CORRELATIONS

Correlation for the Vapor Pressure of Mercury†

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We present a new correlation for the vapor pressure of mercury that is valid from the triple point to the critical point. The equation is a Wagner-type form, where the terms of the equation are selected using a simulated annealing optimization algorithm. To improve the reliability of the equation at low temperatures, heat-capacity data were used in addition to vapor-pressure data. We present comparisons with available experimental data and existing correlations. The estimated uncertainty at a coverage factor of 2 varies from 3% near the triple point to 1% for temperatures from 273 to 400 K; 0.15% for the intermediate temperature region from 400 K to the normal boiling point at 629.77 K; for temperatures above the normal boiling point but below ~900 K, it is 0.5%; and for temperatures between 900 K and the critical point, we estimate that the uncertainty is 5%.

Introduction

Concerns about mercury as an industrial pollutant have led to increased interest in the detection and regulation of mercury in the environment.1 The recent Clean Air Mercury Rule2 will permanently cap and reduce mercury emissions from coal-fired power plants. The development of standardized equations for the thermophysical properties of mercury can aid in the implementation of this task. A critical evaluation of density, thermal expansion coefficients, and compressibilities, as a function of temperature and pressure, was conducted by Holman and ten Seldam.3 Bettin and Fehlauer4 recently reviewed the density of mercury for metrological applications. Vukalovich and Fokin’s book5 including tabulations of available experimental data, and a more-complete description of the work; a more-complete description, and we estimate the uncertainty of the correlation. This manuscript summarizes the work; a more-complete description, including optical and magnetic characteristics. To aid in the development of standards for the concentration of mercury in air, it is important to have an accurate representation of the vapor pressure of mercury. Numerous compilations and correlations of the vapor pressure of mercury have been published,6–25 however, there is no consensus on which is the best one to use for a given purpose. To address this issue, we review the existing experimental data and correlations and provide a new representation of the vapor pressure of mercury that is valid from the triple point to the critical point. We also present comparisons with both experimental data and correlations, and we estimate the uncertainty of the correlation. This manuscript summarizes the work; a more-complete description, including tabulations of available experimental data, and a more-detailed discussion of the results for the temperature range of 273–333 K, is presented in a NIST Internal Report.27

Experimental Vapor-Pressure Data

Experimental measurements of the vapor pressure of mercury have a long history, dating all the way back to the 1800s. Table 1 gives a detailed compilation of sources of vapor-pressure data from 1862 to the present, along with the temperature range of the measurements, the experimental method used, and an estimate of the uncertainty of these measurements. Generally, determinations of the purity of the mercury were not available; however, methods for the purification of mercury have been known for a long time, and high-purity samples were prepared before it was possible to quantify the purity.19 The estimates of uncertainty were obtained by considering the experimental method and conditions, the original author’s estimates (when available), and the agreement with preliminary correlations. These correspond to our estimate of a combined expanded uncertainty with a coverage factor of 2.

As indicated in Table 1, many measurements have been made on the vapor pressure of mercury. However, only a limited number of these are comprehensive and have uncertainty levels of 1% or less. These sets have been identified as primary data sets in our work and are indicated by boldface type in Table 1. Generally, the most-accurate measurements were those made with ebulliometric methods. Ambrose and Sprake19 used an ebulliometric technique for their measurements over a temperature range of 380–771 K. These data have an uncertainty of ~0.03% or lower, with the largest uncertainty at the lowest temperatures. Beattie et al.28 very accurately determined the boiling point of mercury over a temperature range of 623–636 K. Spedding and Dye81 used an isoteniscope to measure the vapor pressure over a temperature range of 534–630 K, with uncertainties on the order of 0.03%, except at the lowest temperatures, where they are larger. Menzies52,88 used an isoteniscope at temperatures of 395–708 K; however, these data show more scatter and have larger uncertainties than the sets previously mentioned; however, the uncertainties are still <0.5%. Shpil’rain and Nikanorov80 used an ebulliometric method, extending from 554 K to 883 K. Their data are more consistent with the measurements

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of Ambrose and Sprake\(^{19}\) in their region of overlap than are other high-temperature sets, such as those by Sugawara et al.,\(^{10}\) Bernhardt,\(^{29}\) or Cailletet et al.,\(^{33}\) and thus were selected as the primary data for the high-temperature region from \(~700\) K to \(900\) K. In addition, although the uncertainty is \(\sim 1\%\), we have selected the data of Schoenherr and Hensel\(^{78}\) for the highest-temperature region from \(~6\) to \(400\) K, much higher for lower \(T\).

Table 1. Summary of Available Data for the Vapor Pressure of Mercury\(^{a}\)

