Correlation for the Vapor Pressure of Heavy Water From the Triple Point to the Critical Point

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A new formulation has been developed to represent the vapor pressure of heavy water (D_2O) from its triple point to its critical point. This work takes advantage of several developments since the publication of the best previous formulation: the availability of some new data in the lower part of the temperature range, the adoption of the ITS-90 temperature scale, and the adoption of recommended values for the critical constants by the International Association for the Properties of Water and Steam (IAPWS). The new formulation fits the available data within their scatter across the entire temperature range, and is constrained to pass through the values recommended by IAPWS for the critical point. The previous formulation can be made to provide a similarly good fit if its input temperatures are converted from ITS-90 to IPTS-68 before the vapor pressure is computed. The new formulation offers the advantage of computation without having to perform a temperature conversion. © *2002 American Institute of Physics.*

Key words: D_2O; heavy water; ITS-90; vapor pressure.

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1. Introduction

Heavy water (D_2O) is a fluid of some industrial importance and much scientific interest. In 1979, Hill and MacMillan[1] published what was then the definitive correlation for its vapor pressure from the triple point to the critical point.

Subsequent advances include: new measurements of differential vapor pressures between D_2O and ordinary water,[2–4] a determination of the vapor pressure of D_2O at its triple point,[5] and the adoption of recommended values for its critical constants by the International Association for the Properties of Water and Steam (IAPWS).[6,7] In addition, a new representation of the thermodynamic temperature scale, known as ITS-90,[8] was adopted as an international standard in 1990. A standard correlation for the vapor pressure of ordinary water[9] has been produced on ITS-90. The object of this work is to produce a similar equation for D_2O, taking into account the new data.

2. Data Sources

Hill and MacMillan[1] analyzed the data published up to 1979. They make a case for discarding several (mostly pre-1955) data sets; we followed their judgment here. Table 1 lists the sources of data included in our study.

Oliver and Grisard[10] reported differences in saturation temperature between D_2O and H_2O at the same pressure. We followed Hill and MacMillan[1] in discarding their data above 368 °C, since Oliver and Grisard[10] considered these points to be less accurate and since they do not extrapolate well toward the accepted critical point. In order to convert these

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TABLE 1. Data sources for D_2O vapor pressures

Reference	Year	No. of points considered (Used)	T_{min}/K	T_{max}/K
Oliver and Grisard[10]	1956	32(32)	481.37	639.03[a]
Rivkin and Akhundov[12]	1962	8(8)	548.20	638.15
Zieborak[11]	1966	16(16)	354.81	494.16
Jones[13]	1968	43(43)	334.42[b]	387.44
Liu and Lindsay[14]	1970	12(12)	379.12	573.11
Pupezin et al.[16]	1972	96(67)	273.41[c]	371.47
Besley and Bottomley[15]	1973	37(37)	277.84	298.09
Jancsó and Jákli[3]	1980	157(153)	280.89	361.82
Jákli and Van Hook[2]	1981	57(53)	280.03	362.66
Markó et al.[5] (triple pt.)	1989	1(1)	276.967	276.967
Jákli and Markó[4]	1995	101(101)	281.51	352.50

[a]Seven points at higher temperatures not considered in fit (see text).
[b]21 points at lower temperatures not considered in fit (see text).
[c]Four points at lower temperatures not considered in fit (see text), but shown in Fig. 1.

data to D_2O vapor pressures, the correlation for saturation pressure versus temperature of H_2O from Wagner and Pruss[9] was used.

Zieborak[11] also measured isobaric differences in saturation temperature between D_2O and H_2O. The actual data were not reported; instead a table gives smoothed data (stated to be obtained from a much larger number of measurements) at 10 K intervals ranging from 80 to 220 °C. We use these values in our fit. The paper also locates the temperature (221.00 °C on the temperature scale in use at the time) where the vapor pressures of H_2O and D_2O are equal; this provides one more data point. The conversion of the data to D_2O vapor pressures was the same as for the Oliver and Grisard data. This paper was evidently missed in the survey of Hill and MacMillan.[1]

Rivkin and Akhundov[12] reported isothermal measurements of pressure versus density at high temperatures. The flat portions of their isotherms indicate vapor–liquid coexistence. We took the coexistence points from the original isotherms (Table 2 of their paper) rather than the values from their Table 1, which reports values adjusted to integer Celsius temperatures.

Jones[13] and Liu and Lindsay[14] reported vapor–pressure differences $[p(H_2O)-p(D_2O)]$ at various temperatures. In these and other cases where vapor–pressure differences were reported, we obtained $p(D_2O)$ by adding the difference to $p(H_2O)$ computed from the correlation of Wagner and Pruss,[9] after converting the reported temperatures to the ITS-90 scale. Since the scatter of the Jones data at low temperatures is much greater than that of several more recent low-temperature studies, we only included his data above 330 K.

Besley and Bottomley[15] made direct measurements of $p(D_2O)$ at low temperatures; no additional processing of these data was needed except for the correction of the reported temperatures to ITS-90.

Pupezin et al.[16] measured vapor–pressure differences, but they reported values of the ratio $R = p(H_2O)/p(D_2O)$ as a function of temperature. We calculated $p(H_2O)$ from the same expression of Goff[17] that they used (at the reported temperature) in order to convert that ratio back to a vapor–pressure difference. While the paper of Pupezin et al. says the temperatures are on the IPTS-68 scale, the temperature calibration is that described in an earlier paper by Jancsó et al.,[18] which actually corresponds to the IPTS-48 scale.[19] The difference between the two scales is negligible for the vapor–pressure ratios R with which Pupezin et al. were concerned, but not necessarily for the absolute vapor pressures. This study was unique in that it reported data for the supercooled liquid below the triple point of D_2O, a few of which were even below the triple point of H_2O. The latter points were not included in our fit, but the points between the triple points of D_2O and H_2O were included because knowledge of $p(D_2O)$ in this region could be useful for work involving H_2O/D_2O mixtures.

