Correlation for the Second Virial Coefficient of Water

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(Received 18 November 2002; revised 26 March 2003; accepted 7 May 2003; published online 4 March 2004)

A new correlation has been developed to represent the second virial coefficient of water (H_2O) as a function of temperature. The formulation was fitted to experimental data, both for the second virial coefficient itself and for a quantity related to its first temperature derivative, at temperatures between approximately 310 and 1170 K. The high-temperature extrapolation behavior was guided by results calculated from a high-quality intermolecular pair potential. The new correlation agrees well with the experimental data deemed to be reliable, and at high temperatures is a significant improvement over the best previous formulation. © *2004 by the U.S. Secretary of Commerce on behalf of the United States. All rights reserved.* [DOI: 10.1063/1.1587731]

Key words: H_2O, second virial coefficient, steam, thermodynamics, water.

Contents

1. Introduction. 369
2. Data Sources. 370
   2.1. Data for B from pVT Measurements. 370
   2.2. Data for B from Saturated Vapor Measurements. 370
   2.3. Data for $B-T(\mathrm{d}B/\mathrm{d}T)$. 371
   2.4. Estimated Values of B from a Pair Potential. 371
3. Fitting Procedure. 372
4. Results and Comparison with Data. 372
   4.1. Low Temperatures. 373
   4.2. High Temperatures. 373
5. Discussion of Uncertainty in $B(T)$. 375
6. Conclusions. 375
7. Acknowledgments. 375
8. References. 375

List of Tables

1. H_2O second virial coefficients B derived from saturation data of Osborne *et al.*[10,11]. 370
2. Values of $\phi^\circ = B-T(\mathrm{d}B/\mathrm{d}T)$ from μ_{JT} data of Ertle[19]. 371
3. Values of $\phi^\circ = B-T(\mathrm{d}B/\mathrm{d}T)$ from δ_T data of Ertle[19]. 371
4. Parameters for Eq. (6). 372
5. Values of B and of $\phi^\circ = B-T(\mathrm{d}B/\mathrm{d}T)$ calculated from Eq. (6). 372

List of Figures

1. Deviations of B from Eq. (6) at low temperatures. 373
2. Deviations of $\phi^\circ = B-T(\mathrm{d}B/\mathrm{d}T)$ from Eq. (6) at low temperatures. 373
3. Deviations of B from Eq. (6) at high temperatures. 374
4. Deviations of $\phi^\circ = B-T(\mathrm{d}B/\mathrm{d}T)$ from Eq. (6) at high temperatures. 374
5. Deviations of B from Eq. (6) at very high temperatures. 374

1. Introduction

The second virial coefficient of water is a fundamental thermodynamic quantity for an important fluid. In addition to being useful in its own right, knowledge of water's second virial coefficient B [and sometimes its temperature dependence, $B(T)$] is needed in order to extract information on cross second virial coefficients from data for aqueous vapor mixtures; these cross coefficients are important for accurate thermodynamic descriptions in a variety of systems, such as combustion gases and humidity standards. Also, theoretical chemists who develop intermolecular potentials for water often compare second virial coefficients calculated from their potentials to those of real water; such comparisons have not always used the best available values.

Harvey[1] concluded that the best existing representation of $B(T)$ in the range he studied was given by Hill and MacMillan.[2] However, their correlation was fitted only at temperatures up to 573 K. Some applications, such as combustion gases, require $B(T)$ at higher temperatures. Also, new data for $B(T)$ have been published by several groups.[3–7] Our goal was to produce a correlation that took into account these new data and covered a larger temperature range. We limited our work to ordinary water (H_2O). Hill and MacMillan[2] also considered heavy water (D_2O), but we did not seek to improve on their work for D_2O since that fluid is of less importance and few new data have been reported.

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2. Data Sources

2.1. Data for *B* from *pVT* Measurements

The second virial coefficient of a fluid may be extracted from precise pressure–volume–temperature (pVT) measurements, often involving successive expansions of the fluid. However, for water below approximately 500 K, adsorption on the apparatus distorts these experiments significantly. Since the magnitude of this effect was not fully appreciated until relatively recently, second virial coefficients for water published prior to about 1980 are effectively obsolete, especially at lower temperatures. We therefore will use only values of B from recent studies where adsorption has been explicitly taken into account, or from studies at temperatures sufficiently high that adsorption effects are negligible.