<table>
<thead>
<tr>
<th>reference(s)</th>
<th>year</th>
<th>method</th>
<th>number of points</th>
<th>(T) range (K)</th>
<th>estimated uncertainty (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ambrose and Sprake(^{19})</td>
<td>1972</td>
<td>ebulliometer</td>
<td>113</td>
<td>417–771</td>
<td>less than 0.03, greatest at lowest (T) 0.03</td>
</tr>
<tr>
<td>Beattie et al.,(^{28})</td>
<td>1937</td>
<td>boiling tube</td>
<td>42</td>
<td>623–636</td>
<td></td>
</tr>
<tr>
<td>Bernhardt(^{29})</td>
<td>1925</td>
<td>3 static methods</td>
<td>27</td>
<td>694–1706</td>
<td>varies from 2 to (&gt;) 15</td>
</tr>
<tr>
<td>Bessel-Hagen(^{36})</td>
<td>1881</td>
<td>Töpler vacuum pump</td>
<td>2</td>
<td>273–293</td>
<td>(&gt;) 20</td>
</tr>
<tr>
<td>Burlingame(^{31})</td>
<td>1968</td>
<td>transpiration</td>
<td>38</td>
<td>344–409</td>
<td>4</td>
</tr>
<tr>
<td>Busey and Giauque(^{32})</td>
<td>1953</td>
<td>derived from caloric properties</td>
<td>24</td>
<td>234–750</td>
<td>varies from 0.2 to 1.5 at lowest (T)</td>
</tr>
<tr>
<td>Cailletet et al.,(^{33})</td>
<td>1900</td>
<td>Bourdon manometer</td>
<td>11</td>
<td>673–1154</td>
<td>varies from 1 to 7</td>
</tr>
<tr>
<td>Callendar and Griffiths(^{34})</td>
<td>1891</td>
<td>Mayer tube</td>
<td>2</td>
<td>630</td>
<td>0.2</td>
</tr>
<tr>
<td>Cammena(^{35})</td>
<td>1969</td>
<td>effusion</td>
<td>9</td>
<td>299–549</td>
<td>varies from 3 to (&gt;) 20</td>
</tr>
<tr>
<td>Carlso et al.,(^{36})</td>
<td>1963</td>
<td>effusion</td>
<td>18</td>
<td>305–455</td>
<td>5</td>
</tr>
<tr>
<td>Dauphine(^{37,38})</td>
<td>1950, 1951</td>
<td>transpiration</td>
<td>30</td>
<td>234–773</td>
<td>varies from 0.03 (at normal boiling point) to 1.5 at lowest (T)</td>
</tr>
<tr>
<td>Douglas et al.,(^{39})</td>
<td>1951</td>
<td>derived from caloric properties</td>
<td>30</td>
<td>694–1706</td>
<td></td>
</tr>
<tr>
<td>Durrans(^{40})</td>
<td>1920</td>
<td>gives table attributed to Smith and Menzies(^{41})</td>
<td>46</td>
<td>273–723</td>
<td></td>
</tr>
<tr>
<td>Egerton(^{42})</td>
<td>1917</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ersnesberger and Pitman(^{43})</td>
<td>1955</td>
<td>piston manometer</td>
<td>18</td>
<td>285–327</td>
<td>1</td>
</tr>
<tr>
<td>Galchenko and Pelevin(^{44})</td>
<td>1978</td>
<td>static method</td>
<td>14</td>
<td>523–723</td>
<td>3</td>
</tr>
<tr>
<td>Galchenko et al.,(^{45})</td>
<td>1984</td>
<td>atomic absorption correlating equation only</td>
<td>5</td>
<td>723–873</td>
<td>3</td>
</tr>
<tr>
<td>Gebhardt(^{46})</td>
<td>1905</td>
<td>boiling tube</td>
<td>9</td>
<td>403–483</td>
<td>8</td>
</tr>
<tr>
<td>Haber and Kerschbaum(^{47})</td>
<td>1914</td>
<td>vibrating quartz filament</td>
<td>1</td>
<td>293</td>
<td>2</td>
</tr>
<tr>
<td>Hagen(^{48})</td>
<td>1882</td>
<td>differential pressure</td>
<td>5</td>
<td>273–473</td>
<td>(&gt;) 20</td>
</tr>
<tr>
<td>Hensel and Franck(^{49})</td>
<td>1966</td>
<td>electrical resistance</td>
<td>9</td>
<td>363–480</td>
<td>5</td>
</tr>
<tr>
<td>Herza(^{50})</td>
<td>1982</td>
<td>static absolute manometer</td>
<td>3</td>
<td>630</td>
<td>0.2</td>
</tr>
<tr>
<td>Heycock and Lamplough(^{51})</td>
<td>1913</td>
<td>not available</td>
<td>1</td>
<td>295–332</td>
<td>5</td>
</tr>
<tr>
<td>Hildenbrand et al.,(^{52})</td>
<td>1964</td>
<td>torsion-effusion</td>
<td>6</td>
<td>272–308</td>
<td>30</td>
</tr>
<tr>
<td>Hill(^{53})</td>
<td>1922</td>
<td>radiometer principle</td>
<td>19</td>
<td>742–1271</td>
<td>not available</td>
</tr>
<tr>
<td>Hubbard and Ross(^{54})</td>
<td>1982</td>
<td>static</td>
<td>21</td>
<td>479–671</td>
<td>0.1 to (&gt;) 20</td>
</tr>
<tr>
<td>Jenkins(^{55})</td>
<td>1926</td>
<td>isentrope</td>
<td>43</td>
<td>393–493</td>
<td>(&gt;) 10</td>
</tr>
<tr>
<td>Kahlbaum(^{56})</td>
<td>1894</td>
<td>ebulliometer</td>
<td>10</td>
<td>273–324</td>
<td>varies from 5 to 10</td>
</tr>
<tr>
<td>Knudsen(^{57})</td>
<td>1909</td>
<td>effusion</td>
<td>7</td>
<td>263–298</td>
<td>varies from 5 to 10</td>
</tr>
<tr>
<td>Knudsen(^{58})</td>
<td>1910</td>
<td>radiometer principle</td>
<td>2</td>
<td>630–632</td>
<td>4</td>
</tr>
<tr>
<td>Kordes and Raaaz(^{59})</td>
<td>1929</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mayer(^{60})</td>
