

CORRELATIONS

Correlation for the Vapor Pressure of Mercury[†]

Marcia L. Huber,* Arno Laesecke, and Daniel G. Friend

Physical and Chemical Properties Division, National Institute of Standards and Technology,
Boulder, Colorado 80303-3328

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 \sim 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 and the *Gmelin Handbook*⁶ are both thorough treatises on the thermophysical properties of mercury. Thermal properties such as thermal conductivity and heat capacity were reviewed by Sakonidou et al.,⁷ whereas Hensel and Warren⁸ have covered other properties, 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;^{9–26} 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

* To whom correspondence should be addressed. Tel.: 303.497.5252. Fax: 303.497.5224. E-mail: marcia.huber@nist.gov.

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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 \sim 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. Menzies^{62,88} 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

Table 1. Summary of Available Data for the Vapor Pressure of Mercury^a

reference(s)	year	method	number of points	<i>T</i> range (K)	estimated uncertainty (%)
Ambrose and Sprake¹⁹	1972	ebulliometer	113	417–771	less than 0.03, greatest at lowest <i>T</i>
Beattie et al.²⁸	1937	boiling tube	42	623–636	0.03
Bernhardt ²⁹	1925	3 static methods	27	694–1706	varies from 2 to > 15
Bessel-Hagen ³⁰	1881	Töpler vacuum pump	2	273–293	> 20
Burlingame ³¹	1968	transpiration	38	344–409	4
Busey and Giauque ³²	1953	derived from caloric properties	24	234–750	varies from 0.2 to 3.5 at lowest <i>T</i>
Cailletet et al. ³³	1900	Bourdon manometer	11	673–1154	varies from 1 to 7
Callendarand Griffiths ³⁴	1891	Meyer tube	2	630	0.2
Cammenga ³⁵	1969	effusion	graphical results	273–325	
Carlson et al. ³⁶	1963	effusion	9	299–549	varies from 3 to > 20
Dauphinee ^{37,38}	1950, 1951	transpiration	18	305–455	5
Douglas et al. ³⁹	1951	derived from caloric properties	30	234–773	varies from 0.03 (at normal boiling point) to 1.5 at lowest <i>T</i>
Durrans ⁴⁰	1920	gives table attributed to Smith and Menzies ⁴¹	46	273–723	
Egerton ⁴²	1917	effusion	27	289–309	5
Ernsberger and Pitman⁴³	1955	piston manometer	18	285–327	1
Galchenko and Pelevin ⁴⁴	1978	static method	graphical results	523–723	3
Galchenko et al. ⁴⁵	1984	atomic absorption	correlating equation only	723–873	3
Gebhardt ⁴⁶	1905	boiling tube	9	403–483	8
Haber and Kerschbaum ⁴⁷	1914	vibrating quartz filament	1	293	2
Hagen ⁴⁸	1882	differential pressure	5	273–473	> 20
Hensel and Franck ⁴⁹	1966	electrical resistance	graphical results	1073–critical	not available
Hertz ⁵⁰	1882	static absolute manometer	9	363–480	5
Heycock and Lamplough ⁵¹	1913	not available	1	630	0.2
Hildenbrand et al. ⁵²	1964	torsion-effusion	6	295–332	5
Hill ⁵³	1922	radiometer principle	19	272–308	30
Hubbard and Ross ⁵⁴	1982	static	graphical results	742–1271	not available
Jenkins ⁵⁵	1926	isotenoscope	21	479–671	0.1 to > 20
Kahlbaum ⁵⁶	1894	ebulliometer	43	393–493	> 10
Knudsen ⁵⁷	1909	effusion	10	273–324	varies from 5 to 10
Knudsen ⁵⁸	1910	radiometer principle	7	263–298	varies from 5 to 10
Kordes and Raaz ⁵⁹	1929	temperature scanning evaporation method	2	630–632	4
Mayer ⁶⁰	1930	effusion	82	261–298	5, except greater at <i>T</i> < 270 K
McLeod ⁶¹	1883	transpiration	1	293	> 20
Smith and Menzies,⁴¹ Menzies⁶²	1910, 1927	isotenoscope	46	395–708	0.5
Millar ⁶³	1927	isotenoscope	6	468–614	2
Morley ⁶⁴	1904	transpiration	6	289–343	varies from 8 to > 20
Murgulescu and Topor ⁶⁵	1966	quasi-static	9	301–549	3
Neumann and Völker ⁶⁶	1932	torsion balance	19	290–344	6
Pedder and Barratt ⁶⁷	1933	transpiration	3	559–573	2
Pfaundler ⁶⁸	1897	gas saturation	3	288–372	12
Poindexter ⁶⁹	1925	ionization gauge	17*	235–293	5–20, greatest at lowest <i>T</i>
Raabe and Sadus ⁷⁰	2003	computer simulation	20	408–1575	varies from 0.5 to > 20
Ramsay and Young ⁷¹	1886	isotenoscope	13	495–721	varies from 0.3 to 10 at highest <i>T</i>
Regnault ⁷²	1862	isotenoscope	29	297–785	~6 for <i>T</i> > 400 K, much higher for lower <i>T</i>
Rodebush and Dixon ⁷³	1925	quasi-static	7	444–476	1
Roeder and Morawietz ⁷⁴	1956	quartz spiral manometer	7	413–614	2
Ruff and Bergdahl ⁷⁵	1919	temperature scanning evaporation method	12	478–630	> 20
Schmahl et al. ⁷⁶	1965	static method	43	412–640	1.5
Schneider and Schupp ⁷⁷	1944	gas saturation	23	484–575	10
Schönherr and Hensel⁷⁸	1981	electrical conductivity	13	1052–1735	3
Scott ⁷⁹	1924	vibrating quartz filament	1	293	2
Shipil'rain and Nikanorov⁸⁰	1971	ebulliometer	50	554–883	0.6–0.8
Spedding and Dye⁸¹	1955	isotenoscope	13	534–630	0.03
Stock and Zimmermann ⁸²	1929	transpiration	3 ^b	253–283	20
Sugawara et al. ¹⁰	1962	static method	14	602–930	2
van der Plaats ⁸³	1886	transpiration	26	273–358	
Villiers ⁸⁴	1913	ebulliometer	12	333–373	6
Volmer and Kirchhoff ⁸⁵	1925	effusion	10	303–313	3
von Halban ⁸⁶	1935	resonance light absorption	1 ^b	255	7
Young ⁸⁷	1891	static	11	457–718	2

