leq T_k \), we get for the three excess Gibbs energies the sums

\[
\Delta g_{\text{A,M,B}}(T) = g_{13} + (T_{13} - T) \cdot s_{13} - g_{\text{in}}(T, 0)
\]

\[
= \sum_{i=13}^{k+1} \int_{T_i}^{T_{i+1}} \left( 1 - \frac{T}{T_i} \right) \cdot c_{\text{A,M,B}}(T') \, dT' - g_{\text{in}}(T, 0)
\]

and find eventually upon integration

\[
\Delta g_{\text{A}}(T) = g_{13} + (T_{13} - T) \cdot s_{13} - g_{\text{in}}(T, 0)
\]

\[
+ \sum_{i=13}^{k+1} c_{i-1} \left[ T_{i-1} - T_i + T \ln \frac{T_i}{T_{i-1}} \right]
\]

\[
\Delta g_{\text{B}}(T) = g_{13} + (T_{13} - T) \cdot s_{13} - g_{\text{in}}(T, 0)
\]

\[
+ \sum_{i=13}^{k+1} c_i \left[ T_{i-1} - T_i + T \ln \frac{T_i}{T_{i-1}} \right]
\]

\[
\Delta g_{\text{M}}(T) = g_{13} + (T_{13} - T) \cdot s_{13} - g_{\text{in}}(T, 0)
\]

\[
+ \sum_{i=13}^{k+1} \left[ p_{i-1} \left( T_{i-1} - T_i + T \ln \frac{T_i}{T_{i-1}} \right) \right]
\]

\[
\frac{q_{k-1}}{2} (T_{k-1} - T_k) \left( T_{k-1} - T_k - 2T_k \right)
\]

\[
+ p_{k-1} \left( T - T_k + T \ln \frac{T_k}{T} \right) - \frac{q_{k-1}}{2} (T^2 - T_k^2)
\]

The corresponding solutions of Eq. (3.6) are listed in Table 3.
4. Correlation equations

For temperatures \( T \) sufficiently close to the zero point, the specific heat capacity of vapor is \( c_p(T) = c_r(T) = 3R/2 \) due to the translational degrees of freedom, before first rotational-quantum states become excited at higher temperatures (Landau and Lifschitz, 1966; Flaud and Camy-Peyret, 1973). In order to carry out the limit \( T \to 0 \), we can formally introduce into (3.7) a very small but finite temperature \( T_0 > 0 \) subject to the condition \( c_p(T_0) = 3R/2 \), yielding

\[
\Delta g(T) = g_{13} + (T_{13} - T) \cdot s_{13} - g^\text{th}(T, 0)
\]

\[
+ \int_{T_0}^T c_p(T') \, dT' + \frac{3}{2} R \int_{T_0}^T dT' - T \int_{T_0}^T c_p(T') \frac{dT'}{T'} - \frac{3}{2} RT \int_{T_0}^T \frac{dT'}{T'}.
\]

Expanding into a power series with respect to temperature and neglecting higher powers of \( T \), we get

\[
\Delta g(T) = g_{13} + T_{13} \cdot s_{13} - g^\text{th}(0, 0) - \frac{3}{2} RT \ln T
\]

\[
+ \int_{T_0}^T c_p(T') \, dT' + O(T).
\]

We obtain from Eqs. (4.2) and (3.6) the low-temperature limiting law of sublimation pressure,

\[
\ln P_{\text{sub}}(T) = -\frac{\Delta h_0}{RT} + \frac{3}{2} \ln T + O(T^0),
\]

with the zero-point sublimation enthalpy \( \Delta h_0 \) defined as

\[
\Delta h_0 = g_{13} + T_{13} \cdot s_{13} + \int_{T_0}^T c_p(T') \, dT' - g^\text{th}(0, 0).
\]
The approximate Clausius–Clapeyron sublimation law at the triple point \((T_t, P_t)\) reads (Feistel and Wagner, 2006),

\[
P_{\text{subl}}^{\text{CC}}(T) = \frac{P_t}{C_1} \exp \left( \frac{D_h(T_t)}{R \left( \frac{T}{T_t} - 1 \right)} \right).
\]

