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P. G. Hill, and R. D. Chris MacMillan

Saturation States of Heavy Water

P. G. Hill and R. D. Chris MacMillan
Department of Mechanical Engineering, University of British Columbia, Vancouver, Canada V6T 1W5

A study has been made of the saturation properties of D_2O from the triple point temperature to 325 °C, in the light of information on the saturation properties of H_2O. Saturated liquid volumes have been determined by extrapolation to saturation pressure of relatively abundant liquid phase data (corrected to 100% D_2O). Saturated liquid enthalpy has been determined by extrapolation of liquid phase specific heat data, and integration along the saturation line, allowing for the compressibility effect. Saturated vapor volumes have been determined by use of an extended virial equation formulated for H_2O and corrected for D_2O. Saturated vapor enthalpies have been determined by use of the Clapeyron equation, and compared to vapor enthalpies calculated from the extended virial equation. Saturated liquid and vapor volumes have been extrapolated to the critical temperature to allow an inference of the critical density.

Key words: Enthalpy of water; heavy water; *PvT*; saturation states; thermodynamic properties of water; vapor pressure; virial coefficients; water.

Contents

1. Introduction

The main problem in establishing saturation states for D_2O is the absence of heat of vaporization or other calorific measurements and the scarcity of vapor volume measurements for nearly-saturated states. However, data on liquid volumes are relatively abundant and virial coefficients are available, as well as saturation vapour pressures and zero pressure specific heats.

The feasibility of using these data to establish saturation states for D_2O has been tested by using the same procedure with corresponding data on H_2O for which the saturation states are now quite well known.

The first step was the extrapolation of liquid volumes to saturation vapor pressure, both for H_2O and D_2O. Volume data for the latter must be corrected for isotopic effects. This process provides saturation liquid volumes up to about 340 °C.

The second step was determination of the saturation liquid enthalpy by extrapolating corrected specific heats to saturation states and integrating along the saturation line, after allowing for compressibility effects. Again this process was followed for both H_2O and D_2O and proved to be feasible for temperatures from the triple point value up to about 325 °C.

Next the saturation vapor volumes were estimated from virial coefficient information. For H_2O it appears that only the second virial coefficient is necessary up to 100 °C, but third and fourth virial coefficients are needed to match saturation volumes from 200 to 300 °C. For D_2O, correlations of the experimentally determined second and third virial coefficients have been used, and the effective fourth virial coefficient has been assumed the same as for H_2O with respect to molar volumes. With this procedure it appears feasible to determine saturation vapor volumes to about 300 °C. A few saturation vapor volumes at higher temperature were obtained by extrapolation along experimental isotherms.

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The next stage of the process was to determine saturation vapor enthalpies, employing both the Clapeyron equation and previously determined saturation quantities for one set of results, and the virial coefficients, zero pressure specific heats, and the vapor pressure equation for another. The agreement of these two sets of results for both H_2O and D_2O was within 4 J/g up to 300 °C.

By these methods a set of saturation quantities consistent with the Clapeyron equation and estimates of uncertainties was obtained.

It is assumed that the absolute temperature scale may be satisfactorily represented by

$$T/\mathrm{K} = t(°\mathrm{C}, \text{IPTS-68}) + 273.15.$$

2. Saturated Liquid Volumes

2.1. Light Water

Saturated liquid volumes were obtained for H_2O and D_2O using simple extrapolation formulae for each isotherm in the form

$$\ln v = \sum_{i=0}^{4} a_i P^i. \tag{1}$$

For H_2O, extrapolations were performed with the liquid phase PVT data of Kell and Whalley [1][1] for the range 0 to 150 °C, and Kell, McLaurin and Whalley [2] for the range 175 to 350 °C. The saturation pressure was calculated from the formula provided by Wagner [3], which is as follows:

$$\ln\left[\frac{P}{P_c}\right] = \frac{T_c}{T}\left[n_1\tau + n_2\tau^{1.5} + n_3\tau^{2.5} + n_4\tau^{6.5} + n_5\tau^{7.5}\right] \tag{2}$$

with

$T_c = 647.25\ \mathrm{K}(\text{IPTS 68})$ n_1: -7.863889
$P_c = 22.093\ \mathrm{MPa}$ n_2: 1.898527
$\tau = \left[1. - \frac{T}{T_c}\right]$ n_3: -2.364891
n_4: -9.911414
n_5: 9.982952

A discussion of the uncertainties introduced by the process of extrapolation is provided in Appendix A.1.

The results of those extrapolations are shown in table 1 along with the saturation liquid volumes given by Kell [4] and Osborne, Stimson and Ginnings [5] (adjusted to the IPTS-68).

The close agreement of these determinations indicates little difficulty in finding liquid saturation volumes by the above extrapolation formulae, for temperatures up to 325 °C. In view of these results it was decided to determine v_f for D_2O by the same technique, for the same temperature range. The subscripts f and g are used to denote saturated liquid and vapor phases, respectively.

TABLE 1. Saturated liquid volumes of H_2O. Comparison of Extrapolated values with the determinations of Kell [4] and Osborne, Stimson and Ginnings [5]

t °C (IPTS-68)	v_f OSG[5][a] cm^3/g	v_f Kell [4]	v_f Extrapolated
0.	1.00021	1.0002117	1.000211
10.	1.00035	1.0003483	1.000343
20.	1.00184	1.0018446	1.001842
30.	1.00442	1.0044154	1.004413
50.	1.0121	1.0121483	1.012148
70.	1.0228	1.022768	1.022769
80.	1.0290	1.029046	1.029047
100.	1.0435	1.043445	1.043442
110.	1.0515	1.051561	1.051559
120.	1.0603	1.060298	1.060289
130.	1.0697	1.069675	1.069669
150.	1.0906	1.090463	1.090456
175.	1.1208		1.120672
200.	1.1564		1.156470
225.	1.1991		1.199309
250.	1.2511		1.251572
275.	1.3166		1.317277
300.	1.4033		1.403971
325.	1.5284		1.527736
350.	1.740		1.722171

[a] Adjusted to IPTS-68.

2.2. Heavy Water

Saturation liquid volumes of D_2O have been cited by Whalley [6] Hebert, MacDuffie and Secoy [7] and Grossman-Doerth [8] [9]. However these values differ by as much as 0.5%, for temperatures above 200 °C, and do not constitute an adequate base for establishing the liquid saturation line. The redetermination of saturated liquid volumes reported here utilizes the compressed liquid data of Emmet and Millero [10], Tsederberg et al. [11] [12] and Rivkin and Akhundov [13].

All of these volume data were corrected to 100% D_2O using stated impurities, and calculation of the H_2O volumes from Keenan, Keyes, Hill and Moore [14]. For the Emmet and Millero [10] data the impurity level (taken as H_2O) was unstated, and was inferred from a comparison of these data with the one-atmosphere volumes of Steckel and Szapiro [15] corrected to 100% D_2O. This implied that the Emmet and Millero [10] data pertained to 99.8% D_2O.

Figure 1 shows the degree of consistency between the corrected Emmet and Millero [10] and Tsederberg [11] data, and the one-atmosphere specific volumes correlated by Kell [16] for D_2O. The agreement is within a part in 10^4 up to 50°, and 3×10^4 at 100 °C.

The extrapolation to saturation pressure was performed using, for each isotherm, a least squares fit of the data to (1) and the D_2O saturation vapour pressure equation of Hill and MacMillan [17], which is as follows:

$$\ln\left[\frac{P}{P_c}\right] = \frac{T_c}{T}\left[n_1\tau + n_2\tau^{1.9} + n_4\tau^2 + n_{11}\tau^{5.5} + n_{20}\tau^{10}\right] \tag{3}$$

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[1] Figures in brackets indicate literature references at the end of this paper.