The temperature calibration used by Pupezin et al.[16] was also used by Jákli and Van Hook,[2] whose temperatures are therefore also on IPTS-48. Their reported values of R were converted back to pressure differences with the equation for $p(H_2O)$ of Wexler and Greenspan[20] that Jákli and Van Hook used in computing R.

Jancsó and Jákli[3] also measured $p(H_2O)-p(D_2O)$. The raw data are tabulated in a separate report.[21] Two of the tabulated points are clearly typographical errors; these points were discarded since the correct values could not be recovered. The temperature measurement of Jancsó and Jákli[3] requires special comment. Their thermometer was not calibrated to any temperature scale; instead it was calibrated against measurements of $p(H_2O)$, where these pressures were converted to saturation temperatures by the equation of Goff.[17] Since the reported temperatures really correspond to values of $p(H_2O)$, it is appropriate to use $p(H_2O)$ from the Goff equation to convert the measured pressure differences to $p(D_2O)$. In order to convert the reported temperatures to ITS-90, we found the temperature at which the equation of Wagner and Pruss[9] gives the same vapor pressure as that given by the Goff equation at the temperature reported in the paper.

Similar measurements were reported by Jákli and Markó.[4] The data were not tabulated in the paper, but values of R that had been derived from the measurements were supplied by one of the authors.[22] Their temperature calibration was also indirect, identical to the procedure used by Jancsó and Jákli.[3] The data were therefore handled as described above. Because these data have not been published, we tabulate them here with the permission of the authors so that they will be available for future workers. Table 2 shows $p(H_2O)-p(D_2O)$ [converted back to this measured quantity from the values of R supplied by the authors with the equation[17] used to calculate $p(H_2O)$ in the original work] as a function of temperature, with the temperatures converted to ITS-90.

All temperatures were converted to the ITS-90 scale using standard procedures. In some cases the purity was reported, and a small correction based on Raoult's law was applied as in previous work[1] to correct the data to 100% D_2O. Some

TABLE 2. Vapor–pressure differences derived from unpublished data measured in connection with the work of Jákli and Markó.[a] Temperatures have been converted to ITS-90 and values of R converted to vapor–pressure differences as described in the text

T/K	$p(H_2O)-p(D_2O)/kPa$	T/K	$p(H_2O)-p(D_2O)/kPa$	T/K	$p(H_2O)-p(D_2O)/kPa$
281.511	0.1841	304.758	0.5821	327.159	1.4139
281.939	0.1882	305.251	0.5965	328.158	1.4639
285.155	0.2248	307.239	0.6514	329.661	1.5429
285.652	0.2304	307.239	0.6506	329.661	1.5414
285.652	0.2302	308.728	0.6941	331.168	1.6248
285.660	0.2307	308.766	0.6946	332.169	1.6804
287.425	0.2532	309.722	0.7217	332.169	1.6809
288.121	0.2620	309.741	0.7226	332.169	1.6769
288.611	0.2689	310.713	0.7549	334.670	1.8315
289.606	0.2837	311.216	0.7704	334.670	1.8257
289.900	0.2876	312.207	0.8021	334.771	1.8243
289.900	0.2868	312.236	0.8011	335.265	1.8639
290.396	0.2949	313.833	0.8578	335.366	1.8640
291.378	0.3102	314.692	0.8856	337.175	1.9797
291.378	0.3104	314.692	0.8852	337.175	1.9731
291.378	0.3098	317.187	0.9764	338.476	2.0520
292.374	0.3264	317.187	0.9758	339.684	2.1379
292.374	0.3252	317.238	0.9814	339.684	2.1305
293.455	0.3437	319.682	1.0754	340.180	2.1829
293.455	0.3433	319.815	1.0789	342.183	2.3169
294.345	0.3598	321.273	1.1423	342.183	2.3003
294.839	0.3674	321.273	1.1423	342.687	2.3428
295.388	0.3780	322.174	1.1792	344.695	2.5000
297.320	0.4153	322.174	1.1792	344.695	2.4775
297.984	0.4283	322.174	1.1834	344.755	2.5086
298.901	0.4463	323.173	1.2238	347.209	2.6774
299.304	0.4564	323.665	1.2471	347.209	2.6774
299.797	0.4675	324.169	1.2714	347.233	2.6732
299.797	0.4663	324.600	1.2927	349.722	2.8703
300.292	0.4769	324.663	1.2931	349.759	2.8708
300.292	0.4766	325.170	1.3182	352.298	3.0795
301.778	0.5102	326.167	1.3645	352.397	3.0834
302.271	0.5229	326.668	1.3900	352.496	3.0872
302.271	0.5218	327.159	1.4139		

[a]See Jákli.[4,22]

authors made this correction before reporting the data; in these cases we accepted the numbers as reported.