^a References in boldface indicate primary data sets (see text). ^b Excludes points below the triple point.

of Ambrose and Sprake¹⁹ 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 > 1%, we have selected the data of Schönherr and Hensel⁷⁸ for the highest-

Table 2. Critical Temperature and Pressure of Mercury^a

reference	year	T_c (K)	p_c (MPa)
Koenigsberger ⁹²	1912	~1543	
Menzies ⁸⁸	1913	> 1548	
Bender ⁹³	1915	1923	
Meyer ⁹⁴	1921	1747	
Bernhardt ²⁹	1925	1923	294.2–343.2
Birch ⁹⁵	1932	1733 ± 20	161 ± 5
Hensel and Franck, ⁴⁹ Franck and Hensel ⁹⁶	1966	1763.15 ± 15	151 ± 3
Kikoin and Senchenkov ⁹⁷	1967	1753 ± 10	152 ± 1
Neale and Cusack ⁹⁸	1979	1768 ± 8	167.5 ± 2.5
Hubbard and Ross ⁹⁹	1983	1750	172
Götzlaff ¹⁴	1988	1751 ± 1	167.3 ± 0.2
Kozhevnikov et al. ⁹¹	1996	1764 ± 1	167 ± 3

^a Uncertainties are expressed in units of K and MPa for the temperature and pressure, respectively.

temperature region, 1052–1735 K. This data set was obtained by observing changes in the electrical conductivity. At fixed pressures, the temperature was increased, and when a discontinuity was observed, this was considered to be an indication of phase change.

All of the sets mentioned thus far are given for temperatures of >380 K. At lower temperatures, the measurements are much more uncertain and display significant scatter. In the low-temperature range, we considered the measurements of Ernsberger and Pitman⁴³ to be the most accurate. These measurements were made with an absolute manometer method, with 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.⁸⁹

The triple point of mercury has been designated as a fixed point of the ITS-90 temperature scale,⁹⁰ 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.⁹¹

Correlation Development

Numerous expressions have been used to represent the vapor pressure of a pure fluid; many are reviewed in Růžička and Majer.¹⁰⁰ Equations of the general form

$$\ln\left(\frac{p}{p_c}\right) = \left(\frac{T_c}{T}\right) \sum_i a_i \tau^{i/2} \quad (1)$$

where $\tau = 1 - (T/T_c)$, are attributed to Wagner and co-workers^{101–104} and have been used successfully to represent the vapor pressures of a wide variety of fluids. Lemmon and Goodwin¹⁰⁵ 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 C₃₆. 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,^{101,102} which we call Wagner 3–6. The Wagner 2.5–5 form has emerged as the generally preferred form.¹⁰⁶ 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 acetone-trile,¹⁰⁷ 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 water¹⁰⁸ 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^{109,110} 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.^{100,106,111} 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.¹¹² Both of these approaches can be used to ensure that the vapor pressure is thermodynamically consistent with other thermodynamic data.