<td>1930</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>McLeod(^{61})</td>
<td>1883</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Smith and Menzies(^{41, 1910, 1927})</td>
<td>1910, 1927</td>
<td>isentrope</td>
<td>46</td>
<td>395–708</td>
<td>0.5</td>
</tr>
<tr>
<td>Menzies(^{62})</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Millar(^{63})</td>
<td>1927</td>
<td>isentrope</td>
<td>6</td>
<td>468–614</td>
<td>2</td>
</tr>
<tr>
<td>Morley(^{64})</td>
<td>1904</td>
<td>transpiration</td>
<td>6</td>
<td>289–343</td>
<td>varies from 8 to (&gt;) 20</td>
</tr>
<tr>
<td>Murgeulescu and Topon(^{65})</td>
<td>1966</td>
<td>quasi-static</td>
<td>9</td>
<td>301–549</td>
<td>3</td>
</tr>
<tr>
<td>Neumann and Völker(^{66})</td>
<td>1932</td>
<td>torsion balance</td>
<td>19</td>
<td>290–344</td>
<td>6</td>
</tr>
<tr>
<td>Pedder and Barratt(^{67})</td>
<td>1933</td>
<td>transpiration</td>
<td>3</td>
<td>559–573</td>
<td>2</td>
</tr>
<tr>
<td>Pfaundler(^{68})</td>
<td>1897</td>
<td>gas saturation</td>
<td>3</td>
<td>288–372</td>
<td>12</td>
</tr>
<tr>
<td>Poindexter(^{69})</td>
<td>1925</td>
<td>ionization gauge</td>
<td>17*</td>
<td>235–293</td>
<td>5–20, greatest at lowest (T)</td>
</tr>
<tr>
<td>Raabe and Sadus(^{70})</td>
<td>2003</td>
<td>computer simulation</td>
<td>20</td>
<td>408–1575</td>
<td>varies from 0.5 to (&gt;) 20</td>
</tr>
<tr>
<td>Ramsay and Young(^{71})</td>
<td>1886</td>
<td>isentrope</td>
<td>13</td>
<td>495–721</td>
<td>varies from 0.3 to 10 at highest (T)</td>
</tr>
<tr>
<td>Regnault(^{72})</td>
<td>1862</td>
<td>isentrope</td>
<td>29</td>
<td>297–785</td>
<td>(~6) for (T \geq 400) K, much higher for lower (T)</td>
</tr>
<tr>
<td>Rodebush and Dixon(^{73})</td>
<td>1925</td>
<td>quasi-static</td>
<td>7</td>
<td>444–476</td>
<td>1</td>
</tr>
<tr>
<td>Roeder and Morawietz(^{74})</td>
<td>1956</td>
<td>quartz spiral manometer</td>
<td>7</td>
<td>413–614</td>
<td>2</td>
</tr>
<tr>
<td>Ruff and Bergdahl(^{75})</td>
<td>1919</td>
<td>temperature scanning</td>
<td>12</td>
<td>478–630</td>
<td>(&gt;) 20</td>
</tr>
<tr>
<td>Schmal et al.,(^{76})</td>
<td>1965</td>
<td>static method</td>
<td>43</td>
<td>412–640</td>
<td>1.5</td>
</tr>
<tr>
<td>Schneider and Schopp(^{77})</td>
<td>1944</td>
<td>gas saturation</td>
<td>23</td>
<td>484–575</td>
<td>10</td>
</tr>
<tr>
<td>Schönherr and Hensel(^{78})</td>
<td>1981</td>
<td>electrical conductivity</td>
<td>13</td>
<td>1052–1735</td>
<td>3</td>
</tr>
<tr>
<td>Scott(^{79})</td>
<td>1924</td>
<td>vibrating quartz filament</td>
<td>1</td>
<td>293</td>
<td>2</td>
</tr>
<tr>
<td>Shiply'rain and Nikanorov(^{80})</td>
<td>1971</td>
<td>ebulliometer</td>
<td>50</td>
<td>554–883</td>
<td>0.6–0.8</td>
</tr>
<tr>
<td>Spedding and Dyke(^{81})</td>
<td>1955</td>
<td>isentrope</td>
<td>13</td>
<td>534–630</td>
<td>0.03</td>
</tr>
<tr>
<td>Stock and Zimmermann(^{82})</td>
<td>1929</td>
<td>transpiration</td>
<td>3*</td>
<td>253–283</td>
<td>20</td>
</tr>
<tr>
<td>Sugawara et al.,(^{83})</td>
<td>1962</td>
<td>static method</td>
<td>14</td>
<td>602–930</td>
<td>2</td>
</tr>
<tr>
<td>van der Plaats(^{84})</td>
<td>1886</td>
<td>transpiration</td>
<td>26</td>
<td>273–358</td>
<td></td>
</tr>
<tr>
<td>Villiers(^{85})</td>
<td>1913</td>
<td>ebulliometer</td>
<td>12</td>
<td>333–373</td>
<td>6</td>
</tr>
<tr>
<td>Volmer and Kirchhoff(^{86})</td>
<td>1925</td>
<td>effusion</td>
<td>10</td>
<td>303–313</td>
<td>3</td>
</tr>
<tr>
<td>von Halban(^{87})</td>
<td>1935</td>
<td>resonance light absorption</td>
<td>1*</td>
<td>255</td>
<td>7</td>
</tr>
<tr>
<td>Young(^{88})</td>
<td>1891</td>
<td>static</td>
<td>11</td>
<td>457–718</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^{a}\) References in boldface indicate primary data sets (see text). \(^{b}\) Excludes points below the triple point.
emerged as the generally preferred form. When the data set has been described as reliable and confirmed by heat-capacity measurements, the uncertainties on the order of 1%, and they cover the temperature range of 285–327 K. This data set has been adopted in the metrology community for use in precision manometry, and it has been described as reliable and confirmed by heat-capacity measurements.