In addition, some data have recently become available on the derivatives of $p(D_2O)$ with respect to temperature. A direct measurement of $dp(D_2O)/dT$ at approximately the critical temperature was reported by Polikhronidi et al.[23] Their value was 0.276 MPa·K^{-1}; the uncertainty is approximately 5%.[24] Additional measurements by the same authors[25] of the isochoric heat capacity in the two-phase region were processed according to the Yang–Yang[26] relation to yield values of the second derivative $d^2p(D_2O)/dT^2$. Polikhronidi et al.[25] also show graphically values of $d^2p(D_2O)/dT^2$ extracted in the same manner from the measurements of Mursalov et al.;[27] we obtained the numerical data from one of the authors.[24] These second derivatives are estimated to have an uncertainty of 10%.[24]

3. Fitting Procedure

There are two reasonable ways to correlate D$_2$O vapor pressures. If all the data were measurements of $p(D_2O)$, the right approach would be to correlate $p(D_2O)$ directly. On the other hand, if all the data were of the vapor–pressure difference $p(H_2O)-p(D_2O)$, one might prefer to correlate that difference (or perhaps the vapor–pressure ratio R), so that any improvement in the knowledge of $p(H_2O)$ would automatically improve values of $p(D_2O)$. Here, we have some data of each type, so either approach would require recalculation of some data (and, in principle, refitting) if better values of $p(H_2O)$ were obtained. We chose to fit $p(D_2O)$ directly, so that the intermediate step of calculating $p(H_2O)$ would not be necessary in order to compute $p(D_2O)$. Those interested in the vapor–pressure difference or in the ratio R will need to use a correlation for $p(H_2O)$; to be consistent with this study they should use the correlation of Wagner and Pruss.[9]

The fit was constrained to the ITS-90 values of the critical temperature and pressure of D$_2$O ($T_c=643.847$ K, $p_c=21.671$ MPa) as adopted by IAPWS.[7] Initially, we also attempted to constrain the fit to reproduce the value of 659.3 Pa obtained at the triple point (276.97 K, which becomes 276.967 K on ITS-90) by Markó et al.[5] However, as ex-

plained below, this made it impossible to fit the vapor-pressure data at temperatures near the triple point. Since these vapor pressures came from two independent studies,[15,16] we could not justify ignoring them in favor of one triple-point value. We therefore did not fix the triple-point pressure, but included the value of Markó et al.[5] as another vapor–pressure point in the fit, with a relative weight of 3 (since it is stated to be the average of three measurements).

We minimized the sum of squares of the relative deviations between calculated and experimental values of $p(D_2O)$. Because the data of Pupezin et al.[16] have more scatter than do other low-temperature data, those points were given a relative weight of 0.5. Points above 400 K were given larger relative weights in order to keep the large number of points at low temperatures from dominating and distorting the fit; the extra weight is also justified by the smaller scatter (in terms of relative deviation) these data display compared to the low-temperature data. The calorimetric data for $d^2p(D_2O)/dT^2$ were not included in the fit; their agreement with the correlation will be discussed in Sec. 4.

The fit was performed repeatedly, with outliers discarded. Outliers were identified by plotting the data and identifying points deviating from the fit by more than approximately a factor of 2 compared with the remaining points at nearby temperatures. Table 1 lists the number of points from each study considered and the number used in the final fit.

The fitting procedure was similar to that used by Wagner and Pruss[9] for $p(H_2O)$. $\ln[p(D_2O)/p_c]$ was expressed as a function of $\tau = 1 - T/T_c$. The equation was structurally optimized by selecting terms with powers of τ rounded to the nearest tenth, with terms added until the addition of more terms did not significantly improve the fit.

A final constraint on the fit was the theoretically expected weak divergence of the second derivative $d^2p(D_2O)/dT^2$ near the critical point.[28] This derivative diverges as $\tau^{-\alpha}$, where the currently accepted value of the critical exponent α is 0.11.[29] In order to produce the correct divergence, the equation was required to have terms with $\tau^{1.89}$ and τ^2.

4. Results

While a four-term equation was able to fit $p(D_2O)$ over most of the range, it was not quite able to reproduce the high-temperature data. A five-term equation provided an excellent fit all the way from the triple point to the critical point. The final equation is

$$\ln[p(D_2O)/p_c] = (T_c/T)(a_1\tau + a_2\tau^{1.89}$$
$$+ a_3\tau^2 + a_4\tau^3 + a_5\tau^{3.6}). \quad (1)$$

The coefficients for Eq. (1) are listed in Table 3.

Before comparing Eq. (1) with the experimental data, we briefly mention how we will compare it to the formulation of Hill and MacMillan.[1] The most straightforward approach is to compute the vapor pressure directly from the equation given in that paper. This will introduce some error, since Hill

TABLE 3. Coefficients for Eq. (1)

i	a_i
1	$-7.896\,657$
2	$24.733\,08$
3	$-27.811\,28$
4	$9.355\,913$
5	$-9.220\,083$

and MacMillan used the IPTS-68 temperature scale and we are considering data on ITS-90. We can, however, produce a modified equation, compatible with ITS-90, by converting input temperatures in ITS-90 back to IPTS-68 by using the standard conversion equation[30] before putting them into the equation of Hill and MacMillan. In the following comparisons, we show both of these approaches.

Figure 1 shows the deviations of the data from Eq. (1) in the range from 270 to 290 K. It is apparent that the triple-point measurement of Markó et al.[5] cannot be reconciled with the nearby vapor–pressure data of Besley and Bottomley[15] and Pupezin et al.[16] Since these two vapor–pressure studies are in fair agreement with each other (although there is more scatter in the data of Pupezin), and since their data also blend smoothly into the three additional data sets[2–4] that begin at temperatures near 280 K, forcing the correlation to pass through this triple-point measurement would not be justified. At the higher temperatures in this range, we have five studies in mutual agreement within a scatter of approximately 0.2%, although some systematic differences between individual sets are visible. We defer further discussion of these data sets until we consider the next higher temperature range.