Eubank *et al.*[3] reported the results of Burnett expansion experiments at temperatures from approximately 348 to 623 K, taking great pains to correct the results for adsorption. Two different sets of results were recommended, reflecting two different methods of dealing with adsorption. Set II covered a wider range of temperatures; Set III covered a subset of the points in Set II and was said to have smaller adsorption corrections (though the reported uncertainties were somewhat larger for Set III). Agreement between the two sets is excellent, well within their estimated uncertainties. At temperatures where values for both Set II and Set III were given, we took their arithmetic mean; otherwise the Set II values were used. Three of these points were later duplicated in a different analysis by Warowny and Eubank;[4] we did not add these points to our study since they were essentially identical to those from the earlier work.

Kell *et al.*[5] reported adsorption-corrected values of B that superseded previous work from the same laboratory.[8] These data range from approximately 423 to 773 K; their claimed uncertainties are for the most part somewhat smaller than those of Eubank *et al.*[3]

Abdulagatov *et al.*[6] extracted second virial coefficients from pVT measurements at four temperatures from approximately 523 to 653 K. While no adsorption corrections were made, the temperatures are high enough that such corrections are likely to be small.

Hendl *et al.*[7] reevaluated older data from their laboratory and derived adsorption-corrected values for B between 381 and 524 K. Their results, while internally consistent, for the most part disagree with the studies mentioned previously; we will discuss this disagreement in a subsequent section.

At high temperatures (above 773 K), the only available data for B appear to be those derived from pVT measurements by Vukalovich *et al.*[9]

2.2. Data for *B* from Saturated Vapor Measurements

The vaporization data of Osborne *et al.*[10,11] can yield reliable values of B at some temperatures; this calculation utilizes the Clapeyron equation relating the enthalpy of vaporization to the slope of the vapor pressure curve and the volume change of vaporization. Osborne *et al.*[10,11] reported calorimetric measurements of the quantity γ, defined by

$$\gamma = v'' T \frac{\mathrm{d}p^{\mathrm{s}}}{\mathrm{d}T}, \tag{1}$$

where v'' is the molar volume of the saturated vapor, T is the absolute temperature, and p^{s} is the saturation pressure. Knowledge of the vapor-pressure curve $p^{\mathrm{s}}(T)$ allows calculation of v'' from γ. Then, the virial expansion can be written for the saturated vapor as

$$\frac{p^{\mathrm{s}} v''}{RT} = 1 + \frac{B}{v''} + \frac{C}{v''^2} + \ldots, \tag{2}$$

where C is the third virial coefficient and R is the molar gas constant. At sufficiently low p^{s}, contributions from the third and higher virial coefficients are negligible and Eq. (2) can be solved directly for B; at somewhat higher pressures, estimated values of C can be used.

In order to calculate B from measurements of γ with Eqs. (1) and (2), we used $p^{\mathrm{s}}(T)$ as correlated by Wagner and Pruß,[12] and $C(T)$ as given by the equation of state of Wagner and Pruß.[13] The original measurements of γ in "international joules" were converted to SI joules by multiplying by 1.000 165; this factor affected γ by an amount slightly larger than the uncertainty in measuring γ. The results of these calculations are given in Table 1. We note that Table 1 does not cover all temperatures for which γ was measured; reliable values of B can be obtained only in a window of temperatures. At low temperatures (and therefore low values of p^{s}), $p^{\mathrm{s}} v''/RT$ is so close to unity that the derived value of B is overly sensitive to the uncertainty in the measurement of γ. At higher temperatures (and therefore high p^{s}), the contributions of higher-order terms are too large.

The uncertainties in Table 1 were computed from three components. The first is the effect on B from the standard deviation in the reported measurements of γ at each temperature. The second contribution is the effect on B from the uncertainty in p^{s} at each temperature; here we used the uncertainties quoted by Wagner and Pruß[12] for their correlation of $p^{\mathrm{s}}(T)$. The third contribution was a rough estimate of the combined effect of uncertainty in C and of ignoring higher-order terms in Eq. (2). This contribution was non-negligible only for the four highest temperatures in Table 1, but it pro-

TABLE 1. H_2O second virial coefficients B derived from saturation data of Osborne *et al.*[10,11]

T (K)	B ($\mathrm{cm^3 \cdot mol^{-1}}$)	Uncertainty in B ($\mathrm{cm^3 \cdot mol^{-1}}$)
323.127	−844	43
333.125	−728	21
343.124	−634	11
353.123	−559	7
363.124	−498	5
373.124	−454	5
423.135	−287	6
473.153	−200	16

vided the majority of the uncertainty for the points at 423 and 473 K. For the points at lower temperatures, the uncertainty from γ and that from p^s were of similar magnitude.

One might think of adding a contribution from the uncertainty in dp^s/dT in Eq. (1). However, these measurements of γ were also used in correlating the temperature dependence of p^s.[12] Therefore, any errors in γ and in dp^s/dT will be highly correlated. Furthermore, because those two quantities appear on opposite sides of Eq. (1), these errors would tend to cancel each other out in the calculation of v''. An extra uncertainty component for dp^s/dT is therefore not needed.