King and Al-Najjar¹¹¹ related heat capacity and vapor pressure, using the relation

$$\frac{d}{dT} \left(T^2 \frac{d \ln p_{\text{sat}}}{dT} \right) = \frac{C_p^0 - C_p^L - G}{R} \quad (2)$$

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 constant¹¹³ ($R = 8.314472$ J/(mol K)), p_{sat} is the vapor pressure, and G approximates vapor-phase nonidealities and is given as

$$G = T \left[p_{\text{sat}} \frac{d^2 B}{dT^2} + 2 \frac{dp_{\text{sat}}}{dT} \left(\frac{dB}{dT} - \frac{dV_L}{dT} \right) + \frac{d^2 p_{\text{sat}}}{dT^2} (B - V_L) \right] \quad (3)$$

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.³⁹ 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 $C_p^0 = 5R/2$.¹¹⁴ 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 $(5R/2 - C_p^L)/R = (T/T_c) \sum_i a_i (i/2) [(i/2) - 1] \tau^{(i/2)-1}$.

Busey and Giauque³² 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.¹¹⁵ 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 3. (a) Fitted Values of the Parameters in Eq 4 and Their Standard Deviations, and (b) Fixed Parameters in Eq 4

<i>i</i>	(a) Fitted Values of the Parameters Used in Eq 4		(b) Fixed Parameters Used in Eq 4	
	<i>a_i</i>	standard deviation	<i>T_c</i> (K)	<i>p_c</i> (MPa)
1	-4.57618368	0.0472	1764	167
2	-1.40726277	0.8448		
3	2.36263541	0.8204		
4	-31.0889985	1.3439		
5	58.0183959	2.4999		
6	-27.6304546	1.1798		

Except for the data of Menzies,⁶² all primary data were measured after 1927. The temperatures of the data of Menzies were first converted to the 1948 temperature scale using the procedure given by Douglas et al.³⁹ 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.^{116,117} 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 τ in increments of 0.5, with terms up to τ^{12} . We followed the recommendation of Harvey and Lemmon¹⁰⁸ 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,¹¹⁸ similar to that of earlier work.¹¹⁹ 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.,⁹¹ rather than determining it by fitting experimental data. The minimization was done with orthogonal distance regression, using the NIST statistical package ODRPACK.¹²⁰ 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.³⁹ 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