Figure 1 also shows data of Pupezin et al.[16] below the triple-point temperature. These data for supercooled D_2O, especially those below the triple point of ordinary water (which were not included in the fit), show a small positive deviation from the trend of Eq. (1). Not shown in Fig. 1 are the measurements of $p(D_2O)$ for the supercooled liquid by Kraus and Greer.[31] Their data [which were not used in fitting Eq. (1)] scatter within about 1% on either side of Eq. (1), with somewhat more of the points lying below our correlation. Bottomley[32] measured the difference in vapor pressure between supercooled D_2O and solid D_2O in this region; unfortunately, the lack of accurate knowledge of the vapor pressure of D_2O ice limits the utility of these data for computing supercooled liquid vapor pressures. Approximate calculations using the measurements of Pupezin et al.[16] for the vapor–pressure difference between solid D_2O and liquid and solid H_2O indicate reasonable consistency between the data of Bottomley and Eq. (1). Because of the lack of precise data for supercooled liquid D_2O, we conclude that Eq. (1) is consistent with the experimental data when extrapolated down at least as far as 270 K, but that there is substantial uncertainty in this region.

The ITS-90 version of the equation of Hill and MacMillan fits the data in Fig. 1 approximately as well as Eq. (1). This
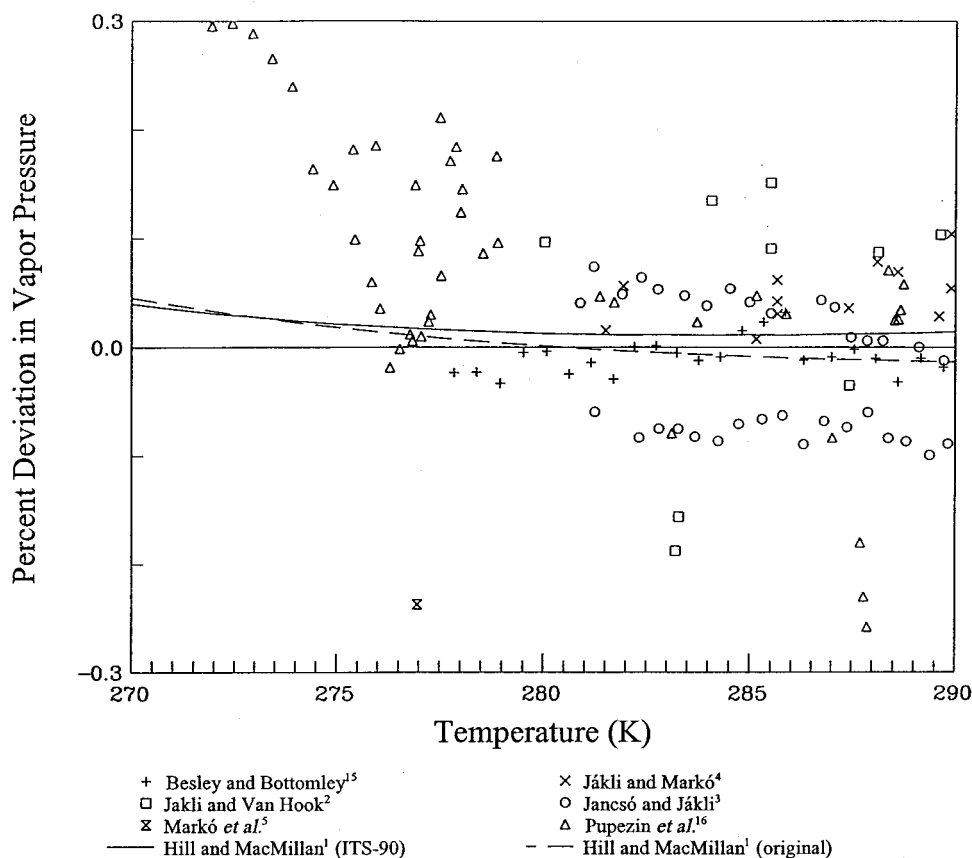
FIG. 1. Deviations from Eq. (1) for 270–290 K.

is not surprising, since both the data of Besley and Bottomley[15] and of Pupezin et al.[16] were used by Hill and MacMillan[1] in their fit. The difference between the modified and original Hill equations is small in this region because the difference between the ITS-90 and IPTS-68 temperature scales is small (passing through zero at 273.16 K).

Figures 2 and 3 cover the regions 290–330 K and 330–375 K, respectively. At these temperatures, the main sources of data are four studies[2–4,16] from overlapping groups of investigators using the differential vapor pressure technique. The three more recent studies[2–4] all exhibit good internal consistency; the systematic differences among them (on the order of 0.1%) most likely reflect different methods of calibration.[22] The data of Jákli and Van Hook[2] and Jancsó and Jákli[3] tend to fall slightly below Eq. (1), while the data of Jákli and Markó[4] fall somewhat above it, as do most of the more-scattered data of Pupezin et al.[16] There is no definitive way to judge which trend is correct, although at the lowest temperatures in Fig. 2 we see that the independent data of Besley and Bottomley[15] are in agreement with the lower trend. At the higher end of the temperature range shown in Fig. 3, the data of Zieborak[11] come closer to the lower trend (and very close to our correlation), while the data of Jones[13] show better agreement with the upper trend. Until more precise measurements are made in this range, this inconsistency will remain unresolved.

At the temperatures represented in Figs. 2 and 3, the correction for temperature scale to the equation of Hill and MacMillan[1] begins to be important in comparison to the scatter of the data. The ITS-90 version of their equation follows the higher-pressure trend mentioned in the previous paragraph; this is not surprising since the main sources of data for Hill and MacMillan in this region were Jones and Pupezin et al. It is in good agreement with one of the sets of data published since then,[4] but not with the other two[2,3] nor with the older data of Zieborak[11] that were not considered by Hill and MacMillan.

Figure 4 covers the region from 360 K to the critical temperature (signified by a dashed vertical line). Equation (1) fits all the data to within better than 0.05% over most of this temperature range. At the lowest end of this range, Eq. (1) is systematically lower than the data of Jones,[13] but data from other sources near 360 K are mostly lower than those of Jones. Equation (1) goes through the IAPWS-accepted critical point, as it was constrained to do.