The triple point of mercury has been designated as a fixed point of the ITS-90 temperature scale, with a value of 234.3156 K. The critical point has been measured by several investigators; these values are listed in Table 2, along with uncertainty estimates provided by the authors. In this work, we adopted the critical point of Kozhevnikov et al.

Correlation Development

Numerous expressions have been used to represent the vapor pressure of a pure fluid; many are reviewed in Růžička and Majer. Equations of the general form

\[
\ln\left(\frac{p}{p_{sat}}\right) = \left(\frac{T}{T_c}\right)^\alpha + \sum_\beta \alpha_\beta T^{\beta/2}
\]

where \( \tau = 1 - (T/T_c) \), are attributed to Wagner and co-workers and have been used successfully to represent the vapor pressures of a wide variety of fluids. Lemmon and Goodwin used the Wagner form with exponents that had values of 1, 1.5, 2.5, and 5 to represent the vapor pressures of normal alkanes up to C10. This form, which we will call Wagner 2.5–5, is one of the most widely used forms, along with the equation with exponents that had values of 1, 1.5, 3, and 6, and which we call Wagner 3–6. The Wagner 2.5–5 form has emerged as the generally preferred form. When the data set is extensive and of high quality, other forms with alternative sets of exponents with additional terms have been used. For example, a Wagner equation with exponents of 1, 1.5, 2, 2.5, and 5.5 was used to represent the vapor pressure of acetonitrile, and another variant of the Wagner equation, with exponents of 1, 1.89, 2, 3, and 3.6 was used to represent the vapor pressure of heavy water from the triple point to the critical point, to within the experimental scatter of the measurements. The International Association for the Properties of Water and Steam (IAPWS) formulation for the vapor pressure of water uses a six-term Wagner equation with exponents of 1, 1.5, 3, 3.5, 4, and 7.5.

Because there is a lack of high-quality experimental vapor-pressure data in the low-temperature region \( T < 285 \) K, liquid heat-capacity measurements at low temperatures can be used to supplement the vapor-pressure data. This permits the simultaneous regression of heat-capacity and vapor-pressure data to determine the coefficients of a vapor-pressure equation that is valid down to the triple point. An alternative method is to use an expression that involves the enthalpies of vaporization, in addition to vapor-pressure data. Both of these approaches can be used to ensure that the vapor pressure is thermodynamically consistent with other thermodynamic data.

King and Al-Najjar related heat capacity and vapor pressure, using the relation

\[
\frac{d}{dT} \left[ T^2 \ln \left(\frac{p_{sat}}{p}\right) \right] = \frac{C_p^0 - C_p^L - G}{R}
\]

where \( C_p^0 \) and \( C_p^L \) are the heat capacities, at constant pressure, of the ideal gas and the saturated liquid, respectively; \( R \) is the molar gas constant \( (\text{8.314472 J/(mol K)}) \), \( p_{sat} \) is the vapor pressure, and \( G \) approximates vapor-phase nonidealities and is given as

\[
G = T \left[ p_{sat} \frac{d^2 B}{dT^2} + 2 \frac{dp_{sat}}{dT} \left( \frac{dB}{dT} - \frac{dV_l}{dT} \right) + \frac{dp_{sat}}{dT} (B - V_l) \right]
\]

In this expression, \( B \) is the second virial coefficient and \( V_l \) is the molar volume of the liquid. We restrict the use of this equation to temperatures of \( < 270 \) K, where vapor pressures are on the order of \( 10^{-5} \) kPa. In this region, we treat the gas phase as ideal, so that the \( G \) term may be neglected. (For example, we applied equations in Douglas et al. for the virial coefficients, liquid volumes, heat capacities, vapor pressures, and their derivatives and estimated that the magnitude of the \( G \) term at 270 K, relative to the heat-capacity difference in eq 2, is on the order of 0.0001%). Assuming that mercury can be considered as an ideal monatomic gas for these low pressures, the ideal-gas heat capacity for mercury is \( C_p^0 = 5R/2 \). With these assumptions, after the derivatives of the vapor pressure in eq 2 are taken analytically, incorporating the specific form of the vapor-pressure correlation function of eq 1, one obtains the simple expression \( (5R/2 - C_p^L)R = (TT_c)\sum_\alpha (i/2)(i(i/2) - 1)T^{i-1-1} \).

Busey and Giauque measured the heat capacity \( C_p \) at atmospheric pressure of solid and liquid mercury from 15 K to 330 K, with estimated uncertainties of 0.1%. Amitin et al. also measured the heat capacity of mercury at temperatures of 5–300 K, with an estimated uncertainty of 1%. The smoothed data over the temperature range of 234–270 K from these two sources were identified as primary data for use in the regression, in addition to the primary vapor-pressure data that have been previously discussed.