2.3. Data for $B-T(dB/dT)$

More information on $B(T)$ can be obtained from expansion experiments on steam. The second virial coefficient and its temperature dependence can be combined into the function $\phi°$, defined by

$$\phi° = B - T\frac{dB}{dT}. \tag{3}$$

$\phi°$ is related to the low-pressure limit of the Joule–Thomson coefficient $[\mu_{JT}=(\partial T/\partial p)_h$, where h is the molar enthalpy] and of the isothermal throttling coefficient $[\delta_T=(\partial h/\partial p)_T]$ by the following relationships:

$$\phi° = \lim_{p\to 0} \delta_T \tag{4}$$

$$\phi° = -c_p^0 \lim_{p\to 0} \mu_{JT}, \tag{5}$$

where c_p^0 is the molar isobaric heat capacity in the ideal-gas state. We use c_p^0 as correlated by Cooper,[14] which is also used in the international standard equation of state for water.[13]

Values of $\phi°$ obtained from isothermal throttling experiments *via* Eq. (4) have been published by Collins and Keyes[15] and by McGlashan and Wormald.[16] The latter paper contains (in reanalyzed form) data from the thesis of Wormald[17] that had been used in some previous formulations of $B(T)$. McGlashan and Wormald diagnosed a probable heat leak that distorted the lowest-temperature values reported by Collins and Keyes and provided corrected numbers; we use those corrected values here. The isothermal throttling measurements of LeFevre *et al.*[18] were too scattered to be of use in this work.

In addition, Ertle[19] reported measurements of both μ_{JT} and δ_T for steam over a range of pressures at temperatures up to 1073 K. At each pressure and temperature, several (usually four) data points were reported. We converted these data to $\phi°$ with Eqs. (4) and (5); the results are given in Tables 2 and 3. In both tables, the uncertainties given (one standard deviation) result both from the scatter among the duplicate points in the original data and from our estimate of the uncertainty in the extrapolation to zero pressure; the scatter in the data is in all cases the dominant contribution.

If one compares Tables 2 and 3, it is apparent that the agreement of the derived values of $\phi°$ at common temperatures is much better than would be expected based on the scatter in the reported measurements. This strongly suggests that the data points reported in Ertle's μ_{JT} experiments and δ_T experiments are not completely independent. In the remainder of this work, we will restrict our attention to the points in Table 2, since the points in Table 3 are effectively redundant.

TABLE 2. Values of $\phi°=B-T(dB/dT)$ from μ_{JT} data of Ertle[19]

T (K)	$\phi°$ ($cm^3\cdot mol^{-1}$)	Uncertainty in $\phi°$ ($cm^3\cdot mol^{-1}$)
431.88	−1197.7	7.2
486.14	−768.1	13.6
521.16	−598.4	3.0
572.25	−453.8	3.7
623.04	−350.1	3.6
673.15	−278.6	3.7
723.27	−229.6	2.4
773.22	−191.3	2.2
822.98	−161.3	2.0
873.00	−137.8	1.8
923.43	−119.1	1.4
973.40	−104.0	1.2
1023.66	−90.7	0.9
1073.80	−79.5	0.7

2.4. Estimated Values of B from a Pair Potential

As mentioned previously, high-temperature data for $B(T)$ are scarce; the only data above 773 K are from Vukalovich *et al.*,[9] and their experimental procedure and uncertainty are not well documented. Above 1173 K, there are no data at all. For applications such as combustion gases, it is desirable to have a good estimate of $B(T)$ at higher temperatures.

It is possible to calculate $B(T)$ from statistical mechanics, provided the intermolecular pair potential is known with sufficient accuracy. For small molecules, it is now possible to derive accurate pair potentials from *ab initio* quantum mechanics; such potentials have been used to derive values of $B(T)$ considered more reliable than those obtainable experimentally for helium[20] and for cross second virial coefficients of water with noble gases.[21–23] For pure water, Harvey[1] determined that this route to $B(T)$, with quantum effects in-

TABLE 3. Values of $\phi°=B-T(dB/dT)$ from δ_T data of Ertle[19]

T (K)	$\phi°$ ($cm^3\cdot mol^{-1}$)	Uncertainty in $\phi°$ ($cm^3\cdot mol^{-1}$)
622.45	−352.4	3.1
673.31	−279.0	4.1
723.43	−229.1	2.8
773.42	−190.9	2.4
823.12	−161.1	2.0
873.15	−137.7	1.8
923.55	−119.2	1.4
973.52	−103.8	0.9
1023.78	−90.7	0.9
1073.97	−79.5	0.5

cluded to first order, was not sufficiently accurate at low and moderate temperatures. This was attributed in part to large rotational quantum corrections (due to water's large intermolecular torques and small moment of inertia) that at the time could not be calculated to sufficiently high order [subsequently, Schenter[24] presented a method for incorporating rotational degrees of freedom in a fully quantum calculation of $B(T)$]. Because these quantum effects are much smaller at high temperatures, they can be treated to first order and still produce reliable values to guide the high-temperature behavior of our correlation.