In this range, the original equation of Hill and MacMillan[1] clearly produces unacceptable results. The modified equation on the ITS-90 basis is consistent with all the data, except at the low-temperature end of the figure where it passes through the data of Jones and misses the Zieborak data and the more recent data near 360 K. The modified equation does not pass through the IAPWS critical point; the difference is approxi-
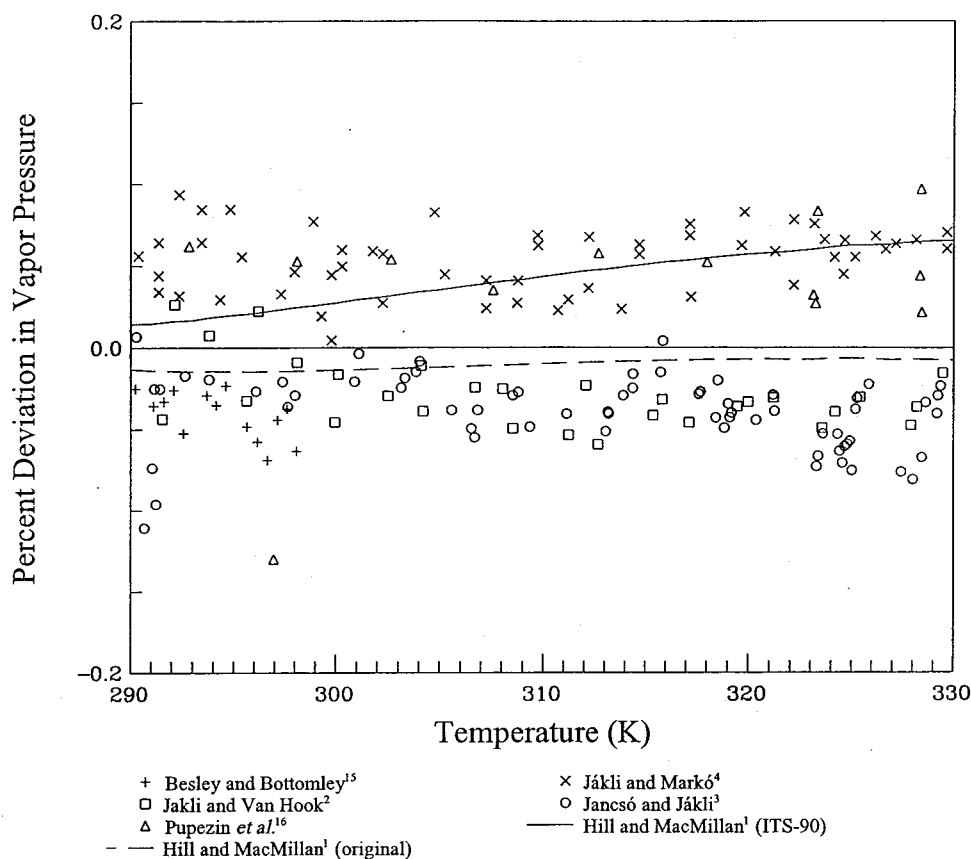
FIG. 2. Deviations from Eq. (1) for 290–330 K.

mately equal to the uncertainty of 0.01 MPa assigned to the IAPWS value.

We compare our results to the calorimetric data[25,27] for $d^2p(D_2O)/dT^2$ in Fig. 5, where one can see the beginnings of the weak critical divergence. Equation (1) (and therefore the underlying vapor–pressure data) agrees well with the data of Mursalov *et al.*[27] Agreement is only fair with the derivatives obtained by Polikhronidi *et al.*[25] For most points we are within their stated experimental uncertainty of 10%, but there seems to be a systematic difference in the trend of the data. It was not possible to significantly improve the agreement of Eq. (1) with these second-derivative data without making the fit of the high-temperature vapor–pressure data much worse. We note that a slight upward adjustment of the critical pressure in Eq. (1) (by an amount smaller than the uncertainty in p_c) would somewhat improve the agreement with the data of Polikhronidi *et al.*[25] at higher temperatures (above about 630 K) without harming the fit of the vapor–pressure data, but the disagreement at lower temperatures would remain. We also note that one would expect values of $d^2p(D_2O)/dT^2$ to be very similar (at the same reduced temperature) to those evaluated from the vapor pressure of H_2O (which is known with more certainty). We find good agreement between the two, lending further support to the second derivatives of Eq. (1).

Figure 5 also shows $d^2p(D_2O)/dT^2$ from the modified equation of Hill and MacMillan, which yields results similar to Eq. (1). Values from the original Hill–MacMillan equation differ negligibly from the ITS-90 version (except extremely close to the critical point), so they are not shown in the figure.

Finally, our value of $dp(D_2O)/dT$ at the critical point is $0.266\ \text{MPa}\cdot\text{K}^{-1}$, in agreement with the value of 0.276 measured by Polikhronidi *et al.*[23] within its experimental uncertainty.

5. Uncertainty of the Fit

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.