Table 4. Vapor Pressure of Mercury Calculated Using Eq 4 for 273–333 K

<i>T</i> (K)	<i>t</i> (°C)	<i>p</i> (MPa)	ideal gas density ^a	
			(mol/L)	(ng/mL)
273.15	0	2.698829 × 10 ⁻⁸	1.188337 × 10 ⁻⁸	2.383684
274.15	1	2.979392 × 10 ⁻⁸	1.307088 × 10 ⁻⁸	2.621887
275.15	2	3.286720 × 10 ⁻⁸	1.436675 × 10 ⁻⁸	2.881826
276.15	3	3.623129 × 10 ⁻⁸	1.577990 × 10 ⁻⁸	3.165289
277.15	4	3.991118 × 10 ⁻⁸	1.731989 × 10 ⁻⁸	3.474196
278.15	5	4.393376 × 10 ⁻⁸	1.899698 × 10 ⁻⁸	3.810605
279.15	6	4.832795 × 10 ⁻⁸	2.082217 × 10 ⁻⁸	4.176720
280.15	7	5.312487 × 10 ⁻⁸	2.280723 × 10 ⁻⁸	4.574903
281.15	8	5.835798 × 10 ⁻⁸	2.496477 × 10 ⁻⁸	5.007682
282.15	9	6.406319 × 10 ⁻⁸	2.730825 × 10 ⁻⁸	5.477762
283.15	10	7.027907 × 10 ⁻⁸	2.985209 × 10 ⁻⁸	5.988031
284.15	11	7.704698 × 10 ⁻⁸	3.261169 × 10 ⁻⁸	6.541579
285.15	12	8.441128 × 10 ⁻⁸	3.560348 × 10 ⁻⁸	7.141702
286.15	13	9.241950 × 10 ⁻⁸	3.884501 × 10 ⁻⁸	7.791920
287.15	14	1.011225 × 10 ⁻⁷	4.235498 × 10 ⁻⁸	8.495986
288.15	15	1.105749 × 10 ⁻⁷	4.615334 × 10 ⁻⁸	9.257899
289.15	16	1.208348 × 10 ⁻⁷	5.026135 × 10 ⁻⁸	10.08192
290.15	17	1.319646 × 10 ⁻⁷	5.470161 × 10 ⁻⁸	10.97260
291.15	18	1.440308 × 10 ⁻⁷	5.949822 × 10 ⁻⁸	11.93475
292.15	19	1.571046 × 10 ⁻⁷	6.467678 × 10 ⁻⁸	12.97352
293.15	20	1.712619 × 10 ⁻⁷	7.026452 × 10 ⁻⁸	14.09436
294.15	21	1.865835 × 10 ⁻⁷	7.629036 × 10 ⁻⁸	15.30308
295.15	22	2.031558 × 10 ⁻⁷	8.278502 × 10 ⁻⁸	16.60585
296.15	23	2.210708 × 10 ⁻⁷	8.978112 × 10 ⁻⁸	18.00919
297.15	24	2.404265 × 10 ⁻⁷	9.731323 × 10 ⁻⁸	19.52006
298.15	25	2.613271 × 10 ⁻⁷	1.054180 × 10 ⁻⁷	21.14581
299.15	26	2.838837 × 10 ⁻⁷	1.141344 × 10 ⁻⁷	22.89423
300.15	27	3.082141 × 10 ⁻⁷	1.235036 × 10 ⁻⁷	24.77358
301.15	28	3.344440 × 10 ⁻⁷	1.335691 × 10 ⁻⁷	26.79262
302.15	29	3.627066 × 10 ⁻⁷	1.443770 × 10 ⁻⁷	28.96059
303.15	30	3.931433 × 10 ⁻⁷	1.559763 × 10 ⁻⁷	31.28729
304.15	31	4.259045 × 10 ⁻⁷	1.684185 × 10 ⁻⁷	33.78306
305.15	32	4.611495 × 10 ⁻⁷	1.817581 × 10 ⁻⁷	36.45885
306.15	33	4.990473 × 10 ⁻⁷	1.960527 × 10 ⁻⁷	39.32620
307.15	34	5.397770 × 10 ⁻⁷	2.113631 × 10 ⁻⁷	42.39732
308.15	35	5.835283 × 10 ⁻⁷	2.277535 × 10 ⁻⁷	45.68508
309.15	36	6.305024 × 10 ⁻⁷	2.452917 × 10 ⁻⁷	49.20305
310.15	37	6.809117 × 10 ⁻⁷	2.640489 × 10 ⁻⁷	52.96556
311.15	38	7.349813 × 10 ⁻⁷	2.841004 × 10 ⁻⁷	56.98770
312.15	39	7.929493 × 10 ⁻⁷	3.055255 × 10 ⁻⁷	61.28535
313.15	40	8.550671 × 10 ⁻⁷	3.284075 × 10 ⁻⁷	65.87527
314.15	41	9.216005 × 10 ⁻⁷	3.528344 × 10 ⁻⁷	70.77506
315.15	42	9.928302 × 10 ⁻⁷	3.788986 × 10 ⁻⁷	76.00327
316.15	43	1.069052 × 10 ⁻⁶	4.066972 × 10 ⁻⁷	81.57939
317.15	44	1.150580 × 10 ⁻⁶	4.363324 × 10 ⁻⁷	87.52391
318.15	45	1.237743 × 10 ⁻⁶	4.679116 × 10 ⁻⁷	93.85838
319.15	46	1.330888 × 10 ⁻⁶	5.015475 × 10 ⁻⁷	100.6054
320.15	47	1.430383 × 10 ⁻⁶	5.373585 × 10 ⁻⁷	107.7888
321.15	48	1.536613 × 10 ⁻⁶	5.754690 × 10 ⁻⁷	115.4333
322.15	49	1.649985 × 10 ⁻⁶	6.160093 × 10 ⁻⁷	123.5653
323.15	50	1.770928 × 10 ⁻⁶	6.591162 × 10 ⁻⁷	132.2121
324.15	51	1.899890 × 10 ⁻⁶	7.049329 × 10 ⁻⁷	141.4025
325.15	52	2.037347 × 10 ⁻⁶	7.536097 × 10 ⁻⁷	151.1666
326.15	53	2.183795 × 10 ⁻⁶	8.053040 × 10 ⁻⁷	161.5359
327.15	54	2.339760 × 10 ⁻⁶	8.601806 × 10 ⁻⁷	172.5436
328.15	55	2.505789 × 10 ⁻⁶	9.184118 × 10 ⁻⁷	184.2242
329.15	56	2.682462 × 10 ⁻⁶	9.801783 × 10 ⁻⁷	196.6140
330.15	57	2.870385 × 10 ⁻⁶	1.045669 × 10 ⁻⁶	209.7507
331.15	58	3.070193 × 10 ⁻⁶	1.115081 × 10 ⁻⁶	223.6740
332.15	59	3.282555 × 10 ⁻⁶	1.188620 × 10 ⁻⁶	238.4253
333.15	60	3.508170 × 10 ⁻⁶	1.266503 × 10 ⁻⁶	254.0478

^a Assuming that the ideal gas law applies.