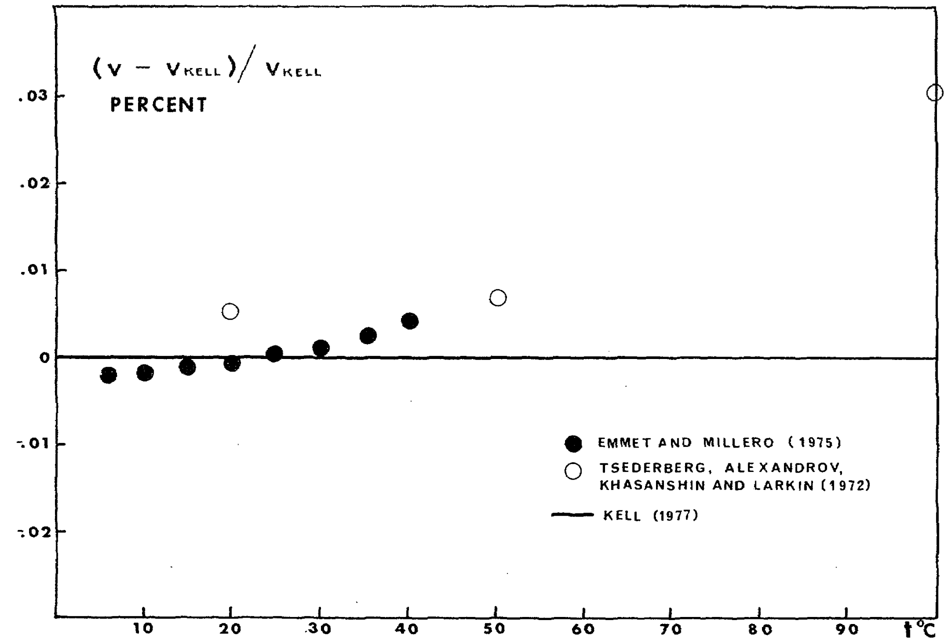

FIGURE 1. Specific volumes of D_2O at one atmosphere. Comparison of interpolated data with formulation of Kell [16].

in which

$$\tau = \left[1 - \frac{T}{T_c}\right]$$

$T_c =$ 643.89 K (IPTS-68)

$P_c =$ 21.66 MPa

$n_1 = -7.81583$ (± 0.00168)

$n_2 = 17.6012$ (± 0.0700)

$n_4 = -18.1747$ (± 0.0736)

$n_{11} = -3.92488$ (± 0.0420)

$n_{20} = 4.19174$ (± 0.291)

The critical parameters T_c and P_c are from Blank [18]. The number in parenthesis with each coefficient is the estimate of standard error.

Table 12 contains the extrapolated liquid volumes obtained. The uncertainties due to extrapolation are discussed in Appendix A.1. Figure 2 shows the relative consistency of the saturation liquid volumes obtained by extrapolation. The ratio v_{fD_2O}/v_{fH_2O} has been plotted to demonstrate smoothness to within 10^{-4} in relative volume. (Again the equation of Keenan, Keyes, Hill and Moore [14] has been used to obtain v_{fH_2O}.)

3. Saturated Liquid Enthalpy

3.1. Light Water

For H_2O the specific heat values of Sirota [19] along each of 9 isotherms were extrapolated to saturation vapor pressure by means of the formula

$$\ln C_p = \sum_{i=0}^{3} \alpha_i P^i \qquad (4)$$

These extrapolated values are shown in table 2 and were fitted to the following formula

$$C_{pt} = \sum_{i=0}^{2} \beta_i T^i \qquad (5)$$

in which, for $25 < t$ °C < 150

$\beta_0 = 5.844$ kJ/kg·K

$\beta_1 = -.0101$

$\beta_2 = .0000153$

and, for $150 \leqslant t$ °C $\leqslant 300$

$\beta_0 = 17.515$ kJ/kg·K

$\beta_1 = -.0611$

$\beta_2 = .0000708$

The uncertainties due to extrapolation to saturation are discussed in Appendix A.2 for both H_2O and D_2O.

TABLE 2. Specific heat of saturated liquid H_2O. Extrapolations from data of Sirota, Belyakov and Shrago [19]

t °C (IPTS-48)	C_{pt} J/g °C
50.	4.1822
100.	4.2149
150.	4.3124
200.	4.4980
250.	4.8656
300.	5.7594
310.	6.0648
320.	6.5091
330.	7.1223

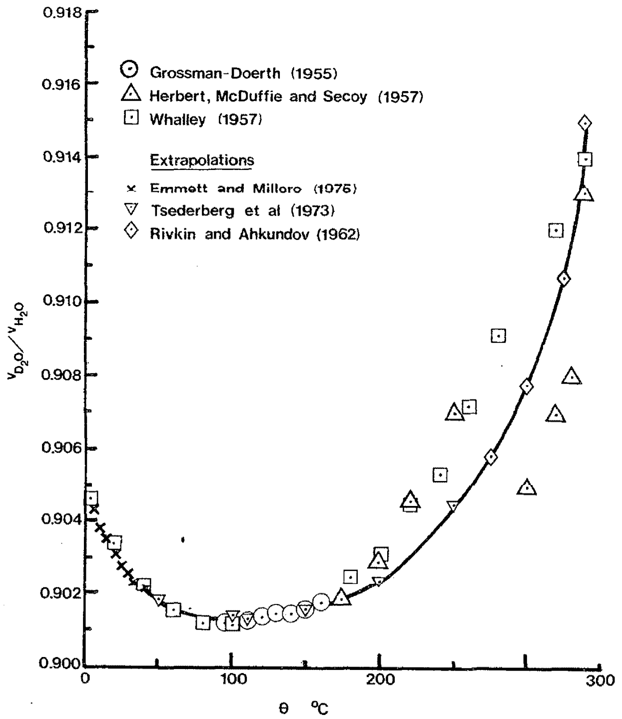

FIGURE 2. Saturation liquid volumes.

To determine the saturation liquid enthalpy h_f, use was made of the following equation, whose derivation is given in Appendix B.

$$\frac{dh_f}{dT} = C_{pf} + \left[\frac{d(v_f\tau)}{d\tau} + \left(\frac{\partial v}{\partial P}\right)_T T\frac{dP_{sat}}{dT}\right]\frac{dP_{sat}}{dT}. \tag{6}$$

Table 3 shows the comparison of the values of h_f integrated from eq (6) (taking h_f at 25 °C as 104.98 kJ/kg) with the values presented by Osborne, Stimson, and Ginnings [5], and indicates that up to 275 °C the value of h_f can be determined by the above equation well within 1 J/g. For 300 °C and 325 °C (for which the calculated value of h_f was obtained by a separate fit for C_{pf}) the uncertainty in the calculated value of h_f appears to be 2 J/g. The uncertainties in the values of h_f due to integration of eq (6) are discussed in Appendix A.3.

TABLE 3. Comparison of saturated liquid enthalpy calculated from eq (6) with values given by Osborne, Stimson and Ginnings [5] for H_2O

t °C (IPTS-68)	h_f OSG [5][a]	h_f Equation (4)
30.	125.74	125.87
50.	209.34	209.63
100.	419.11	419.25
110.	461.32	461.46
150.	632.12	632.35
200.	852.20	852.28
250.	1085.55	1084.92
275.	1210.51	1210.72
300.	1344.47	1346.45
325.	1493.08	1495.2

[a] Adjusted to IPTS-68.