At low temperatures, the inconsistency between a careful triple-point measurement and the surrounding vapor–pressure measurements is troubling. Markó *et al.*[5] note this inconsistency in their triple-point paper, but have no definitive explanation. While it is possible that the inconsistency arises from systematic errors in the vapor–pressure measurements, this is made less likely by the existence of two independent studies,[15,16] one by an absolute method and one by a differential method, both of which disagree with the triple-point measurement. We therefore conservatively estimate the
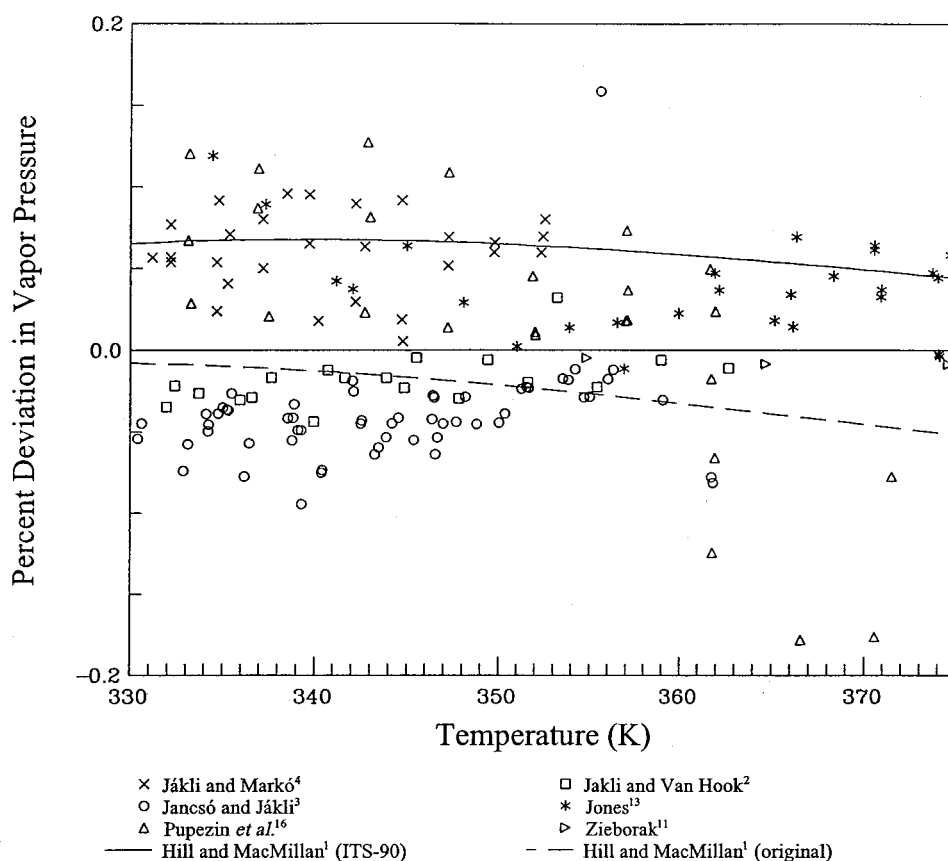
FIG. 3. Deviations from Eq. (1) for 330–375 K.

uncertainty in $p(D_2O)$ near the triple point as approximately 0.3%.

At somewhat higher temperatures, between about 280 and 360 K, there are four data sets[2–4,16] of fairly high quality and internal consistency, and a fifth[15] in the low-temperature portion of this range. These exhibit systematic deviations from one another on the order of 0.1%, and are all fitted to within that amount by Eq. (1). It would be tempting to consider 0.1% to be the uncertainty in this range, but because the triple-point measurement disagrees with Eq. (1) by almost 0.3%, an uncertainty of 0.1% could be considered overly optimistic in the lower portion of this range.

At temperatures above 360 K, the available data are fitted within 0.05% across the whole range. For almost all of this region, independent investigations agree closely, lending more confidence to the results. The only significant discrepancy is in the region between about 360 and 390 K, where the data of Liu and Lindsay[14] and those of Jones[13] follow a higher trend, while the data of Zieborak[11] follow a lower trend that joins more smoothly with the data from studies at lower temperatures.

At high temperatures, we must also consider the uncertainty in the critical pressure p_c to which Eq. (1) is constrained. There are two components to this uncertainty.[6] The first is proportional to the uncertainty in T_c, representing the effect on p_c if the vapor–pressure curve extends to a slightly

higher temperature or stops at a slightly lower temperature; this is not relevant for our purposes. The second component is an absolute uncertainty of 0.1 MPa, which is 0.046% of p_c. It is therefore reasonable to assign an uncertainty of 0.05% to the entire high-temperature range.

One additional source of uncertainty in $p(D_2O)$ is the vapor pressure of ordinary water, where the equation for $p(H_2O)$ of Wagner and Pruss[9] was used to convert differential measurements to $p(D_2O)$. Wagner and Pruss refer to another document[33] that contains uncertainties in $p(H_2O)$ considered to be identical to those of their correlation. These uncertainties are near 0.025% at most temperatures, with somewhat smaller uncertainties near the triple point and the normal boiling point. This is small compared to the scatter of the $p(D_2O)$ data at low temperatures, but is significant at the higher temperatures shown in Fig. 4. Of the high-temperature data sources, Oliver and Grisard,[10] Zieborak,[11] and Liu and Lindsay[14] all made differential measurements and therefore are subject to this additional uncertainty. The absolute measurements of Rivkin and Akhundov[12] are not affected.