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,

$$\ln\left(\frac{p}{p_c}\right) = \left(\frac{T_c}{T}\right)(a_1\tau + a_2\tau^{1.89} + a_3\tau^2 + a_4\tau^8 + a_5\tau^{8.5} + a_6\tau^9) \quad (4)$$

The regressed coefficients and their standard deviations are given in Table 3a, and fixed parameters for eq 4 are given in

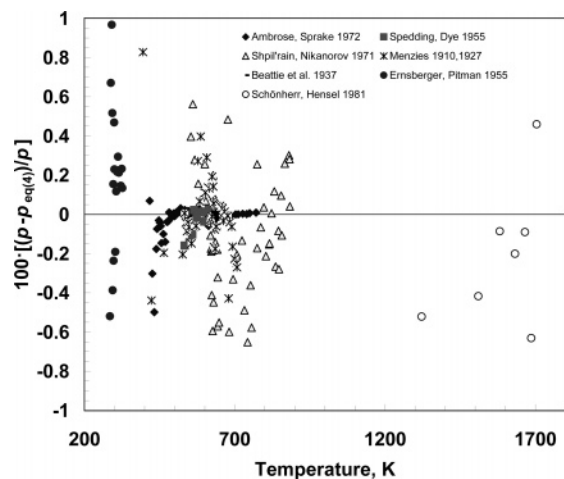


Figure 1. Deviations between the correlation given in eq 4 and the primary data set.

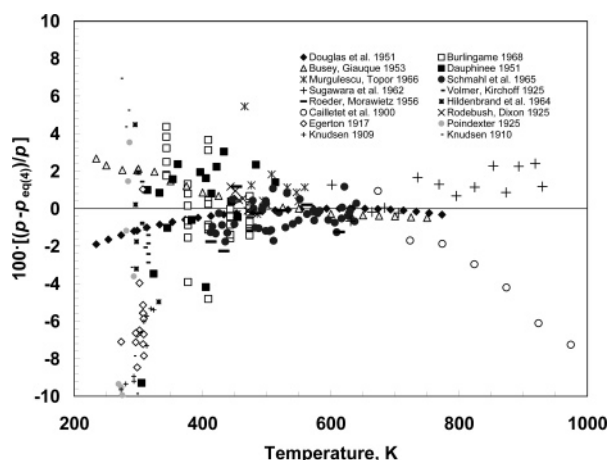


Figure 2. Deviations between the correlation given in eq 4 and selected secondary data.

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 ($\rho = p/(RT)$). We use the currently accepted values of the molar gas constant¹¹³ ($R = 8.314\,472\text{ J}/(\text{mol K})$) and the atomic mass of mercury¹²¹ (200.59 g/mol).

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 $\text{AAD} = (100/n) \sum \text{abs}(p_i^{\text{calc}}/p_i^{\text{expt}} - 1)$, $\text{BIAS} = (100/n) \sum (p_i^{\text{calc}}/p_i^{\text{expt}} - 1)$, and $\text{RMS}^2 = (100/n) \times \sum (p_i^{\text{calc}}/p_i^{\text{expt}} - 1)^2 - ((100/n) \sum (p_i^{\text{calc}}/p_i^{\text{expt}} - 1))^2$, 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 Pitman⁴³ 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%). The very accurate measurements of Beattie et al.²⁸ 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 Menzies⁴¹ and Menzies⁶² are also represented to within their estimated uncertainty. The highest-temperature data of Schönherr and Hensel⁷⁸ 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 $\sim 1360\text{ K}$, 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.³² Both of these sets were not obtained from direct vapor-pressure measurements, but rather were calculated based on caloric 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 Dauphinee³⁷ 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 $100 \times (p_{\text{eq4}} - p_{\text{corr}})/p_{\text{eq4}}$, where p_{corr} is the vapor pressure from correlations in the literature and p_{eq4} 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 $\sim 400\text{ K}$ 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* correlation^{122,123} is based on the *International Critical Tables* of 1928,¹²⁴ whereas the most recent *CRC Handbook*¹²⁵ values are based on the work of Vargaftik et al.,⁹ which itself is based upon the 1972 book of Vukalovich and Fokin.⁵ 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-

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

reference(s)	number of points	<i>T</i> range (K)	estimated uncertainty (%)	Deviation (%)	
				AAD ^a	RMS ^b
Ambrose and Sprake ¹⁹	113 ^c	417–771	<0.03, greatest at lowest <i>T</i>	0.02	0.06
Beattie et al. ²⁸	42	623–636	0.03	0.01	0.01
Ernsberger and Pitman ⁴³	18	285–327	1	0.33	0.35
Smith and Menzies, ⁴¹ Menzies ⁶²	46 ^d	395–708	0.5	0.14	0.20
Schönherr and Hensel ⁷⁸	13	1052–1735	3	1.06	1.42
Shpil'rain and Nikanorov ⁸⁰	50	554–883	0.6–0.8	0.25	0.29
Spedding and Dye ⁸¹	13	534–630	0.03	0.05	0.06

^a Average absolute deviation. ^b Root-mean-square deviation. ^c Two outliers, at 380 and 400 K, were not included in the statistics. ^d One outlier, at 395 K, was not included in the statistics.