For this purpose, we used the SAPT-5s potential of Mas *et al.*[25] Other pair potentials of similarly high quality exist in the literature;[26–28] we chose SAPT-5s because computer code was available in convenient form and because it produced values of $B(T)$ that closely matched the data of Kell *et al.*[5] above 700 K and that agreed reasonably well with the data of Vukalovich *et al.*[9] Second virial coefficients, including first-order quantum corrections, were calculated at temperatures up to 3000 K by procedures identical to those described by Hodges *et al.*[21] The uncertainty in the numerical evaluation of $B(T)$ from the pair potential is less than 0.1 $\mathrm{cm^3 \cdot mol^{-1}}$.

3. Fitting Procedure

All temperatures for experimental data were converted to the ITS-90 scale by standard procedures. Effects of temperature scales were insignificantly small except in the processing of the saturation measurements of Osborne *et al.*[10,11]

The functional form to which $B(T)$ was fit was that used previously for correlating cross second virial coefficients of water with nonpolar gases.[21,22] This form obeys the necessary boundary conditions that $B(T)$ is bounded from above and goes to negative infinity in the low-temperature limit. The number of terms was increased until additional terms did not improve the fit significantly. Data points that appeared to be outliers were excluded if omitting them significantly improved the root-mean-square deviation of the fit.

The fit was primarily determined by the $B(T)$ data of Eubank *et al.*,[3] Kell *et al.*[5] and Osborne *et al.*,[10,11] and to a lesser extent by the $B(T)$ data of Abdulagatov *et al.*[6] and Vukalovich *et al.*,[9] the values of $B(T)$ generated from the SAPT-5s potential,[25] and the $\phi°$ data of McGlashan and Wormald.[16] Other data not included in the fit will be discussed in Sec. 4.

4. Results and Comparison with Data

The final equation is

$$B(T)/B^0 = \sum_{i=1}^{4} a_i (T^*)^{b_i}, \tag{6}$$

where $B^0 = 1000\ \mathrm{cm^3 \cdot mol^{-1}}$, $T^* = T/100$ K, and the coefficients a_i and b_i are listed in Table 4. For easy reference, in Table 5 we give values of B and $\phi° = B - T(\mathrm{d}B/\mathrm{d}T)$ calculated from Eq. (6) at selected temperatures. The number of digits printed in Table 5 should not be taken as an indication of uncertainty; Section 5 should be consulted for that information.

TABLE 4. Parameters for Eq. (6)

i	a_i	b_i
1	0.344 04	−0.5
2	−0.758 26	−0.8
3	−24.219	−3.35
4	−3978.2	−8.3

In addition to comparing Eq. (6) with experimental data, we will include in our comparisons the correlation of Hill and MacMillan,[2] which was judged previously[1] to be the best existing correlation, at least in its temperature range of validity. We also compare with values of $B(T)$ given by the current international standard equation of state for the properties of water and steam, as documented by Wagner and Pruß.[13] This equation was not specifically fitted to second virial coefficients, so it cannot be expected to reproduce $B(T)$ as well as correlations fitted directly to those data.

TABLE 5. Values of B and of $\phi° = B - T(\mathrm{d}B/\mathrm{d}T)$ calculated from Eq. (6)

T (K)	B ($\mathrm{cm^3 \cdot mol^{-1}}$)	$\phi°$ ($\mathrm{cm^3 \cdot mol^{-1}}$)
300	−1163.0	−6980.9
325	−795.94	−4364.0
350	−580.11	−2938.4
375	−443.32	−2101.9
400	−351.11	−1578.0
425	−285.75	−1230.9
450	−237.52	−989.54
475	−200.75	−814.88
500	−171.97	−684.12
525	−148.94	−583.45
550	−130.18	−504.11
575	−114.67	−440.34
600	−101.66	−388.22
625	−90.64	−345.02
650	−81.20	−308.77
675	−73.04	−278.03
700	−65.94	−251.72
725	−59.72	−229.00
750	−54.23	−209.24
775	−49.35	−191.94
800	−45.00	−176.70
850	−37.58	−151.17
900	−31.51	−130.74
950	−26.47	−114.11
1000	−22.22	−100.37
1100	−15.49	−79.12
1200	−10.43	−63.58
1300	−6.50	−51.79
1400	−3.37	−42.60
1500	−0.84	−35.25
1600	1.26	−29.26
1800	4.49	−20.10
2000	6.85	−13.46
2500	10.57	−2.90
3000	12.64	3.21