3.2. Heavy Water

For D_2O, values of C_{pf} have been obtained by extrapolation of the values of C_p given by Rivkin and Egorov [20] and corrected to 100% D_2O. Table 4 shows the values of C_{pf} obtained in this way. These were used in a fit to eq (5) with the results:

For the temperature range $25 < t$ °C < 150

$$\beta_0 = 3.2483 \quad \text{kJ/kg·K}$$
$$\beta_1 = .01049$$
$$\beta_2 = -.3644 \times 10^{-4}$$
$$\beta_3 = .4021 \times 10^{-7}$$

and for $150 \leqslant t$ °C $\leqslant 300$

$$\beta_0 = -32.278 \quad \text{kJ/kg·K}$$
$$\beta_1 = .2433$$
$$\beta_2 = -.5448 \times 10^{-3}$$
$$\beta_3 = .4104 \times 10^{-6}$$

Table 4 also indicates the recommended values of C_{pf} provided by Rosta [21]; the two sets of values agree within 0.6%.

TABLE 4. Specific heat of saturated liquid D_2O. Comparison of extrapolated values with those of Rosta [21]

t °C (IPTS-68)	C_{pf} J/g	C_{pf} Rosta [21]
19.99	4.2048	4.219
39.99	4.1990	4.198
59.99	4.1837	4.182
79.99	4.1816	4.172
100.00	4.1793	4.168
120.01	4.1828	4.174
140.02	4.2023	4.192
160.03	4.2235	4.224
180.03	4.2726	4.273
200.04	4.3400	4.343
220.05	4.4542	4.441
240.06	4.5784	4.577
260.06	4.7710	4.768
280.07	5.0138	5.044
300.07	5.4923	5.470
310.07	5.7791	5.787
320.08	6.2068	6.204
330.08	6.8291	6.784

Evaluation of the term $\left[\quad\right]\frac{dP_{sat}}{dT}$ in eq (6) proceeded as follows. First using the data of table 12 the following formulation was obtained

$$v_f\tau = \sum_{i=0} \gamma_i\tau^i \qquad \tau = 1000/T \tag{7}$$

so that

$$\frac{d(v_f\tau)}{d\tau} = \sum_{i=0} i\gamma_i\tau^{i-1}$$

in which

$$\gamma_0 = .0017230 \quad \mathrm{cm^3/g\cdot K}$$
$$\gamma_1 = -.07568 \quad (25 < t\ {}^\circ\mathrm{C} < 150)$$
$$\gamma_2 = 139.41$$
$$\gamma_0 = .0057892 \quad \mathrm{cm^3/g\cdot K}$$
$$\gamma_1 = -3.7000 \quad (150 \leqslant t\ {}^\circ\mathrm{C} \leqslant 300)$$
$$\gamma_2 = 945.73$$

The term $\left(\frac{\partial v}{\partial T}\right)_P$ was obtained from formulae previously used to extrapolate to liquid saturation volumes. The elements necessary for calculation of $\frac{dh_f}{dT}$ are given in table 5. Figure 3 shows a comparison of C_{pf}, $\frac{dh_f}{dT}$ and the experimental determination of Nowak [22] [23] of $\frac{dh_f}{dT}$. The high temperature point is in good agreement with our inference from eq (6). At lower temperatures Nowak's experimental values are about 1.5% lower than the calculation, but this also means that they are inconsistent to the same extent with the specific heat data of Cockett and Ferguson [24] and Rivkin and Egorov [20]. (See figure 3.) We conclude therefore that our determination of $\frac{dh_f}{dT}$ is about the best that can be done with present experimental information.

Table 5 supplies also the values of h_f integrated from the polynominal representations of $\frac{dh_T}{dT}$ with the difference in enthalpy values between 25 °C and the triple point being set at 89.83 J/g. This value was estimated from $h_0 - h_g$ values at 25 and 3.8 °C, and corresponding values computed from the Clapeyron equation, as shown in section 6. Values of h_f below 25 °C are computed from h_{fg} values from the Clapeyron relationship, and from $h_0 - h_g$ values obtained from the virial equation (again, see sec. 6).

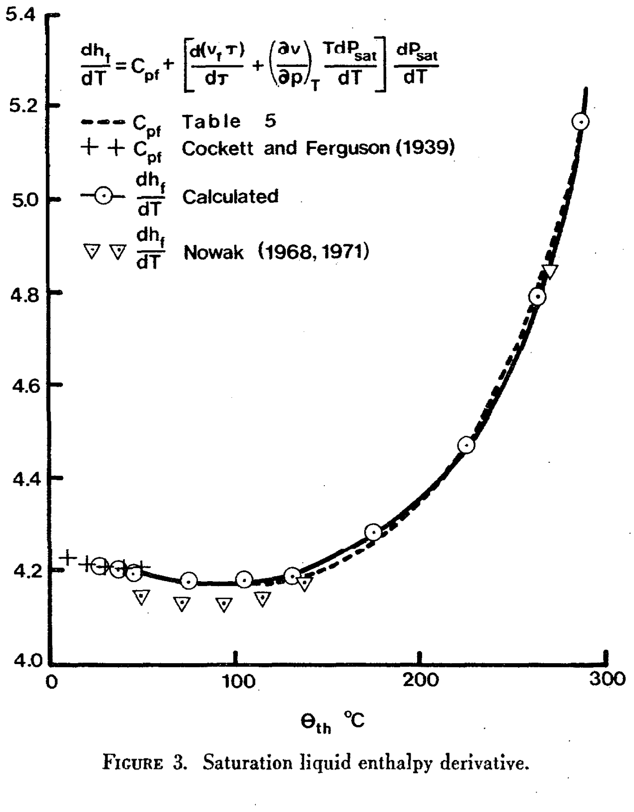

FIGURE 3. Saturation liquid enthalpy derivative.

The value 89.8 J/g is in good agreement with numerical integration of specific heat data of Cockett and Ferguson [24] which gives Δh_f from 3.8 to 25 °C as 89.5 J/g.

TABLE 5. Saturated liquid enthalpy of D_2O. Integration of equation (6).

t °C (IPTS-68)	$\frac{d(v_f\tau)}{d\tau}$	$\left(\frac{\partial v}{\partial p}\right)_T$	$\frac{dP_{sat}}{dT}$	h_f
25.0				89.8
30.0	.8440	—.000416	.000219	110.8
35.0	.8290	—.000412	.000282	131.8
40.0	.8146	—.000410	.000360	152.8
49.99	.7871	—.000409	.000567	194.7
100.	.6714	—.000464	.003509	404.0
111.02	.6500	—.000489	.004835	450.1
150.02	.5831	—.000608	.012684	613.8
200.04	.2972	—.000921	.032771	828.1
250.06	—.0849	—.001639	.068178	1051.9
275.09	—.2500	—.002561	.093010	1171.6
300.10	—.4005	—.004171	.123560	1300.4
325.13	—1.2306	—.007770	.161186	1441.2

4. Saturated Vapor Volumes

4.1. Liquid Water

For H_2O, v_g values were obtained by Osborne, Stimson and Ginnings [5] from direct calorific determinations of the quantity $v_g \frac{TdP_{sat}}{dT}$. These v_g values are shown in table 6 both as determined by Osborne and as revised by us, using the vapor pressure equation of Wagner [3] and the liquid saturation volumes of Kell et al. [14], [25]. Corresponding calorific data is not available for D_2O.

Second virial coefficient formulations for H_2O have been provided by Keyes [26] and by Kell, McLaurin and Whalley [27], who also provide a formulation for the third virial coefficient.