The sublimation enthalpy \(D_h(T)\) is an only weakly varying function of temperature (Table 4, Fig. 5). Moreover, the logarithmic sublimation pressure curve is an almost linear function of reciprocal temperature, Fig. 2. Thus, comparing the asymptotic low-temperature limit, Eq. (4.3), with the triple point formula, Eq. (4.5), it is reasonable to seek a correlation equation,

\[
\ln P_{\text{subl}}^{\text{CE}}(T) = \frac{3}{2} \ln \frac{T}{T_t} + \left( 1 - \frac{T}{T_t} \right) \cdot \eta \left( \frac{T}{T_t} \right),
\]

similar to the empirical equation of Frost and Kalkwarf (1953). The function

\[
\eta = \sum_{i=0}^{6} e_i \cdot (T/T_t)^i
\]

was fitted to Eq. (4.6) with an rms of \(5 \times 10^{-4}\). The coefficients are given in Table 5. Because of the lacking need for practical sublimation formulae below 20 K, the crudity of the linear interpolation of the heat capacity in this range (Fig. 3), and the desired simplicity of the correlation equations, we restricted the regression to the interval 20–273 K.

Next, we derive a correlation equation, \(\Delta h^{\text{CE}}(T)\), from the sublimation enthalpy, \(\Delta h(T)\), listed in Table 4 and plotted in Fig. 5, computed from the Gibbs energy of ice (Feistel and Wagner, 2006) and the Gibbs energy of vapor, for \(T \geq 130 \text{ K}\) from Wagner and Pruss (2002), using Eq. (2.8), and for \(T < 130 \text{ K}\) from Eqs. (3.6) and (3.11). A polynomial

\[
\Delta h^{\text{CE}} = \sum_{i=0}^{6} a_i \cdot (T/T_t)^i
\]

was fitted to the computed curve of sublimation enthalpy \(\Delta h(T)\), Fig. 5, between 20 and 273 K, with an rms deviation of 0.04 kJ kg\(^{-1}\). The coefficients are reported in Table 6.

### 5. Uncertainty estimates

The estimated combined standard uncertainty \(u_c\) (ISO, 1993), briefly called uncertainty further on, of the specific entropy \(s^\text{th}\) of ice below 0.1 MPa, and, therefore, along

### Table 5

<table>
<thead>
<tr>
<th>(i)</th>
<th>(e_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20.996 966 510 789 7</td>
</tr>
<tr>
<td>1</td>
<td>3.724 374 782 713 62</td>
</tr>
<tr>
<td>2</td>
<td>−13.920 548 321 552 4</td>
</tr>
<tr>
<td>3</td>
<td>29.698 876 501 356 6</td>
</tr>
<tr>
<td>4</td>
<td>−40.197 239 263 594 4</td>
</tr>
<tr>
<td>5</td>
<td>1.090 159 935 211 18</td>
</tr>
<tr>
<td>6</td>
<td>−9.130 509 635 477 21</td>
</tr>
</tbody>
</table>

### Table 6

<table>
<thead>
<tr>
<th>(i)</th>
<th>(a_i)</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2 638 742.454 181 07</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>1</td>
<td>400 983.673 912 406</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>2</td>
<td>200 812.111 806 393</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>3</td>
<td>−1 486 203.384 853 36</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>4</td>
<td>2 290 451.502 307 89</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>5</td>
<td>−1 690 159.935 211 18</td>
<td>J kg(^{-1})</td>
</tr>
<tr>
<td>6</td>
<td>479 848.354 373 932</td>
<td>J kg(^{-1})</td>
</tr>
</tbody>
</table>

Fig. 6. Uncertainty of sublimation enthalpy, computed from Eq. (5.2), shown as a cone. The oscillating curve is the deviation of the correlation Eq. (4.8), from the curve given in Table 4 and Fig. 5. The rms (0.04 kJ kg\(^{-1}\)) of the correlation equation is indicated by horizontal lines. The limits 20 and 130 K are shown as vertical lines.
Summing up the ice and vapor parts, the uncertainty estimate of sublimation enthalpy, therefore, is

\[ u_c(\Delta h) = T \cdot u_c(\Delta s) = T \cdot \left( 4 + 3 \ln \frac{T_1}{T} \right) \text{J kg}^{-1} \text{K}^{-1}. \] (5.2)

The additional uncertainty resulting from the interpolation between the data points of vapor heat capacity can be estimated as

\[ \delta h = \frac{d\Delta h}{dT} dP = \frac{d\Delta h}{dT} dP \delta P \]

\[ \approx \frac{d\Delta h}{dT} \frac{RT^2}{\Delta h} |\ln P_A - \ln P_B| \] (5.3)

We infer from Fig. 5 and Table 3 that this term is insignificant in comparison to Eq. (5.2).