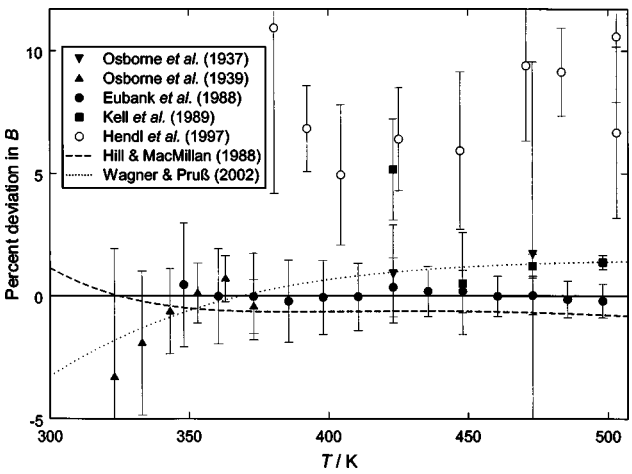

FIG. 1. Deviations of B from Eq. (6) at low temperatures.

However, it made use of data from some of our key sources, notably the pVT data of Kell *et al.*[5] and the saturation data of Osborne *et al.*[10,11] It therefore can be expected to give reasonable values of $B(T)$, and it is interesting to see how accurately such a wide-ranging equation of state can reproduce second virial coefficients.

4.1. Low Temperatures

At low temperatures, Fig. 1 shows the relative deviations from Eq. (6) of both experimental values of B and values calculated from the correlation of Hill and MacMillan[2] and the equation of state of Wagner and Pruß.[13] Figure 2 is a similar figure for $\phi°$.

The most striking aspect of Fig. 1 is the inconsistency of the data of Hendl *et al.*[7] with the other data sources. Because the other three independent sources are in fairly good agreement, and because the $B(T)$ function could not be made to agree with Hendl *et al.*[7] without drastically worsening the prediction of $\phi°$ shown in Fig. 2, we disregarded these data. The data point from Kell *et al.*[5] near 423 K appears to be an outlier and was discarded; apart from this point, the only disagreement outside the stated uncertainties of the data is between Eubank *et al.*[3] and Kell *et al.*[5] near 498 K. Our correlation reproduces all the accepted data within their stated uncertainties except for the two points of Kell *et al.*[5] near 473 and 498 K.

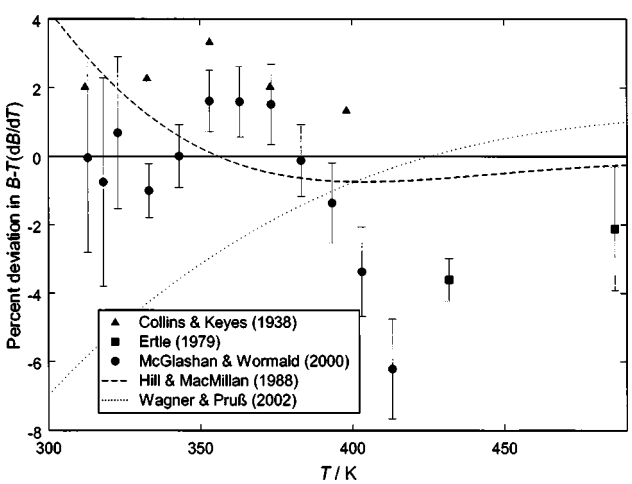

FIG. 2. Deviations of $\phi° = B - T(\mathrm{d}B/\mathrm{d}T)$ from Eq. (6) at low temperatures.

The correlation of Hill and MacMillan[2] also performs well in the temperature range of Fig. 1. The equation of state of Wagner and Pruß[13] differs somewhat at the high-temperature end of Fig. 1, going through the data of Kell *et al.*;[5] this is expected because Kell's pVT data were used to fit that equation.