Use of the virial equation

$$\frac{Pv}{RT} = 1 + B/v + C/v^2 + D/v^3 \tag{8}$$

with $D = 0$, and the above formulations for B and C, proved inadequate to represent the saturation vapour volumes above 200 °C. But it was possible to achieve satisfactory agreement by adding a fourth-virial coefficient term, which could be represented, in the range 195 to 325 °C, by

$$\log_{10} D = 82.204 - 133.12\tau + 71.779\tau^2 - 12.542\tau^3 \tag{9}$$

in which $\tau = 1000/(273.15 + t^\circ{}_{48}\mathrm{C})$ and D is in $(\mathrm{cm^3/g})^3$.

For $t < 195$ °C the value of D was set equal to zero. The formulation for C is taken from Kell, McLaurin and Whalley [27] and is

$$C = [-423{,}960 + 4381.5t - 16.919t^2 + 0.029t^3 - 18.615 \times 10^{-6}t^4]/18.016^2\ (\mathrm{cm^3/g})^2. \qquad (10)$$

This formulation is based on experimental measurements down to 200 °C. For $t < 145$ °C the value of C is set equal to zero. The formulation for B is taken from Keenan, Keyes, Hill, and Moore [14] and is

$$B = 2.0624 - 2.61204\,\tau\,10^{\left(\frac{0.1008\tau^2}{1 + 0.0349\tau^2}\right)}\ (\mathrm{cm^3/g}). \qquad (11)$$

This H_2O formulation is used for the entire temperature range.

As shown in table 6, a simple virial equation with $C = D = 0$ will produce values of v_g which agree with the determinations of Osborne, Stimson, and Ginnings [5] to within one part in 1000 up to 150 °C. The use of formulations for C and D above that temperature renders good agreement up to 325 °C.

The values of B, C, and D are shown in table 7.

TABLE 6. Saturated vapor volumes of H_2O; comparison of values from Osborne, Stimson and Ginnings [5] with values obtained from a virial equation (8).

t °C (IPTS-68)	v_g[5] OSG (Revised) cm³/g	v_g[5] OSG	v_g Equation (8)
0.0	206233.	206288.	206058
19.99		57836.	57819
20.0	57796.		57793
49.99		12045.	12046
50.0	12037.		12040.6
100.0	1673.8	1673.0	1674.8
150.0	392.94		393.11
150.02		392.57	393.91
200.0	127.35		127.35
200.04		127.19	127.24
225.0	78.467		78.463
225.05		78.372	78.386
250.0	50.115		50.112
250.06		50.056	50.059
275.0	32.788		32.795
275.07		32.745	32.759
300.0	21.667		21.676
300.07		21.643	21.650
325.0	14.182		14.111
325.07		14.167	14.092

4.2. Heavy Water

For D_2O the values of v_g were obtained from the virial equation, using the vapor pressure equation of Hill and MacMillan [17].

The virial coefficients used were the same as for H_2O (in terms of molar volumes) except that allowance was made for the differences in B for D_2O and H_2O given by Kell, McLaurin, and Whalley [28] and Kell [29] which were represented by

TABLE 7. Virial coefficients for H_2O

t °C (IPTS-68)	B cm³/g	C (cm³/g)²	D (Cm³/g)³
0	−77.56	0.0	0.0
20	−58.76	0.0	0.0
50	−40.69	0.0	0.0
100	−24.48	0.0	0.0
150	−16.20	−181.72	0.0
200	−11.48	− 68.48	1177.
225	− 9.846	− 37.11	580.8
250	− 8.533	− 17.33	257.8
275	− 7.460	− 5.875	122.1
300	− 6.572	− 0.017	67.67
325	− 5.826	+ 2.437	46.00

$$B_{H_2O} - B_{D_2O} = 41.6016 - 38.2913\tau + 4.8814\tau^3\ \mathrm{cm^3/mol} \qquad (12)$$

in which $\tau = 1000/(273.15 + t°_{48}\mathrm{C})$.

Table 8 shows the values of B, C, and D and the values of v_g which were calculated from the virial equation for D_2O.

Table 9 shows values of v_g which were obtained by extrapolation to saturation pressure of the data of Rivkin and Ahkundov [13], on 4 isotherms. To test the consistency of the Rivkin and Ahkundov [13] isotherms with the virial coefficients of Kell, McLaurin and Whalley [28], a plot of $v \ln\left(\frac{Pv}{RT}\right)$ vs ρ was made (see fig. 4) following the derivation of Keyes [26] of

$$B = \lim_{\rho \to 0} v \ln \frac{Pv}{RT}.$$

The resulting B coefficients are shown in figure 5 to be in excellent agreement with eq (11) and (12).

Uncertainties due to extrapolation of limited data on vapor volumes are discussed in Appendix A.4.

TABLE 8. Virial coefficients for D_2O and saturated vapor volumes obtained from eq (8) with the vapor pressure equation of Hill and MacMillan [17]

t °C (IPTS-68)	B cm³/g	C (cm³/g)²	D (cm³/g)³	v_g cm³/g
3.8	−72.68	0.0	0.0	174119.
6.0	−70.42	0.0	0.0	149649.
10.0	−66.57	0.0	0.0	114465.
15.0	−62.13	0.0	0.0	82896.
20.0	−58.08	0.0	0.0	60820.
25.0	−54.38	0.0	0.0	45177.
30.0	−51.00	0.0	0.0	33950.
35.0	−47.89	0.0	0.0	25797.
40.0	−45.04	0.0	0.0	19807.
49.99	−39.99	0.0	0.0	12030.
100.0	−23.67	0.0	0.0	1585.4
111.02	−21.36	0.0	0.0	1101.8
150.02	−15.35	−146.99	0.0	360.83
200.04	−10.66	− 55.36	855.67	114.68
250.06	− 7.798	− 13.99	187.30	44.525
275.09	− 6.777	− 4.731	88.63	28.947
300.10	− 5.944	− 0.0013	49.15	18.978

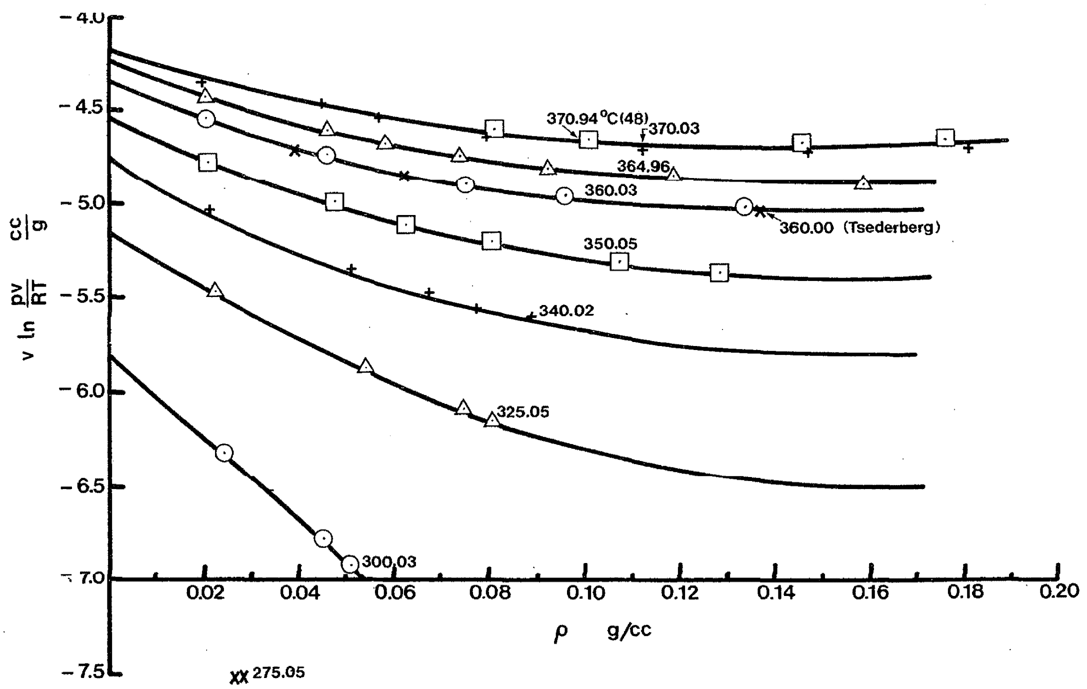

FIGURE 4. Determination of second virial coefficient from data of Rivkin and Ahkundov [13] D_2O.