Table 6. Summary of Comparisons of the Correlation Given in Eq 4 with Secondary Data for the Vapor Pressure of Mercury

reference(s)	number of points	temperature range (K)	estimated uncertainty (%)	Deviation (%)	
				AAD ^a	RMS ^b
Bernhardt ²⁹	27	694–1706	varies from 2 to >15	14.13	17.26
Bessel-Hagen ³⁰	2	273–293	>20	96.12	2.50
Burlingame ³¹	38	344–409	4	1.44	1.92
Busey and Giauque ³²	24	234–750	varies from 0.2 to 3.5 at lowest <i>T</i>	0.90	1.03
Cailliet et al. ³³	11	673–1154	varies from 1 to 7	3.97	2.26
Callendar and Griffiths ³⁴	2	630	0.2	0.17	0.14
Cammenga ³⁵	graphical results	273–325			
Carlson et al. ³⁶	9	299–549	varies from 3 to >20	19.74	16.83
Dauphinee ^{37,38}	18	305–455	5	2.14	2.94
Douglas et al. ³⁹	30	234–773	varies from 0.03 (at normal boiling point) to 1.5 at lowest <i>T</i>	0.45	0.54
Durrans ⁴⁰	19	290–344		4.63	3.06
Egerton ⁴²	27 ^c	289–309	5	6.99	2.34
Galchenko et al. ⁴⁴	graphical results	523–723	3	na ^d	na ^d
Gebhardt ⁴⁶	9	403–483	8	3.34	4.03
Haber and Kerschbaum ⁴⁷	1	293	2	1.84	na ^d
Hagen ⁴⁸	5	273–473	>20	51.02	57.44
Hensel and Franck ⁴⁹	graphical results	1073–critical	na ^d	na ^d	na ^d
Hertz ⁵⁰	9	363–480	5	4.50	1.94
Heycock and Lamplough ⁵¹	1	630	0.2	0.21	na ^d
Hildenbrand et al. ⁵²	6	295–332	5	2.76	3.16
Hill ⁵³	19	272–308	30	29.40	4.38
Hubbard and Ross ⁵⁴	graphical results	742–1271	na	na ^d	na ^d
Jenkins ⁵⁵	21	479–671	varies from 0.1 to >20	5.08	5.67
Kahlbaum ⁵⁶	43	393–493	>10	8.89	9.47
Knudsen ⁵⁷	10	273–324	varies from 5 to 10	7.36	1.67
Knudsen ⁵⁸	7	263–298	varies from 5 to 10	7.12	7.64
Kordes and Raaz ⁵⁹	2	630–632	4	2.59	1.84
Mayer ⁶⁰	82	261–298	5, except greater at <i>T</i> < 270 K	6.72	8.86
McLeod ⁶¹	1	293	>20	77.65	na ^d
Millar ⁶³	6	468–614	2	1.27	1.84
Morley ⁶⁴	6	289–343	varies from 8 to >20	17.58	11.82
Murgulescu and Topor ⁶⁵	9	301–549	3	1.41	1.56
Neumann and Völker ⁶⁶	19	290–344	6	4.63	3.06
Pedder and Barratt ⁶⁷	3	559–573	2	1.14	0.94
Pfaundler ⁶⁸	3	288–372	12	8.06	5.76
Poindexter ⁶⁹	17	235–293	>5–20; greatest at lowest <i>T</i>	28.23	29.19
Ramsay and Young ⁷¹	13	495–721	varies from 0.3 to 10 at highest <i>T</i>	3.23	3.02
Regnault ⁷²	29	297–785	~6 for <i>T</i> > 400 K, much higher for lower <i>T</i>	24.74	34.03
Rodebush and Dixon ⁷³	7	444–476	1	0.53	0.54
Roeder and Morawietz ⁷⁴	7	413–614	2	1.00	1.11
Ruff and Bergdahl ⁷⁵	12	478–630	>20	22.49	25.78
Schmahl et al. ⁷⁶	43	412–640	1.5	0.70	0.71
Schneider and Schupp ⁷⁷	23	484–575	10	4.04	5.02
Scott ⁷⁹	1	293	2	1.11	na ^d
Stock and Zimmermann ⁸²	3	253–283	20	15.05	16.80
Sugawara et al. ¹⁰	14	602–930	2	1.15	0.95
van der Plaats ⁸³	26	273–358	>20	86.65	23.03
Villiers ⁸⁴	12	333–373	6	4.76	3.24
Volmer and Kirchhoff ⁸⁵	10	303–313	3	1.57	1.13
von Halban ⁸⁶	2	220–255	7	8.15	2.21
Young ⁸⁷	11	457–718	2	1.40	1.30