In Fig. 2, we see that our correlation is fairly consistent with the low-temperature $\phi°$ data of McGlashan and Wormald.[16] It was not possible to obtain a smooth fit that passed through all their data points, especially for the points above 400 K where this would have greatly increased the disagreement with data for B in Fig. 1. Equation (6) is also fairly consistent (though with an apparent systematic deviation) with the data of Collins and Keyes;[15] these points are shown without error bars because their uncertainty was not reported. The two points from Ertle[19] are also missed to some extent. Again, Eq. (6) could not be made to pass through these without seriously degrading the fit of the $B(T)$ data. Since the error bars we have assigned to Ertle's data represent only the scatter in the measurements at each temperature, it is likely that the actual uncertainties are larger than implied in Fig. 2, especially for the point near 430 K.

The correlation of Hill and MacMillan[2] behaves similarly to Eq. (6), although at the lowest temperatures it is less consistent with the data of McGlashan and Wormald[16] and more consistent with those of Collins and Keyes.[15] Wagner and Pruß[13] deviate significantly from the $\phi°$ data of McGlashan and Wormald[16] at temperatures below about 380 K. The reason for this can be seen in Fig. 1, where Wagner and Pruß[13] follow more closely the low-temperature data of Osborne *et al.*,[11] to which their equation was fitted in part. This causes their values of $\phi°$ to be lower. In fitting Eq. (6), we chose to accept slightly worse agreement with the two lowest $B(T)$ points of Osborne *et al.*[11] (though our fit still lies within their uncertainties) in order to be consistent with the $\phi°$ data of McGlashan and Wormald.[16]

4.2. High Temperatures

Figures 3 and 4 are similar deviation plots to Figs. 1 and 2, except that they cover a higher temperature range. Unlike Figs. 1 and 2, Figs. 3 and 4 report absolute deviations in B and $\phi°$ rather than relative deviations; this is because $B(T)$ passes through zero at a high temperature, making a relative deviation meaningless.

In Fig. 3, we see that there is some inconsistency among the different data sets between about 500 and 650 K, although the differences are not much larger than the mutual uncertainties of the experiments. At the temperatures in Fig. 3 where data from Eubank *et al.*[3] are reported, Eq. (6) gives values intermediate between those data and the data of Kell *et al.*[5] At higher temperatures, it closely follows the data of

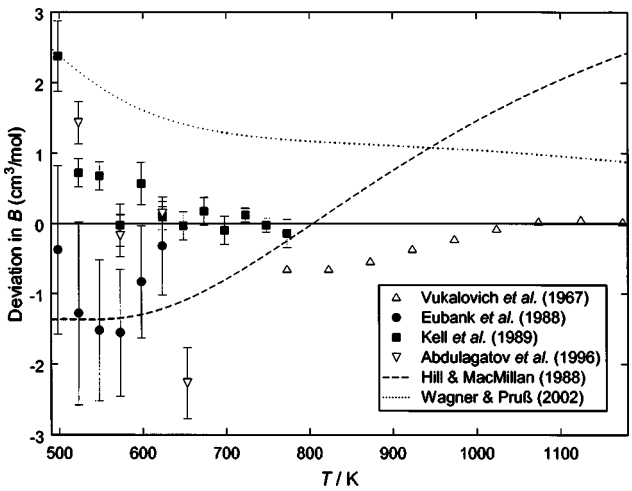

FIG. 3. Deviations of B from Eq. (6) at high temperatures.

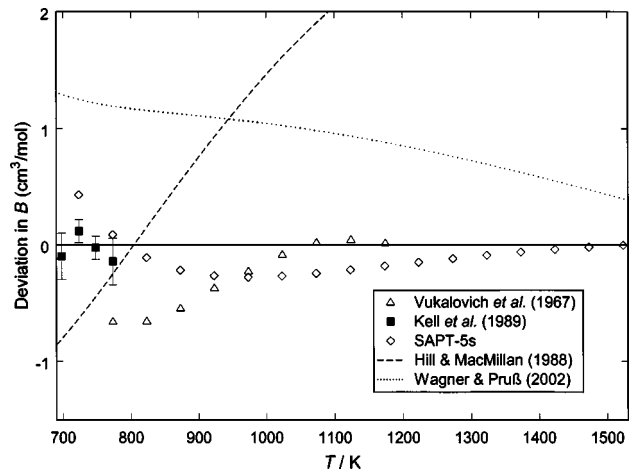

FIG. 5. Deviations of B from Eq. (6) at very high temperatures.

Kell *et al.*[5] Two of the four points from Abdulagatov *et al.*[6] deviate from Eq. (6), but no systematic trend is evident. At higher temperatures, Eq. (6) is consistent with the data of Vukalovich *et al.*[9] The smooth systematic trend for these data in Fig. 3 is probably due to the use of a smoothing equation by Vukalovich *et al.*;[9] unfortunately no uncertainties for these values were reported.