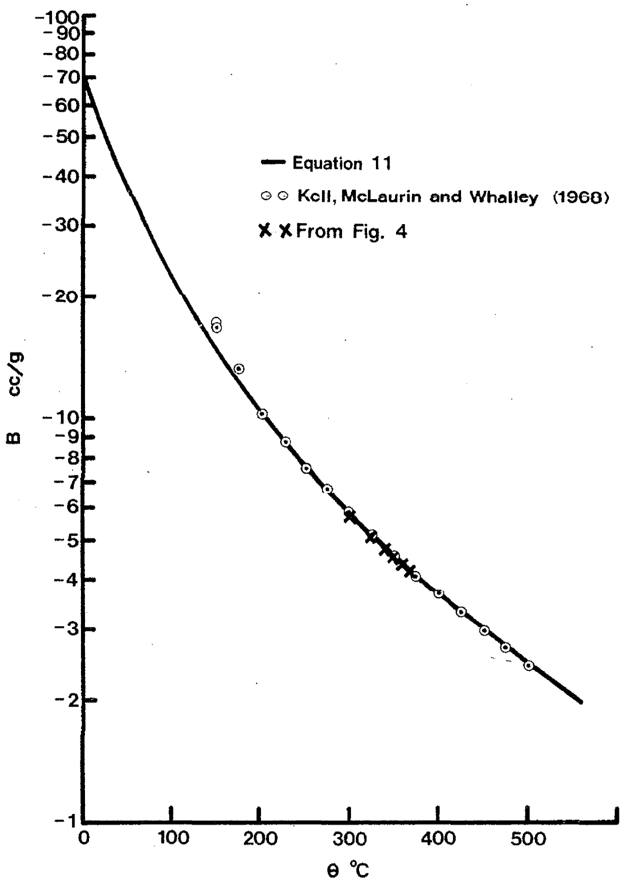

FIGURE 5. Second virial coefficients.

TABLE 9. Saturated vapor volumes of D_2O. Values obtained by extrapolations of data of Rivkin and Ahkundov [13]

t °C (IPTS-68)	v_g Extrapolations cm³/g
325.13	12.27183
340.10	9.30522
350.13	7.49275
360.06	5.79188

5. Saturation Vapor Enthalpies

5.1. Light Water

Two methods of estimating saturation vapor enthalpy were employed. The first uses previously determined values of v_g, h_f and saturation pressure with the Clapeyron equation to obtain

$$h_g = h_f + (v_g - v_f)\, T\, \frac{dP_{sat}}{dT}. \qquad (13)$$

A second method utilizes the virial equation and the thermodynamic relationship

$$\left(\frac{\partial h}{\partial P}\right)_T = \left(\frac{\partial (v\tau)}{\partial \tau}\right)_P$$

or

$$h_g = h_0 + \int_0^{P_{sat}} \left[\frac{\partial (v\tau)}{\partial \tau}\right]_P dP \qquad (14)$$

in which the integration proceeds along an isotherm from the zero pressure enthalpy h_0.

From the virial equation it may shown that

$$\left[\frac{\partial (v\tau)}{\partial \tau}\right]_P = \frac{\frac{\partial}{\partial \tau}(B\tau) + \frac{1}{(v\tau)}\frac{\partial}{\partial \tau}(C\tau^2) + \frac{1}{(v\tau)^2}\frac{\partial}{\partial \tau}(D\tau^3)}{1 + \frac{2B}{v} + \frac{3C}{v^2} + \frac{4D}{v^3}}. \tag{15}$$

Table 10 shows the results of using the second method for calculating the values of h_g for H_2O, using the values of B, C, and D given in table 8, and the derivatives from equations (9), (10) and (11), along with h_0 from Keenan, Keyes, Hill and Moore [14]. These indicate agreement with the Osborne, Stimson and Ginnings [5] values within 4 J/g up to 300 °C. Owing to the importance of the derivative terms in eq (15) closer agreement is difficult to obtain.

TABLE 10. Saturated liquid enthalpies of H_2O. Comparison of values of Osborne, Stimson, and Ginnings [5] with values estimated from eq (14).

t °C (IPTS-48)	h_g OSG [5] J/g	h_g Equation (14)
0	2500.8	2501.3
20	2537.6	2538.0
50	2591.6	2592.3
100	2675.8	2677.6
150	2746.5	2749.1
200	2793.0	2795.9
225	2802.6	2805.8
250	2801.0	2803.7
275	2785.1	2787.4
300	2749.1	2753.1

5.2. Heavy Water

For D_2O table 11 shows the degree of agreement between the calculations of h_g from equation (13) and those from equation (14).

The D_2O virial coefficients are given by eqs (9), (10), (11) and (12) and the values of h_0 were determined by

$$h_0 = \sum_{i=1}^{6} \frac{C_i\,(2-i)T^{i-1}}{1000^{i-1}} + C_7\,(\ln T - 1) + \left(R - \frac{C_8}{1000}\right)T \quad \text{J/g} \tag{16}$$

with the following values for c_i representing a fit to the ideal gas specific heats of Friedman and Haar [30]. The constant of integration was set to be consistent with zero internal energy at the triple point.

$c_1 =$ 1866.86

$c_2 =$ 4661.99

$c_3 =$ 64.6050

$c_4 =$ −284.8833

$c_5 =$ 100.1333

$c_6 =$ −13.1350

$c_7 =$ .32684

$c_8 =$ −1211.253

TABLE 11. Saturated vapor enthalpies of D_2O. Comparison of values calculated from the virial and Clapeyron equations.

t °C (IPTS-68)	h_g Equation (14) Isothermal integration from zero pressure J/g	h_g Equation (13) (Clausius-Clapeyron)
3.8	2324.0	
6.0	2327.7	
10.0	2334.5	
15.0	2342.9	
20.0	2351.3	
25.0	2359.7	
30.0	2368.1	2367.9
35.0	2376.4	2376.0
40.0	2384.7	2384.1
49.99	2401.2	2400.2
100.0	2480.0	2478.5
111.02	2496.1	2494.8
150.02	2546.0	2545.3
200.04	2589.1	2590.2
250.06	2596.9	2599.8
275.09	2582.5	2586.8
300.10	2551.5	2554.4

6. Saturation States of D_2O

Table 12 provides the recommended values of v_f, v_g, h_f and h_g, the latter being obtained using the Clapeyron equation with previously quoted values of h_f, v_f and v_g, for the temperature range above 25 °C. Below 25 °C (in the presence of liquid C_p data) the values of h_f were obtained as follows: First the value of h_g was obtained from equations (14) and (15); then the Clapeyron equation was used (with existing values of v_f and v_g) to obtain h_f. The values of v_f, v_g, h_f, h_g are thus thermodynamically consistent with the vapour pressure equation of Hill and MacMillan [17].