The uncertainty of sublimation enthalpy is shown in Fig. 6, together with the deviation of the correlation equation (4.8), from the curve given in Table 4 and Fig. 5.
For an estimate of the uncertainty of the sublimation pressure above 100 Pa, we adopt the value \( u_c(P_{\text{subl}}) = 0.4 \text{ Pa} \) as reported by Jancso et al. (1970) for his experiment.

Below 100 Pa, we use the Clausius–Clapeyron differential equation

\[
\frac{dP_{\text{subl}}}{dT} = \frac{\Delta s}{\Delta v}
\]

in approximate form with the specific volume difference \( \Delta v = v - v^1 \approx v \approx RT/P \),

\[
\frac{u_c(P_{\text{subl}})}{P_{\text{subl}}} \approx \int_{T_r}^{T} \frac{u_c(\Delta s)}{RT} \left[ R \int_{0}^{\ln(T_r/T)} u_c(\Delta s) \ d\left( \frac{\ln T}{T} \right) \right],
\]

and, making use of \( u_c(\Delta s) \) from Eq. (5.2), obtain finally the sublimation pressure uncertainty estimate for \( P_{\text{subl}} < 100 \text{ Pa} \), i.e. \( T < 253 \text{ K} \), as

\[
\frac{u_c(P_{\text{subl}})}{P_{\text{subl}}} = \left( 0.8\% + 0.3\% \cdot \ln \frac{T_r}{T} \right) \cdot \ln \frac{T_r}{T} + \left| \ln P_B - \ln P_A \right|.
\]

The last term represents the additional uncertainty from the interpolation between the data points of vapor heat capacity below 130 K, Eq. (3.6), as given in Table 3.

The uncertainty dependence of Eq. (5.6) on temperature is funnel-shaped (Fig. 7b) and is shown in Fig. 7 together with the experimental data scatter, which is much higher than the theoretical value (5.6) for temperatures below 253 K.

6. Conclusion

A thermodynamic method is proposed for the computation of the sublimation curve \( P_{\text{subl}}(T) \) of water below 130 K. Neither by theory nor by experiment has this very low pressure range been quantitatively described thus far. The formulae extend to arbitrarily low temperatures and pressures due to the supposed validity of the employed thermodynamic functions for vapor and ice, including the asymptotic zero-temperature limiting law.

We prove that sublimation temperature is a monotonically decreasing functional of water vapor heat capacity. Based upon this, and owing to the physically possible range of heat capacity values of water vapor below 130 K, we find that the region of possible locations of the sublimation curve is a narrow stripe in the \((T, P)\) space. Using available heat capacity data and the manifold of possible interpolation functions between them, this region further shrinks significantly, making different interpolations almost equivalent.

The sublimation curve based on linear interpolation of heat capacity data is proposed as the new sublimation pressure function. Since sublimation pressures below \( 10^{-30} \text{ Pa} \) are unlikely to be observed in nature, we have restricted the correlation equations for the sublimation pressure and enthalpy to the range 20–273 K. The uncertainty of the new formulation is estimated, which is much smaller than the scatter of published measurements.

Acknowledgments

The authors thank Jens Biele for information about cosmic subsurface probes, and Allan H. Harvey for hints on new water vapor heat capacity computations. They are grateful to the editors, Frank A. Podosek and David J. Wesolowski, and the referees for improving several details of the paper.

Associate Editor: David J. Wesolowski

References


Flaud, J.M., Camy-Peyret, C., 1973. The 2\(\nu_2\), \(v_1\) and \(v_3\) bands of H\(_2\)\(\text{O}\). Rotational study of the (0\(00\)) and (0\(20\)) states. Mol. Phys. 26, 811–823.