The correlation of Hill and MacMillan[2] is in fair agreement with the data (less so with the values of Kell *et al.*[5]) up to about 800 K, after which it produces increasingly larger deviations. This is not surprising, since it was fitted only up to 573 K. The equation of state of Wagner and Pruß[13] agrees with the data of Kell *et al.*[5] near 500 K, after which it systematically overpredicts $B(T)$, though not by a very large amount.

Figure 4 shows deviations for $\phi°$. While Eq. (6) is fairly consistent with the data of Ertle,[19] it was not possible to obtain complete agreement with these data without significantly degrading the agreement with values of B shown in Fig. 3. The correlation of Hill and MacMillan[2] is reasonably consistent with Ertle's data in the range where the correlation

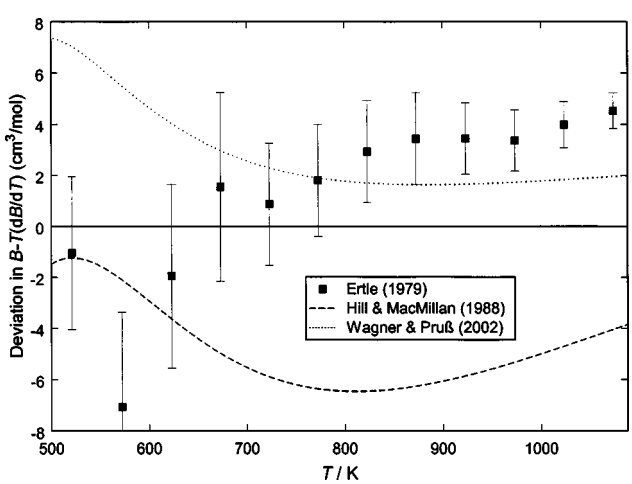

FIG. 4. Deviations of $\phi° = B - T(\mathrm{d}B/\mathrm{d}T)$ from Eq. (6) at high temperatures.

was fitted, but deviates more at higher temperatures. The equation of state of Wagner and Pruß[13] disagrees more with the data of Ertle[19] at the lower temperatures in Fig. 4, but is in better agreement at the higher temperatures.

Finally, we examine the behavior of Eq. (6) at very high temperatures. Figure 5 shows the deviations from Eq. (6) of the four highest-temperature points of Kell *et al.*[5] and of the data of Vukalovich *et al.*[9] It also shows values of B calculated from the SAPT-5s pair potential[25] (these values were omitted from Fig. 3 for clarity). The SAPT-5s values are consistent with the two experimental data sets in this range, increasing our confidence in the accuracy of the pair potential and resulting values of $B(T)$. Equation (6) follows the SAPT-5s values closely at high temperatures (up to 3000 K); we believe these values provide as trustworthy an extrapolation as can be obtained for $B(T)$. The correlation of Hill and MacMillan,[2] which was not intended for such high temperatures, is increasingly inaccurate in this region, while the equation of state of Wagner and Pruß[13] gives reasonable behavior of $B(T)$ at very high temperatures despite being systematically high compared to the data at intermediate temperatures. The Boyle temperature (where $B(T)=0$) for Eq. (6) is 1538 K; this compares to 1408 K for Hill and MacMillan[2] and 1519 K for Wagner and Pruß.[13]

After this work was completed, Abdulagatov *et al.*[29] published values of the quantity

$$2T\frac{\mathrm{d}B}{\mathrm{d}T} + T^2\frac{\mathrm{d}^2B}{\mathrm{d}T^2}$$

derived from analysis of existing isochoric heat-capacity data between approximately 578 and 1024 K. Their values are in good agreement with those from Eq. (6) above 700 K. At lower temperatures, there is a systematic deviation of their values not only from Eq. (6), but also from other correlations for $B(T)$. Since $B(T)$ in this range is fairly well determined, this suggests problems in the heat-capacity measurements. In reporting their comprehensive equation of state for water, Wagner and Pruß[13] commented on apparent inconsistencies below 725 K in some of these isochoric heat-capacity data.

5. Discussion of Uncertainty in $B(T)$

While a formal uncertainty analysis is impractical for a correlation fitted to a variety of data such as this, we can make reasonable estimates of the quality of the correlation. The uncertainty in $B(T)$ is governed by the scatter and uncertainties in the original experimental data, including regions where data from different sources are not mutually consistent.

At temperatures below 500 K, the uncertainty in $B(T)$ can be estimated from Fig. 1. Below 350 K, a reasonable estimate of uncertainty is given by the error bars on the data of Osborne *et al.*[11] Between 350 and 500 K, it appears that $B(T)$ is determined to within 2% or better. The values of $\phi°$ shown in Fig. 2 generally confirm this analysis, although a few $\phi°$ points between 400 and 450 K are not consistent with the $B(T)$ measurements.