6. Conclusions

We have converted to the ITS-90 temperature scale all data included in the previous formulation[1] for $p(D_2O)$, plus
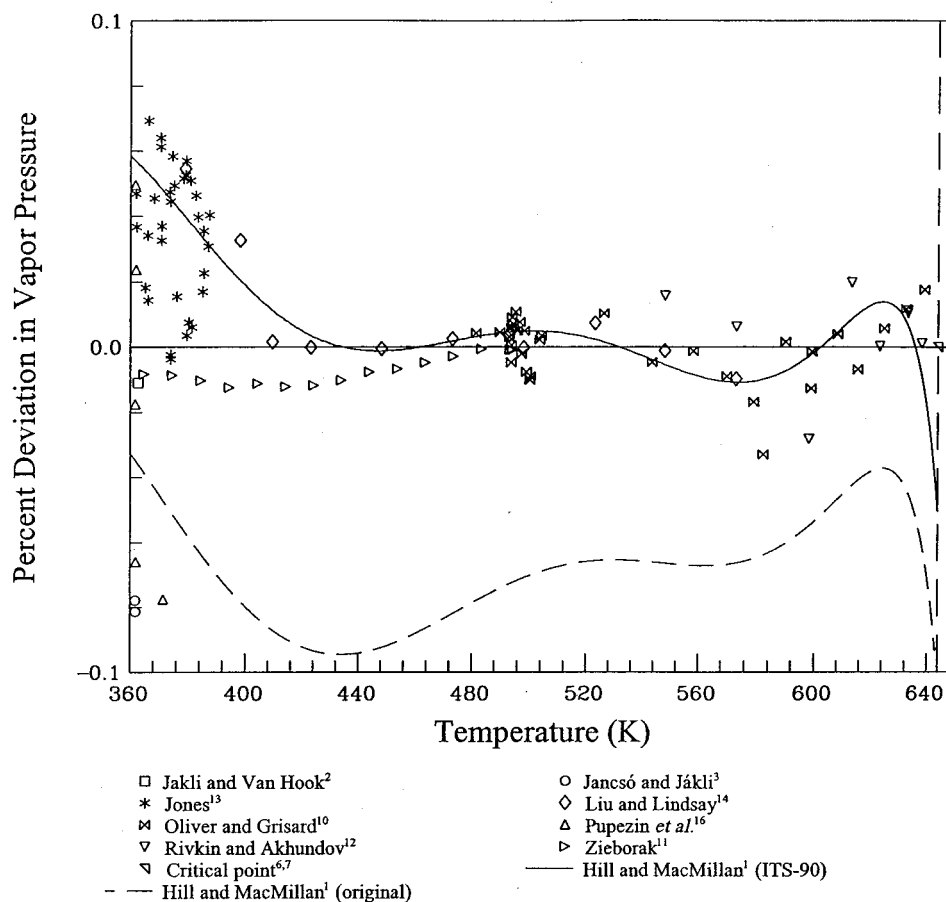
FIG. 4. Deviations from Eq. (1) above 360 K.

one set of data[11] that was missed in the previous work, and some new data[2–5] reported since that correlation was published. The current standard vapor–pressure equation for ordinary water[9] was used to convert differential measurements where appropriate. Equation (1) was fitted to these data and constrained to pass through the coordinates recommended by IAPWS for the critical point of D_2O. The uncertainty in $p(D_2O)$ as given by Eq. (1) is conservatively estimated at 0.3% near the triple point (because of a discrepancy between vapor–pressure measurements and a measurement of the triple-point pressure), and decreases gradually to approximately 0.05% at the critical point. Extrapolation to supercooled liquid states below the triple point of D_2O appears to be reasonable, based on the limited data available.

The equation of Hill and MacMillan,[1] as published, does not adequately describe these data, especially at high temperatures, because it is based on the IPTS-68 temperature scale. However, if one converts temperatures from ITS-90 to IPTS-68 before using their equation, it describes the data approximately as well as Eq. (1). This modified Hill–MacMillan equation does differ from Eq. (1) in the range from 300 to 370 K where new data now exist, but it is not clear which is better because of systematic differences among data sets. The ITS-90 modification of the Hill–MacMillan equation also does not pass through the accepted

critical point, although the difference is similar to the uncertainty of p_c. An advantage of Eq. (1) is that it allows accurate values of $p(D_2O)$ to be calculated directly without requiring any temperature conversions.

The vapor pressure is not known as accurately as that of ordinary water; this is especially the case at lower temperatures. The greatest reduction in uncertainty of $p(D_2O)$ could be accomplished by an independent, precise determination of the triple-point pressure of D_2O. Good measurements at temperatures between approximately 300 and 370 K could resolve the systematic discrepancies among data sets observed in that region.
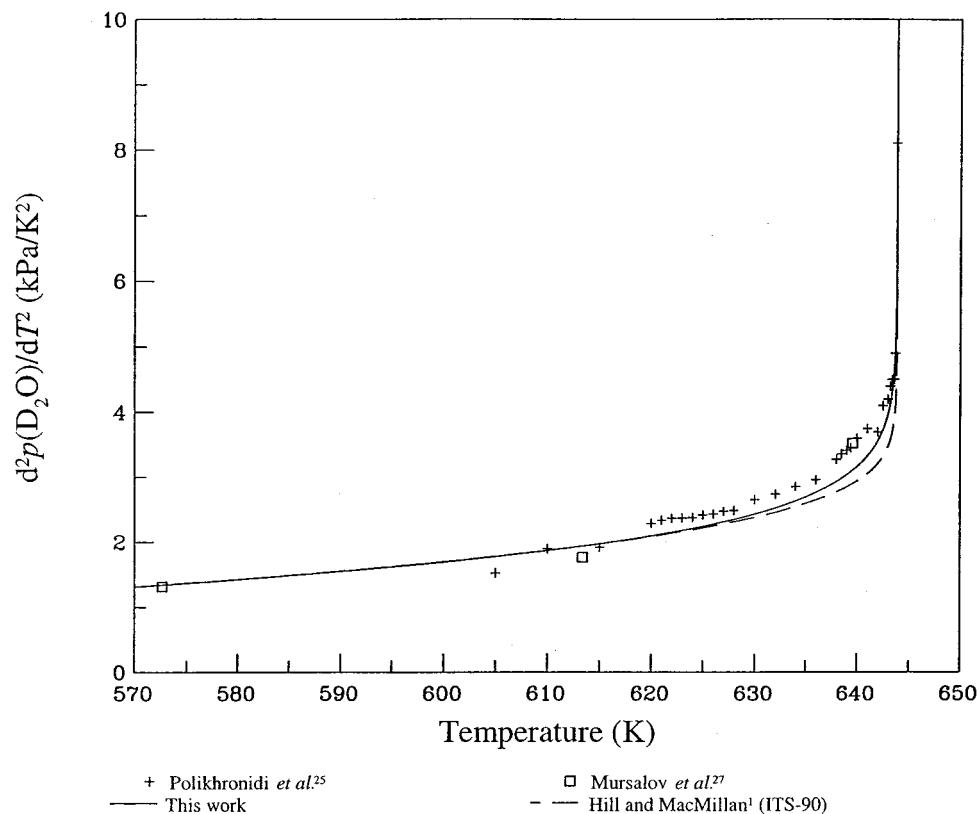
7. Acknowledgments