The value of h_{fg} for 25 °C from table 12 (2270 J/g) is in quite close agreement with the determination of Rossini, Knowlton and Johnston [31] who obtained

$$h_{fg} = 45{,}391 \pm 36 \text{ int j/mol at } 25\ ^\circ\text{C}$$

Using 1 int j = 1.0003 J and a molecular weight value of 20.0284, this value becomes

$$h_{fg} = 2267.0 \pm 1.8 \text{ J/g, at } 25\ ^\circ\text{C}$$

which compares with 2269.9 from table 12 at the same temperature.

7. Comparison of Saturated Molar Densities of D_2O and H_2O

Figures 6 and 7 show the values of, and the differences between, the molar densities of D_2O and H_2O for both saturated liquid and saturated vapor. For H_2O the saturation states have been taken from Keenan, Keyes, Hill, and Moore [14].

For the saturated liquid states of D_2O, values have been obtained from the equation of state of Ikeda, Kageyama, and Nagashima [32] for liquid D_2O, along with the saturation vapor equation of Hill and MacMillan [17]. A few extrapolations from unpublished data of Kell [29] are also shown for temperatures between 150° and 300 °C. These are in agreement with table 12 to within 1 part in 5000.

For the saturated vapor states, values have been obtained from the recent equation of state of Juza [33] (for vapor states below 340 °C) along with the saturation vapor equation of Hill and MacMillan [17]. The agreement between these values and those of table 12 is better than about 1 part in 2500, except at 340 °C. This is one of the 4 values from table 9 extrapolated from the vapor state measurements of Rivkin and Ahkundov [13], for 325, 340, 350 and 360 °C. Also shown are extrapolations from a few unpublished data from Kell [29] for temperatures 150, 175, 200, 225, 250, and 275 °C.

8. The Critical Density of D_2O

Figures 8 and 9 show the values of, and the differences between, the mean molar saturation densities $(\rho_f + \rho_g)/2$ of D_2O and H_2O. The values for H_2O have been taken from Keenan, Keyes, Hill, and Moore [14] except that the critical density for H_2O has been taken as 0.324 g/cm^3, i.e., 18.0 kmol/m^3.

For temperatures between 200 °C and the critical temperature (as well as below 100 °C) there appear to be significant differences in mean molar density of D_2O and H_2O, at the same reduced temperature. However, the absence of reliable saturation densities for D_2O above 330 or 340 °C means that one cannot conclude that the critical molar density of D_2O is appreciably different from that of H_2O. Hence our best estimate of the critical density of D_2O at this time is 0.361 g/cm^3 = 18.0 kmol/m^3.

Figure 10 shows 2 experimental isotherms of Rivkin and Ahkundov [13] for D_2O in the vicinity of its critical point. Also shown is a linear interpolation to the 370.74 °C (IPTS 68) isotherm which Blank [18] concluded was the critical temperature. The linearly interpolated isotherm does not have a point of zero slope, nor does the closely subcritical isotherm at 370.53 °C exhibit a zero slope segment for the 2-phase region. The difference between the pressure on the interpolated isotherm at the deduced critical density ρ_c = 0.361 g/cm^3 and the Blank [18] determination of the critical pressure is about 1 part in 3000.

From the foregoing we conclude that while the value of the critical density cited above could differ by 2 percent from the true value, it is in quite reasonable agreement with the critical region PvT data of Rivkin and Ahkundov [13].

TABLE 12. Recommended saturation values for D_2O

t °C (IPTS-68)	P_{sat} MPa	v_f cm^3/g	v_g	h_f J/g	h_g
3.8	.000660	.90464[a]	174119.	0.0	2324.0
6.0	.000774	.90439	149649.	9.3	2327.7
10.0	.001026	.90419	114465.	26.4	2334.5
15.0	.001442	.90428	82896.	47.4	2342.9
20.0	.001999	.90472	60820.	68.6	2351.3
25.0	.002737	.90545	45177.	89.8	2359.7
30.0	.003702	.90645	33950.	110.8	2367.9
35.0	.004950	.90771	25797.	131.8	2376.0
40.0	.006549	.90918	19807.	152.8	2384.1
49.99	.011115	.91274	12030.	194.7	2400.2
100.	.096252	.94057	1585.4	404.0	2478.5
111.02	.14194	.94866	1101.8	450.1	2494.8
150.02	.46558	.98317	360.83	613.8	2545.3
200.04	1.5474	1.0438	114.68	828.1	2590.2
250.06	3.9994	1.1320	44.525	1051.9	2599.8
275.09	6.0054	1.1931	28.947	1171.6	2586.8
300.10	8.7011	1.2746	18.978	1300.4	2554.4
325.13	12.247	1.3925	12.272	1441.2	2490.3
340.10	14.857	1.5006	9.305		
350.13	16.845	1.6044	7.493		

[a] Extrapolated from v_f at higher temperatures.

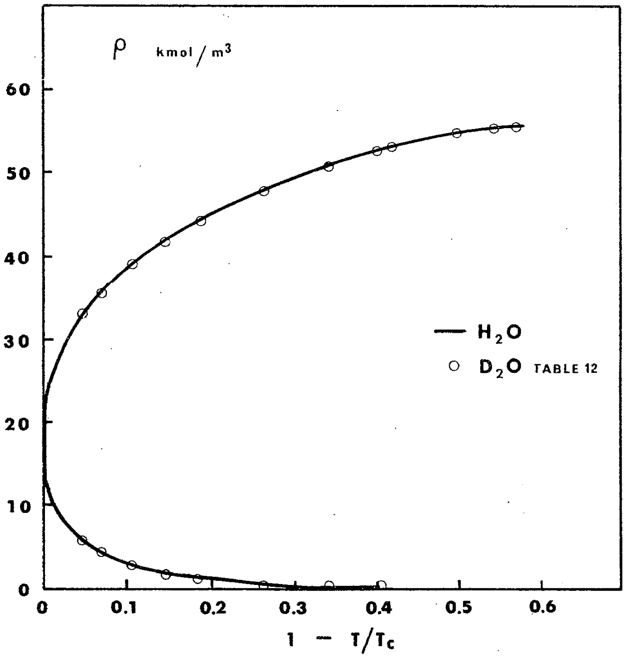

FIGURE 6. Densities of saturated states of D_2O and H_2O.