Between approximately 500 and 650 K, the deviation between different data sets is illustrated in Fig. 3, and we have no way to reconcile the disagreement. It seems that there is an uncertainty of about $1.5\ \mathrm{cm^3 \cdot mol^{-1}}$ for $B(T)$ in this region. At higher temperatures, the data of Kell *et al.*[5] have small reported uncertainties, but the fact that many of their data do not agree with Eubank *et al.*[3] within those uncertainties at lower temperatures suggests caution. However, the agreement with Vukalovich *et al.*[9] where the sources overlap near 773 K is encouraging. We can therefore estimate an uncertainty of $1\ \mathrm{cm^3 \cdot mol^{-1}}$ for $B(T)$ between 650 and 800 K.

At higher temperatures, we have only the data of Vukalovich *et al.*[9] and the calculations from the SAPT-5s potential.[25] Because of their agreement (see Fig. 5), it is reasonable to estimate an uncertainty of $1\ \mathrm{cm^3 \cdot mol^{-1}}$ for $B(T)$ up to 1200 K. At even higher temperatures, all we can say with certainty is that the SAPT-5s potential should provide a physically reasonable extrapolation. Since the magnitude of B is small (on the order of $10\ \mathrm{cm^3 \cdot mol^{-1}}$) at these high temperatures, and since $B(T)$ at high temperatures is relatively insensitive to details of the attractive well of the potential (the most difficult part to get quantitatively correct), $1\ \mathrm{cm^3 \cdot mol^{-1}}$ is also a reasonable estimate of the uncertainty of $B(T)$ at higher temperatures, up to 3000 K.

A final consideration is the validity of extrapolation of Eq. (6) to low temperatures. The lowest temperatures for which data were fitted were 323 K for B and 313 K for $\phi°$. The uncertainty in Eq. (6) (and the underlying data) increases rapidly at low temperatures, as can be seen by the sizes of the error bars at the lowest temperatures in Figs. 1 and 2. Since $\phi°$ contains $\mathrm{d}B/\mathrm{d}T$, the good reproduction of low-temperature $\phi°$ data means that limited extrapolation of $B(T)$ to lower temperatures is reasonable. However, due to the increasing uncertainties, we do not recommend the use of Eq. (6) [or any correlation for $B(T)$] below 300 K. At lower temperatures, Eq. (6) by construction will give correct qualitative behavior, but it cannot be considered quantitative.

6. Conclusions

Equation (6) provides a reliable representation of $B(T)$ for water at temperatures above 300 K. The upper temperature limit of the experimental data on which Eq. (6) is based is 1173 K, but the incorporation in the fit of values of B generated from a high-quality intermolecular pair potential has allowed us to produce a correlation that we believe can be reliably extrapolated to 3000 K. The correlation may be differentiated to produce reliable values of $\mathrm{d}B/\mathrm{d}T$ and the important quantity $\phi° = B - T(\mathrm{d}B/\mathrm{d}T)$.

The best previous correlation (that of Hill and MacMillan[2]) represents the data similarly well in the region where it was fitted (below 573 K), but its accuracy deteriorates at higher temperatures. The international standard equation of state for water[13] gives reasonable values of $B(T)$ throughout the temperature range, but the $B(T)$ data at high temperatures (above about 500 K) and the $\phi°$ data at low temperatures (below about 400 K) are not represented within their uncertainties.

There are some regions where new high-quality data would be desirable to reduce the uncertainty in $B(T)$. At temperatures above about 470 K, the existing data sets[3,5,6] show some significant disagreement, and above 800 K it would be desirable to have some independent validation of the data of Vukalovich *et al.*[9] At temperatures between about 400 and 500 K, the data[16,19] for $\phi°$ appear to be somewhat inconsistent with the data for $B(T)$.

The behavior of Eq. (6) at very high temperatures could be improved if a more accurate pair potential for water became available. A possible deficiency of the SAPT-5s potential[25] is that, like almost all other proposed potentials, it assumes the water molecules are rigid. In reality, higher vibrational and rotational states are activated at high temperatures, causing some stretching of the molecules. Since these effects would be quite small except at very high temperatures (which are of less practical interest), and since incorporating intramolecular degrees of freedom would significantly complicate the calculation of $B(T)$, we do not believe it is worth worrying about the influence of molecular flexibility on $B(T)$ for water at this time.

7. Acknowledgments

The authors thank W. Wagner for providing the data of Ertle[19] in electronic form, I. M. Abdulagatov for making Ref. 29 available prior to publication, and M. P. Hodges for calculating $B(T)$ from the SAPT-5s potential.

8. References

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