FIG. 5. Values of the second derivative of the vapor pressure $d^2 p(D_2O)/dT^2$.

havior of the vapor–pressure curve near the critical point. We also benefitted from input from W. A. Van Hook and P. G. Hill. M. Salehi assisted with data entry.

8. References

[1] P. G. Hill and R. D. C. MacMillan, Ind. Eng. Chem. Fundam. **18**, 412 (1979).

[2] Gy. Jakli and W. A. Van Hook, J. Chem. Eng. Data **26**, 243 (1981).

[3] G. Jancsó and Gy. Jákli, Aust. J. Chem. **33**, 2357 (1980).

[4] Gy. Jákli and L. Markó, ACH–Models in Chemistry **133**, 225 (1995).

[5] L. Markó, Gy. Jákli, and G. Jancsó, J. Chem. Thermodyn. **21**, 437 (1989).

[6] J. M. H. Levelt Sengers, J. Straub, K. Watanabe, and P. G. Hill, J. Phys. Chem. Ref. Data **14**, 193 (1985).

[7] International Association for the Properties of Water and Steam, Release on the Values of Temperature, Pressure and Density of Ordinary and Heavy Water Substances at Their Respective Critical Points. In *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry* (Proceedings, 12th International Conference on the Properties of Water and Steam), edited by H. J. White, Jr., J. V. Sengers, D. B. Neumann, and J. C. Bellows (Begell House, New York, 1995), p. A101.

[8] H. Preston-Thomas, Metrologia **27**, 3 (1990).

[9] W. Wagner and A. Pruss, J. Phys. Chem. Ref. Data **22**, 783 (1993).

[10] G. D. Oliver and J. W. Grisard, J. Am. Chem. Soc. **78**, 561 (1956).

[11] K. Zieborak, Z. Phys. Chem. **231**, 248 (1966).

[12] S. L. Rivkin and T. S. Akhundov, Teploenergetika **9**(5), 62 (1962).

[13] W. M. Jones, J. Chem. Phys. **48**, 207 (1968).

[14] C.-T. Liu and W. T. Lindsay, Jr., J. Chem. Eng. Data **15**, 510 (1970).

[15] L. Besley and G. A. Bottomley, J. Chem. Thermodyn. **5**, 397 (1973).

[16] J. Pupezin, Gy. Jakli, G. Jancso, and W. A. Van Hook, J. Phys. Chem. **76**, 743 (1972).

[17] J. A. Goff, in *Humidity and Moisture*, edited by A. Wexler and W. A. Wildhack (Reinhold, New York, 1965), Vol. 3, p. 289.

[18] G. Jancso, J. Pupezin, and W. A. Van Hook, J. Phys. Chem. **74**, 2984 (1970).

[19] G. Jancsó (private communication, 2001).

[20] A. Wexler and L. Greenspan, J. Res. Natl. Bur. Stand. **75A**, 213 (1971).

[21] Gy. Jákli and H. Illy, Vapour Pressure Isotope Effect of the Equimolar $H_2O–D_2O$ Mixture, KFKI Report 1980-15, Hungarian Academy of Sciences, Budapest, 1980.

[22] Gy. Jákli (private communications, 2001).

[23] N. G. Polikhronidi, I. M. Abdulagatov, J. W. Magee, and G. V. Stepanov, Int. J. Thermophys. **22**, 189 (2001).

[24] I. M. Abdulagatov (private communication, 2001).

[25] N. G. Polikhronidi, I. M. Abdulagatov, J. W. Magee, and G. V. Stepanov, Int. J. Thermophys. (submitted 2001).

[26] C. N. Yang and C. P. Yang, Phys. Rev. Lett. **13**, 303 (1964).

[27] B. A. Mursalov, I. M. Abdulagatov, V. I. Dvoryanchikov, A. N. Kamalov, and S. B. Kiselev, Int. J. Thermophys. **20**, 1497 (1999).

[28] M. Ley-Koo and M. S. Green, Phys. Rev. A **23**, 2650 (1981).

[29] M. A. Anisimov and J. V. Sengers, in *Equations of State for Fluids and Fluid Mixtures*, edited by J. V. Sengers, R. F. Kayser, C. J. Peters, and H. J. White, Jr. (Elsevier, Amsterdam, 2000), p. 381.

[30] R. L. Rusby, J. Chem. Thermodyn. **23**, 1153 (1991).

[31] G. F. Kraus and S. C. Greer, J. Phys. Chem. **88**, 4781 (1984).

[32] G. A. Bottomley, Aust. J. Chem. **31**, 1177 (1978).

[33] International Association for the Properties of Water and Steam, Release on the Skeleton Tables 1985 for the Thermodynamic Properties of Ordinary Water Substance. In *Physical Chemistry of Aqueous Systems: Meeting the Needs of Industry* (Proceedings of the 12th International Conference on the Properties of Water and Steam), edited by H. J. White, Jr., J. V. Sengers, D. B. Neumann, and J. C. Bellows (Begell House, New York, 1995), p. A13.