For our analysis of both \( p_{sat} \) and \( C_p \) experimental data, all temperatures were first converted to the ITS-90 scale. Data taken prior to 1927 were converted to ITS-90, assuming that the older data were on the International Temperature Scale of 1927, although we realize this introduces additional uncertainties.

Table 2. Critical Temperature and Pressure of Mercury

<table>
<thead>
<tr>
<th>Reference</th>
<th>Year</th>
<th>( T_c (K) )</th>
<th>( p_c (MPa) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Koenigsberger</td>
<td>1912</td>
<td>~1543</td>
<td></td>
</tr>
<tr>
<td>Menzies</td>
<td>1913</td>
<td>&gt;1548</td>
<td></td>
</tr>
<tr>
<td>Bendix</td>
<td>1915</td>
<td>1923</td>
<td></td>
</tr>
<tr>
<td>Meyer</td>
<td>1921</td>
<td>1747</td>
<td></td>
</tr>
<tr>
<td>Bernhard</td>
<td>1925</td>
<td>1923</td>
<td>294.2–343.2</td>
</tr>
<tr>
<td>Birch</td>
<td>1932</td>
<td>1733 ± 20</td>
<td>161 ± 5</td>
</tr>
<tr>
<td>Hensel and Franck</td>
<td>1966</td>
<td>1763.15 ± 15</td>
<td>151 ± 3</td>
</tr>
<tr>
<td>Franck and Hensel</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kikoin and Schenkon</td>
<td>1967</td>
<td>1753 ± 10</td>
<td>152 ± 1</td>
</tr>
<tr>
<td>Neale and Cusack</td>
<td>1979</td>
<td>1768 ± 8</td>
<td>167.5 ± 2.5</td>
</tr>
<tr>
<td>Hubbard and Ross</td>
<td>1983</td>
<td>1750</td>
<td>172</td>
</tr>
<tr>
<td>Götzlaff</td>
<td>1988</td>
<td>1751 ± 1</td>
<td>167.3 ± 0.2</td>
</tr>
<tr>
<td>Kozhevnikov et al.</td>
<td>1996</td>
<td>1764 ± 1</td>
<td>167 ± 3</td>
</tr>
</tbody>
</table>

a Uncertainties are expressed in units of K and MPa for the temperature and pressure, respectively.
Except for the data of Menzie, all primary data were measured after 1927. The temperatures of the data of Menzie were first converted to the 1948 temperature scale using the procedure given by Douglas et al. and then were converted to ITS-90.

We regressed the primary data set to three different Wagner-type expressions: the 3–6 form, the 2.5–5 form, and an expression that used variable exponents, where the exponents were selected from a bank of terms, using a simulated annealing procedure. Simulated annealing is an optimization technique that can be used in complex problems where there may be multiple local minima. It is a combinatorial method that does not require derivatives and is not dependent on "traveling downhill"; it also is relatively easy to implement. In this work, the search space contained a bank of terms where the bank contained exponents with powers of \( r \) in increments of 0.5, with terms up to \( \tau^{12} \). We followed the recommendation of Harvey and Lemmon and required the equation to contain terms of orders 1, 1.89, and 2, based on theoretical considerations on the behavior near the critical point. The simulated annealing algorithm was used to determine the optimal terms from the bank of terms. We implemented a Lundy and Mees annealing schedule, similar to that of earlier work. During the regression, one can treat the critical pressure as a variable to be determined in the regression, or it can be fixed. Because of concerns about the quality and amount of experimental data in the temperature range of 930–1764 K, we adopted the critical point of Kozhevnikov et al., rather than determining it by fitting experimental data. The minimization was done with orthogonal distance regression, using the NIST statistical package ODROPACK. For the regression, the data were weighted according to their estimated uncertainty \( (u) \) with weights of \( 1/u^2 \). In addition, the vapor-pressure data were given a relative weight factor of 1, and the heat-capacity data were given a relative weight factor of 0.02. Points that deviated by more than three standard deviations from preliminary fits were considered outliers and were not included in the statistics or the final regression.

The 2.5–5 form of the Wagner equation provided a better fit of the primary data set than the 3.0–6 form; further improvement resulted from the use of the simulated annealing algorithm. Upon closer inspection, we noted that, although one could reasonably reproduce the numerical value of the heat capacity, it was not possible to reproduce well the slope of the saturated liquid heat capacity near the triple point without degrading the fit in other regions. We note that the liquid heat capacity at mercury saturation, as a function of temperature, displays an interesting behavior: a distinct minimum in the curve is observed below the normal boiling point. Douglas et al. noted that other liquid metals such as sodium and potassium also exhibit this behavior. To fit the vapor-pressure and liquid heat-capacity data simultaneously, and to have the correct behavior of the slope of the heat capacity, as a function of temperature along the saturation boundary, we increased the number of terms in the regression from five to six and used the simulated annealing algorithm to obtain our final equation,

\[
\ln \left( \frac{p}{\rho_c} \right) = \left( \frac{T_c}{T} \right) \left( a_1 + a_2 \tau^{0.89} + a_3 \tau^2 + a_4 \tau^{0.8} + a_5 \tau^{0.5} + a_6 \tau^0 \right)
\]

(4)