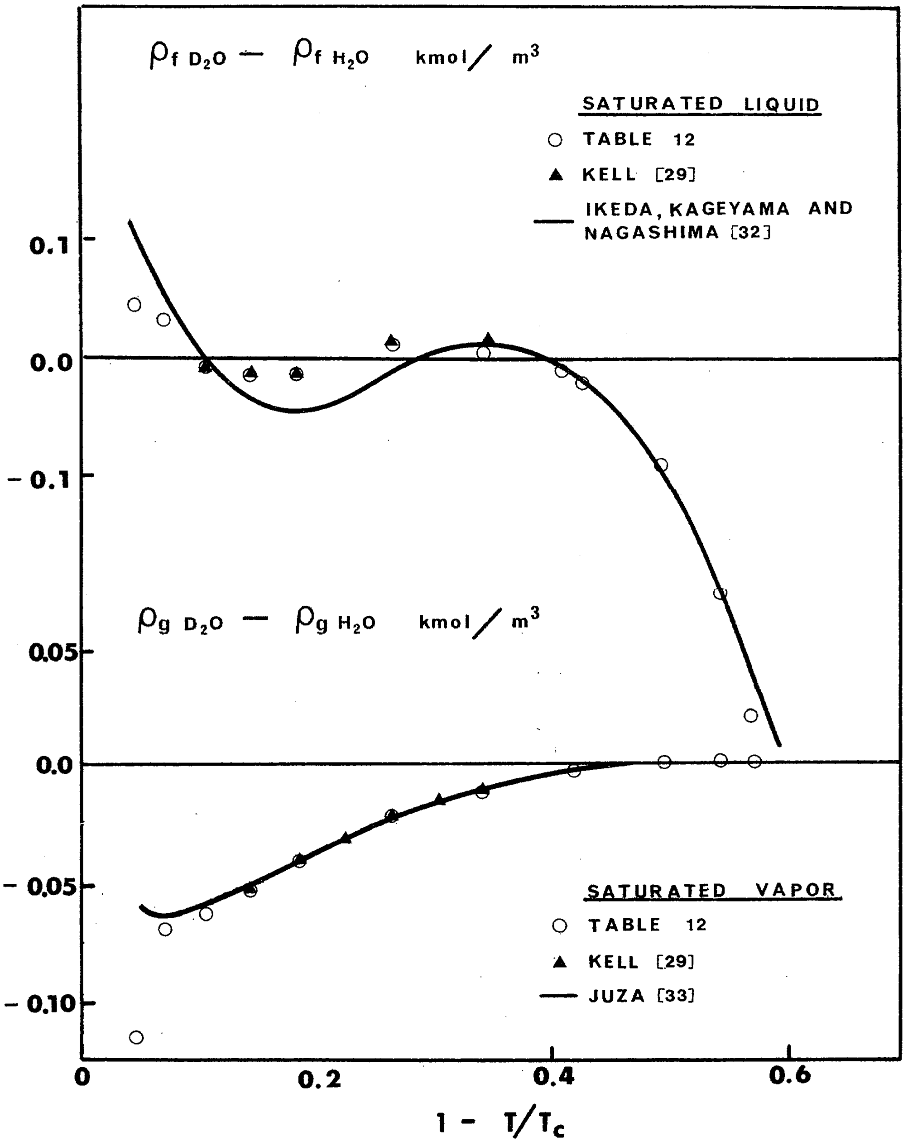

FIGURE 7. Comparison of molar densities of D_2O and H_2O.

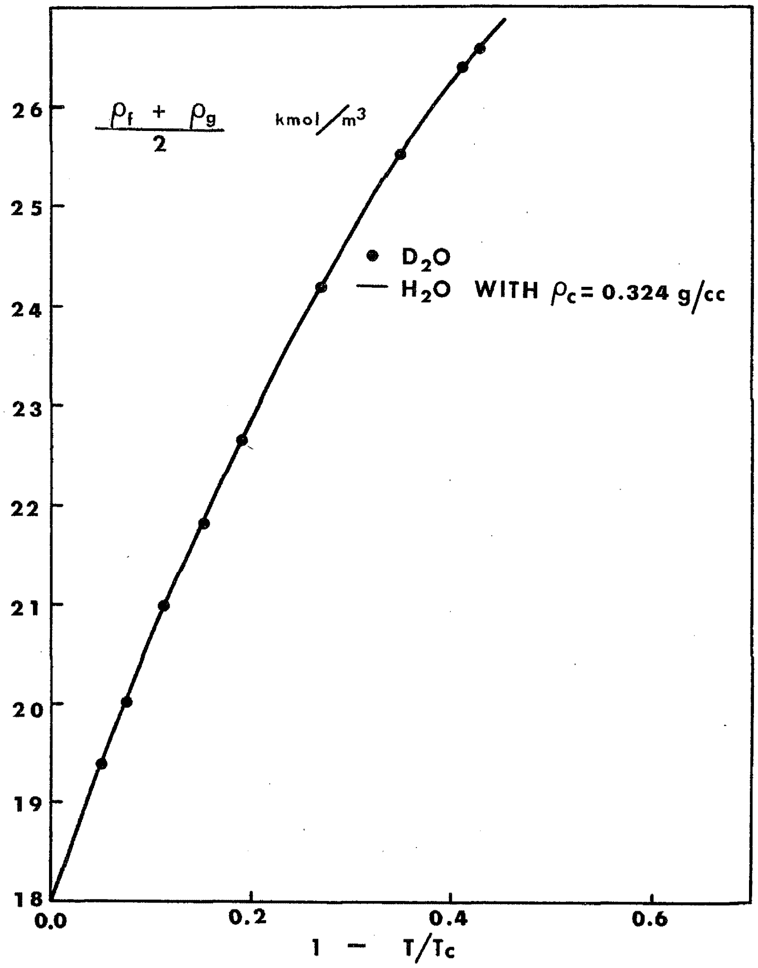

FIGURE 8. Estimation of the critical density of D_2O.

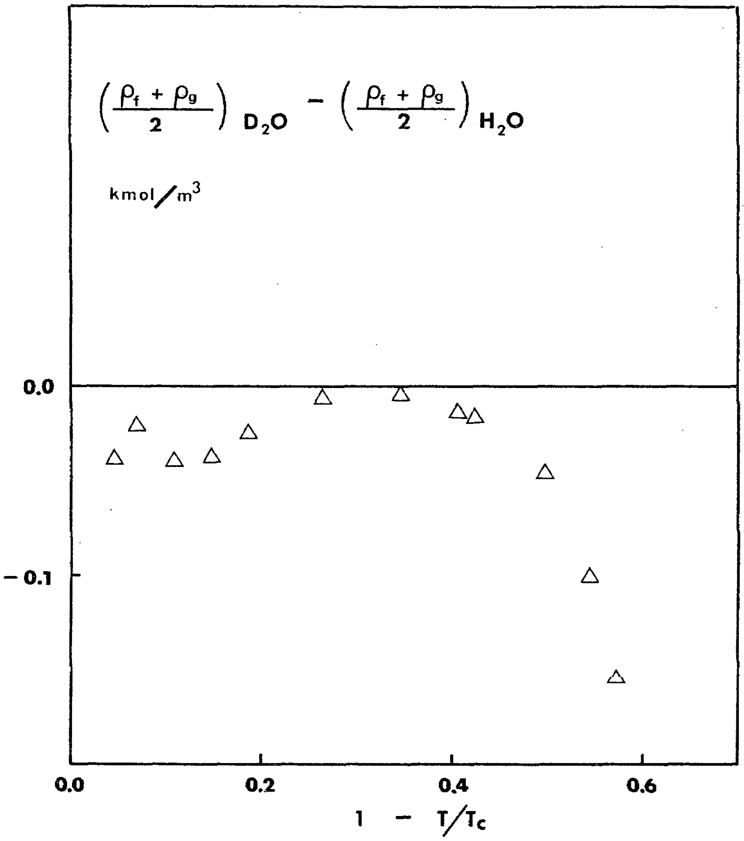

FIGURE 9. Differences in mean saturation densities of H_2O and D_2O values from table 12.