^a Average absolute deviation. ^b Root-mean-square deviation. ^c One outlier, at 288.6 K, was not included in the statistics. ^d Not applicable.

lations should not be extrapolated outside of their given ranges. 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 corre-

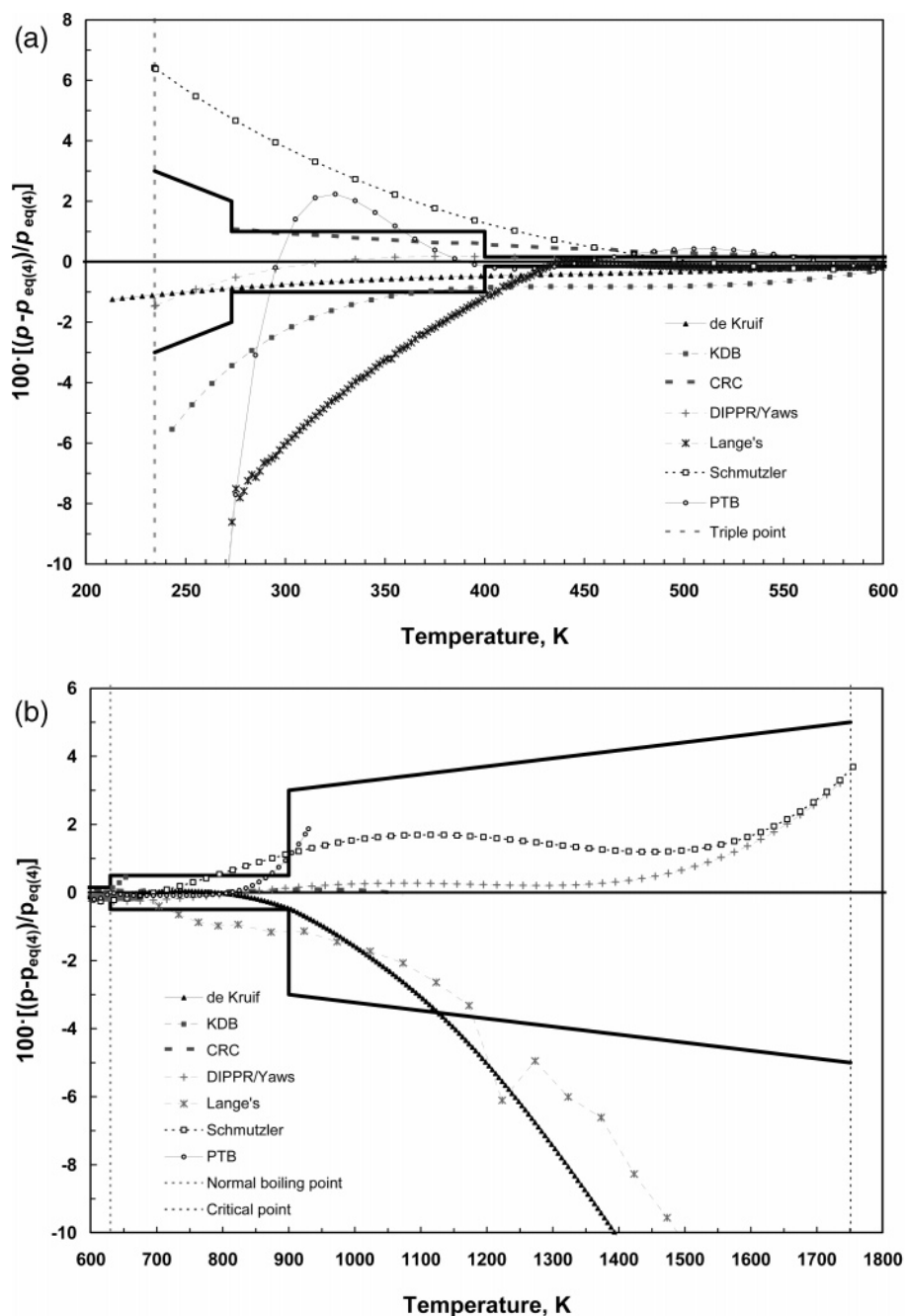


Figure 3. Comparison of the new correlation, eq 4, with previous compilations and correlations in (a) the low-temperature region, up to 600 K, and (b) the high-temperature region, from 600 K to the critical temperature. In each panel, the uncertainty band for eq 4 is indicated by a heavy black solid line.