The coefficients and their standard deviations are given in Table 3a, and fixed parameters for eq 4 are given in Table 4a.
We use the currently accepted values of the molar gas constant1
and the atomic mass of mercury (200.59 g/mol). The data of Ernsberger and Pitman43 display substantial scatter, but the results are
within their estimated uncertainty (0.6%–0.8%). The very accurate measurements of Beattie et al.23 are in the vicinity of the normal boiling point, and the correlation (eq 4) indicates an uncertainty of 0.02%, at a coverage factor of 2. The measurements of Spedding and Dye81 and those of Ambrose and Sprake19 also are represented well by our correlation, although the lowest temperature points display larger scatter than at higher temperatures. The measurements of Smith and Menzies40 and Menzies62 are also represented to within their estimated uncertainty. The highest-temperature data of Schönherr and Hensel128 are represented with an AAD of 1% and a standard deviation of 1.4%; several points are outside of the range of the plot and are not shown. The correlation is valid to the critical point at 1764 K but does not account for a metal–nonmetal transition54 in mercury at ~1360 K, which results in a change of slope in the vapor-pressure curve.

Figure 2 compares selected data not used in the regression (secondary data) with the correlation (eq 4), and Table 6 summarizes comparisons with all secondary data. It is interesting to note that the behavior of the correlation at low temperatures falls between the values of Douglas et al.39 and those of Busey and Giauque.35 Both of these sets were not obtained from direct vapor-pressure measurements, but rather were calculated based on calorimetric measurements combined with vapor-pressure data at higher temperatures. The data of Schmahl et al.76 cover a range of temperatures, from 412 K to 640 K, and are in good agreement with the correlation. The measurements of Burlingame31 and of Dauphine37 were made using a transpiration technique with uncertainties on the order of 4%–5%, and the correlation represents them within this range of deviations. Figure 2 also displays considerably more scatter at both the high- and low-temperature ends of the plot.

Comparisons with Correlations from the Literature

Figures 3a and 3b compare correlations and tables for the vapor pressure of mercury in different temperature regions obtained in the literature. In these figures, we define the percent deviation as 100 × (p_{corr} − p_{expt})/p_{expt}, where p_{corr} is the vapor pressure from correlations in the literature and p_{expt} is that obtained from eq 4. We also show the estimated uncertainty band of the new correlation, eq 4, by a heavy black line. The existing correlations in the literature agree well with each other and with the new correlation in the intermediate temperature region from ~400 K to the normal boiling point. In this region, there is a fair number of high-quality experimental data. At low temperatures, the existing correlations differ from each other and some differ from the new correlation. As mentioned previously, there is a paucity of high-quality direct vapor-pressure measurements in this region, and we feel that simultaneously using low-temperature heat-capacity data allows our new correlation to display the proper behavior in the low-temperature region. We also had access to newer data that some of the earlier correlations did not include. For example, the Lange’s Handbook correlation122,123 is based on the International Critical Tables of 1928,124 whereas the most recent CRC Handbook125 values are based on the work of Vargaftik et al.,3 which itself is based upon the 1972 book of Vukalovich and Fokin.3 Some earlier editions of the CRC Handbook (for example, the 57th Edition, 1976–1977, page D-182) used the values from the International Critical Tables of 1928.124 Few correlations are applicable for higher temperatures. The maximum temperature limit of the Korea Thermophysical Properties Databank (KDB) correlation126 is given as 654.15 K. The maximum of the Physikalisch-Technische Bundesanstalt (PTB) equation23 is 930 K; these corre-

Figure 1. Deviations between the correlation given in eq 4 and the primary data set.

Figure 2. Deviations between the correlation given in eq 4 and selected secondary data.

Table 3b. Table 4 gives sample values of the vapor pressure calculated from eq 4 over the temperature range of 273.15–333.15 K. To validate the computer code, more digits are given than are statistically meaningful. For the calibration community, in Table 4, we also have included the density of saturated mercury vapor in moles per liter and in nanograms per milliliter obtained, assuming that the ideal gas law applies. For the 294 vapor pressure points in the primary data set, the average absolute deviation (AAD) is 0.14%, the bias is 0.028%, and the root-mean-square (RMS) deviation is 0.35%.

Comparison with Experimental Data

For the 294 vapor pressure points in the primary data set, the average absolute deviation (AAD) is 0.14%, the bias is −0.028%, and the root-mean-square (RMS) deviation is 0.35% where we use the definitions AAD = (100/n)Σ|abs(p_{calc}/p_{expt} − 1), BIAS = (100/n)Σ(p_{calc}/p_{expt} − 1), and RMS2 = (100/n)× Σ(p_{calc}/p_{expt} − 1)2 − ((100/n)Σ(p_{calc}/p_{expt} − 1))2, where n is the number of points. The AAD and RMS values for the primary data are given in Table 5. The normal boiling point calculated by this equation is 629.7705 K.

Figure 1 compares the primary data set with our correlation (eq 4). The data of Ernsberger and Pitman13 display substantial scatter, but the results are within their estimated experimental uncertainty of 1%. The data of Shpil’rain and Nikanorov80 also display a fairly high scatter, but, again, it is within their uncertainty estimate (0.6%–0.8%).
At the highest temperatures, there are considerable differences among the various correlations; however, there is also a lack of experimental measurements in this region. The de Kruif correlation varies from 2 to 20; greatest at lowest T. Two outliers, at 380 and 400 K, were not included in the statistics. Ind. Eng. Chem. Res., Vol. 45, No. 21, 2006

### Table 5. Summary of Comparisons of the Correlation with the Primary Data for the Vapor Pressure of Mercury

<table>
<thead>
<tr>
<th>reference(s)</th>
<th>number of points</th>
<th>T range (K)</th>
<th>estimated uncertainty (%)</th>
<th>Deviation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bernhardt</td>
<td>27</td>
<td>694–1706</td>
<td>varies from 2 to 15</td>
<td>14.13</td>
</tr>
<tr>
<td>Bessel-Hagen</td>
<td>2</td>
<td>289–309</td>
<td>5</td>
<td>6.99</td>
</tr>
<tr>
<td>Galchenko et al.</td>
<td>9</td>
<td>533–723</td>
<td>3</td>
<td>3.34</td>
</tr>
<tr>
<td>Gebhardt</td>
<td>5</td>
<td>273–473</td>
<td>&gt; 20</td>
<td>1.84</td>
</tr>
<tr>
<td>Haber and Kerschbaum</td>
<td></td>
<td>630–1154</td>
<td>&gt; 5</td>
<td></td>
</tr>
<tr>
<td>Hagen</td>
<td>9</td>
<td>708–883</td>
<td>&gt; 10</td>
<td>0.14</td>
</tr>
<tr>
<td>Hensel and Franck</td>
<td></td>
<td>363–480</td>
<td>Na</td>
<td>5.00</td>
</tr>
<tr>
<td>Heycock and Lamplough</td>
<td>1</td>
<td>630–1271</td>
<td>Na</td>
<td>0.21</td>
</tr>
<tr>
<td>Hildenbrand et al.</td>
<td>6</td>
<td>295–332</td>
<td>Na</td>
<td>2.76</td>
</tr>
<tr>
<td>Hill</td>
<td>19</td>
<td>272–308</td>
<td>Na</td>
<td>29.40</td>
</tr>
<tr>
<td>Hubbard and Ross</td>
<td></td>
<td>742–1271</td>
<td>Na</td>
<td>4.38</td>
</tr>
<tr>
<td>Jenkins</td>
<td>21</td>
<td>479–671</td>
<td>&gt; 10</td>
<td>5.08</td>
</tr>
<tr>
<td>Knudsen</td>
<td>43</td>
<td>393–493</td>
<td>&gt; 10</td>
<td>8.89</td>
</tr>
<tr>
<td>Knudsen</td>
<td>10</td>
<td>273–324</td>
<td>&gt; 10</td>
<td>7.36</td>
</tr>
<tr>
<td>Kordes and Raaz</td>
<td>7</td>
<td>263–298</td>
<td>&gt; 10</td>
<td>7.12</td>
</tr>
<tr>
<td>Mayer</td>
<td>2</td>
<td>630–632</td>
<td>&gt; 10</td>
<td>2.59</td>
</tr>
<tr>
<td>McLeod</td>
<td>1</td>
<td>293–395</td>
<td>&gt; 20</td>
<td>7.76</td>
</tr>
<tr>
<td>Milicari</td>
<td>4</td>
<td>468–614</td>
<td>2</td>
<td>1.27</td>
</tr>
<tr>
<td>Morley</td>
<td>6</td>
<td>289–343</td>
<td>Na</td>
<td>17.58</td>
</tr>
<tr>
<td>Murgulescu and Topor</td>
<td>9</td>
<td>301–549</td>
<td>Na</td>
<td>1.41</td>
</tr>
<tr>
<td>Neumann and Völker</td>
<td>19</td>
<td>290–344</td>
<td>Na</td>
<td>4.63</td>
</tr>
<tr>
<td>Pedder and Barrant</td>
<td>3</td>
<td>559–573</td>
<td>Na</td>
<td>1.14</td>
</tr>
<tr>
<td>Pfandl</td>
<td>3</td>
<td>288–372</td>
<td>Na</td>
<td>8.06</td>
</tr>
<tr>
<td>Poitouxter</td>
<td>17</td>
<td>235–293</td>
<td>&gt; 5; &gt; 20; greatest at lowest T</td>
<td>28.23</td>
</tr>
<tr>
<td>Ramsay and Young</td>
<td>13</td>
<td>495–721</td>
<td>Na</td>
<td>28.23</td>
</tr>
<tr>
<td>Regnault</td>
<td>29</td>
<td>297–785</td>
<td>Na</td>
<td>29.19</td>
</tr>
<tr>
<td>Rodebush and Dixon</td>
<td>7</td>
<td>444–476</td>
<td>Na</td>
<td>0.53</td>
</tr>
<tr>
<td>Roeder and Morawitz</td>
<td>7</td>
<td>413–614</td>
<td>Na</td>
<td>1.00</td>
</tr>
<tr>
<td>Ruff and Bergdahl</td>
<td>12</td>
<td>478–630</td>
<td>Na</td>
<td>22.49</td>
</tr>
<tr>
<td>Schmidt and Schoppers</td>
<td>23</td>
<td>484–575</td>
<td>Na</td>
<td>0.70</td>
</tr>
<tr>
<td>Scott</td>
<td>1</td>
<td>293–295</td>
<td>Na</td>
<td>4.04</td>
</tr>
<tr>
<td>Stock and Zimmermann</td>
<td>3</td>
<td>253–283</td>
<td>Na</td>
<td>1.11</td>
</tr>
<tr>
<td>Sugawara and coworkers</td>
<td>14</td>
<td>602–930</td>
<td>Na</td>
<td>1.15</td>
</tr>
<tr>
<td>van der Plaats</td>
<td>26</td>
<td>273–358</td>
<td>Na</td>
<td>8.65</td>
</tr>
<tr>
<td>Villiers</td>
<td>12</td>
<td>333–373</td>
<td>Na</td>
<td>4.76</td>
</tr>
<tr>
<td>Volmer and Kirchhoff</td>
<td>10</td>
<td>303–313</td>
<td>Na</td>
<td>1.57</td>
</tr>
<tr>
<td>von Halban</td>
<td>2</td>
<td>220–255</td>
<td>Na</td>
<td>8.15</td>
</tr>
<tr>
<td>Young</td>
<td>11</td>
<td>457–718</td>
<td>Na</td>
<td>1.40</td>
</tr>
</tbody>
</table>