lation^{21,22} does not specifically state the temperature limits of the correlation; however, the very thorough literature survey in the thesis²¹ indicates that the only high-temperature data used in their work were those of Bernhardt²⁹ and Cailletet et al.,³³ and they did not have access to the more-recent measurements of Shpil'rain and Nikanorov,⁸⁰ Sugawara et al.,¹⁰ or Schönherr and Hensel.⁷⁸ *Lange's Handbook*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 DIPPR¹²⁷ and Yaws¹²⁸ 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 Götzlaff¹⁴) 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 Warren⁸ seem to have been generated from the Schmutzler correlation.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 Pitman⁴³ 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

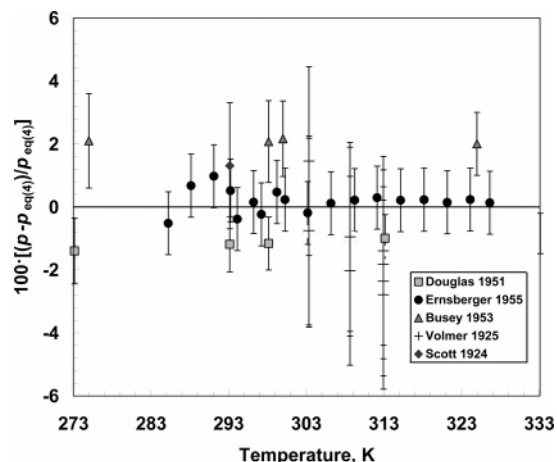


Figure 4. Comparison of the new correlation, eq 4, in the temperature range of 273–333 K with experimental data, with estimated uncertainties of 3% or less.

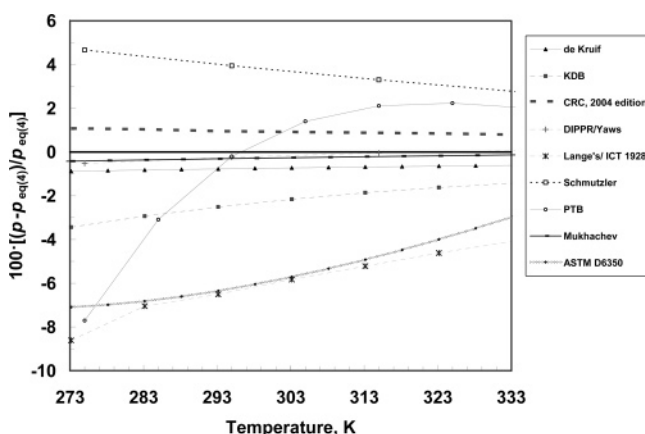


Figure 5. Comparison of the new correlation, eq 4, in the temperature range of 273–333 K with correlations from the literature.

estimated uncertainties of 3% or less in this temperature range. The data of both Busey and Giauque³² and Douglas et al.³⁹ were not direct measurements but rather were 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 have a slightly higher (3%) estimated uncertainty and are represented well by the correlation.

Figure 5 compares correlations in the literature with eq 4 for the temperature range of 273–333 K (0–60 °C). There are four correlations that agree with eq 4 to within our estimated uncertainty of 1%: those by de Kruijf,^{21,22} DIPPR,¹²⁷ Yaws,¹²⁸ and Mukhachev et al.¹⁷ Yaws¹²⁸ does not state the uncertainty of his equation; however, the DIPPR¹²⁷ equation reports an estimated uncertainty of <3%, and the two correlations are almost indistinguishable from each other and are shown here as a single curve. The DIPPR correlation was developed by fitting vapor-pressure data, with a primary data set that consisted of 54 experimental points from Ambrose and Sprake¹⁹ for temperatures of 426–771 K, nine smoothed points from the correlation of Stull¹² for 399–596 K, and 81 points from the tables in Vargaftik¹²⁹ for temperatures of 273–1073 K.¹³⁰ The correlation of de Kruijf^{21,22} was developed using the method of Clark and Glew¹³¹ that, in addition to vapor-pressure data, used

supplementary data such as heat capacities, Gibbs free energies of vaporization, and enthalpies of vaporization to develop the correlation. The curve from the *CRC Handbook* (85th Edition) is based on that of Vargaftik et al.,⁹ which itself is based on the work of Vukalovich and Fokin.⁵ The Vukalovich and Fokin⁵ source lists the data used in the development of the equation, and apparently they were unaware of the data of Ernsberger and Pitman.⁴³ As mentioned previously, Ernsberger and Pitman⁴³ 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 Poindexter⁶⁹ and Neumann and Völker.⁶⁶ 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 $R = 8.314472 \text{ J}/(\text{mol K})$. It agrees well with the values from *Lange's Handbook*^{122,123} 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 Handbook*¹²² 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 point⁹⁰ (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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