a Average absolute deviation. b Root-mean-square deviation. c One outlier, at 380 K, was not included in the statistics. d Not applicable.
relation\textsuperscript{21,22} does not specifically state the temperature limits of the correlation; however, the very thorough literature survey in the thesis\textsuperscript{21} indicates that the only high-temperature data used in their work were those of Bernhardt\textsuperscript{29} and Cailletet et al.,\textsuperscript{33} and they did not have access to the more-recent measurements of Shpil’rain and Nikanorov,\textsuperscript{80} Sugawara et al.,\textsuperscript{10} or Schönherr and Hensel.\textsuperscript{78} Lange’s Handbook\textsuperscript{122} includes a note in their table identifying 900 °C as the critical point; this model deviates substantially from the other correlations at high temperatures. The DIPPR\textsuperscript{127} and Yaws\textsuperscript{128} correlations seem to be indistinguishable on the plot, and both have adopted a critical point of 1735 K and 160.8 MPa. Our correlation agrees very well with these correlations, up to 1500 K, where the differences are probably due to the critical point adopted in the correlations. Also, the correlation of Schmutzler (as presented in Götzlaff\textsuperscript{14}) adopts a different critical point from the selection here; it uses $T_c = 1751$ K and $p_c = 167.3$ MPa. We note that the tabulated values in the book by Hensel and Warren\textsuperscript{5} seem to have been generated from the Schmutzler correlation.\textsuperscript{14}

Detailed Comparisons for the Temperature Range of 0–60 °C

The temperature range of 0–60 °C is of particular interest. Unfortunately, in this region, there are very few vapor-pressure data of high accuracy. Our approach, as detailed previously, was to identify the data sets of highest quality and supplement the vapor-pressure data with low-temperature heat-capacity data, to improve the behavior of the correlation at low temperatures and to ensure thermodynamic consistency. The data of Ernsberger and Pitman\textsuperscript{33} are the only direct vapor-pressure measurements of low uncertainty (1%) available in this region and were the only low-temperature vapor-pressure data used in the regression. Figure 4 shows the deviations of all data with

![Figure 3](image-url)
estimated uncertainties of 3% or less in this temperature range. The data of both Busey and Giauque,32 and Douglas et al.,39 were not direct measurements but rather values obtained from their analysis of heat-capacity data. Our correlation does not agree with these sets to within their estimated uncertainties, nor do the sets agree with each other (to within these uncertainties). The single data point of Scott79 at 293 K, determined with a quartz fiber manometer with an estimated uncertainty of 2%, is represented by our correlation within this margin. The measurements of Volmer and Kirchoff85 gave an estimated uncertainty of 1% for their measurements, and they seem to be the most-reliable vapor-pressure measurements in the 0–60 °C range. The Mukhachev et al.,17 correlation was developed from caloric data such as the heat of vaporization and heat capacities, along with the normal boiling point of mercury. The KDB correlation126 is presented only as a set of coefficients with a range of applicability, and we do not know the data used in its development; it is consistently lower than our correlation. The PTB curve,23 with a reported maximum uncertainty of 4%, is very different in shape from all of the others that have been investigated. This analysis did not incorporate caloric data, and the experimental data in the 0–60 °C range that were used in the regression were those of Pindexter49 and Neumann and Völker.56 The equation recommended in ASTM Standard D6350132 is presented as a concentration, in terms of nanograms per milliliter. We converted the expression to a vapor pressure by applying the ideal gas law and using an atomic mass121 of 200.59 and a gas constant113 value of $R = 8.314472 \text{ J/(mol K)}$. It agrees well with the values from Lange’s Handbook122,123 and deviates the most from our correlation, approaching 10% at 273 K, and gives vapor pressures that are lower than all the other correlations. The curve in Lange’s Handbook122 is based on the 1928 International Critical Tables (ICT)124 and was developed with only the limited data and computational methods available at that time.

Conclusions

We have developed a new correlation for the vapor pressure of mercury that is valid from the triple point89 (234.3156 K) to the critical point91 (1764 K), using a Wagner-type equation. We have determined the uncertainties to be associated with the equation through our comparisons with the primary experimental data and consideration of the uncertainties of these data, as discussed previously. The estimated uncertainty at a coverage factor of 2 varies from 3% near the triple point to 1% for temperatures of 273–400 K, 0.15% for the intermediate temperature region from 400 K to the normal boiling point at 629.77 K, 0.5% for temperatures above the normal boiling point but below ~900 K, and ~5% for temperatures between 900 K and the critical point. The new correlation gives a normal boiling point (at 101.325 kPa) of 629.77 K.

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