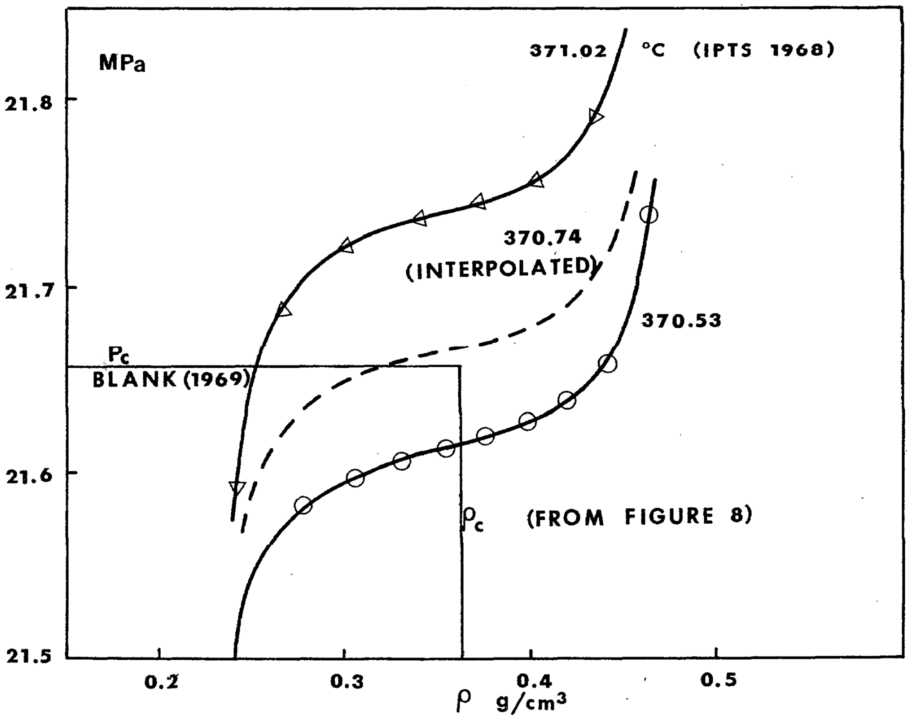

FIGURE 10. Critical region of D_2O.

Appendix A. Uncertainties

A.1. Saturated Liquid Volumes

At 0 °C the 6 H_2O data used to evaluate eq (1) varied from 0.1 to 4.2 MPa and were fit to a standard error of 4×10^{-7} in $\ln v$ or an error of $4 \times 10^{-5}\%$ in v. Given that the error in P_{sat} is of the order of 0.1%, and that the quantity $\frac{v}{P}\frac{\partial P}{\partial v}$ is of the order of 10,000 the uncertainty in the saturated liquid volume (due to the fitting process and the uncertainty in vapour pressure) is expected to be $5 \times 10^{-5}\%$. This uncertainty is of course additional to the effect of systematic error in the data.

At 325 °C the 6 H_2O data used to evaluate eq (1) varied from 13 to 38 MPa and were fit to a standard error of $8 \times 10^{-3}\%$ in v. Since at that temperature $\frac{v}{P}\frac{\partial P}{\partial v}$ is of the order of 20 and the uncertainty in P_{sat} is of the order of 0.1% the uncertainty in the saturation volume introduced by the extrapolation process is expected to be $13 \times 10^{-3}\%$ in v which is considerably less than the uncertainty in the data, if the possibility of systematic errors is allowed for.

At 6 °C the 6 D_2O data used to evaluate eq (1) ranged in pressure from 1 to 50 MPa and the standard error in the fit was $3.6 \times 10^{-4}\%$ in v. Given a std. error in P_{sat} of 0.3% (see Hill and MacMillan [17]) and that $\frac{v}{P}\frac{\partial P}{\partial v}$ is of the order of 10,000, the uncertainty introduced by the extrapolation process is of the order of $4 \times 10^{-4}\%$ in v which is small compared to the uncertainty introduced in adjusting the data to correspond to 100% D_2O (of the order of $10^{-2}\%$).

At 340 °C the 6 D_2O data used to evaluate eq (1) ranged from 15 to 29 MPa and the standard error in the fit was 0.11%. Given that the value of $\frac{v}{P}\frac{\partial P}{\partial v}$ on the saturation line at that temperature was of the order of 20 and that the error in P_{sat} at 340 °C was 0.013% [17], the error in v due to extrapolation is expected to be 0.11% which may be of the same order as the uncertainty in the data. Rivkin [13] provides data for D_2O to within 0.3 MPa of saturation pressure (275 °C to 350 °C) as compared to 1.0 — 4.5 MPa for H_2O data at the same temperatures.

A.2. Specific Heat of Saturated Liquid

At 50 °C the 6 H_2O data used to evaluate eq (5) ranged from 2.5 to 15 MPa and were fit with a standard error of $8.5 \times 10^{-3}\%$ in C_p. Given that, at that temperature $\frac{P}{C_p}\frac{\partial C_p}{\partial P}$ is of the order of 0.01%, and that the vapor pressure uncertainty is less than 0.1% the uncertainty in C_p due to the extrapolation process is expected to be $10^{-2}\%$.

At 300 °C the 6 H_2O data used to evaluate eq (6) ranged from 10 to 22.5 MPa and were fit with a standard error of $1.8 \times 10^{-2}\%$ in C_p. Given that at that temperature $\frac{P}{C_p}\frac{\partial C_p}{\partial P}$ is of the order of —0.1 and that the vapor pressure uncertainty is of the order of .01%, the uncertainty in C_p due to the extrapolation process is expected to be $2 \times 10^{-2}\%$.

At 20 °C the 6 D_2O data used to evaluate eq (6) ranged from 4.9 to 22.1 MPa and were fit with a standard error of $3.1 \times 10^{-2}\%$ in C_p. Given that at that temperature $\frac{P}{C_p}\frac{\partial C_p}{\partial P}$ is of the order of $-10^{-5}\%$ and that the vapor pressure uncertainty is of the order of 0.3%, the uncertainty in C_p due to the extrapolation process is expected to be $8 \times 10^{-2}\%$.

At 300 °C the 6 D_2O data used to evaluate eq (6) ranged from 9.8 to 23.5 MPa and were fit to a standard error of $7.8 \times 10^{-2}\%$ in C_p. Given that at that temperature $\frac{P}{C_p}\frac{C_p}{P}$ is of the order of —0.1 and that the vapor pressure uncertainty is of the order of 0.013% the uncertainty in C_p due to the extrapolation process is $8 \times 10^{-2}\%$.

A.3. Saturated Liquid Enthalpies

These were obtained by the integration of eq (6) in which the first term on the right hand side was typically two orders of magnitude larger than the second term. Hence the main contribution to uncertainty in h_f will be assumed to be due to C_{pf}.

As indicated in section A.2 the uncertainties in C_{pf} for H_2O due to extrapolation are small. In fitting eq (5) to 4 H_2O C_{pf} "data" between 50 and 200 °C the absolute standard error was 0.0052 kJ/kg·K. For a fit to 4 H_2O C_{pf} data points in the range between 150 °C and 300 °C the standard deviation is 0.077 kJ/kg·K. If one arbitrarily estimates that the relative error in the integral of C_{pf} over an interval of 300 ° is at least one order of magnitude less than the maximum error in C_{pf} then the uncertainty in h_f at high temperature due to integration of C_{pf} from the triple point would be less than 2 J/g. This value may be compared with the discrepancy between the Osborne, Stimson and Ginnings results, and the results of the use of eq (6) for H_2O (see table 3).

As indicated in section A.2 the uncertainties in C_{pf} for D_2O were also small. In fitting eq (5) to 8 of these C_{pf} "data" between 20 and 160 °C the standard error was 0.003 kJ/kg·K. For a fit to 9 "data" between 140 and 300 °C the standard error was 0.031 kJ/kg·K. Again, arbitrarily assuming the relative error in the integral of C_{pf} over a range of 300 °C is an order of magnitude less than the relative error in C_{pf}, the uncertainty in h_f at 300 °C due to integration of C_{pf} from the triple point would be of the order of 1 J/g.

A.4. Saturated Vapor Volumes

The test of the method of determining the saturated vapor volumes by a virial equation is the agreement with the extrapolated experimental data of Rivkin and Ahkundov [13] and Kell [29]. As shown in figure 7 these values of v_g appear consistent with each other and with the values of table 12 within about 0.1%. Even though these experimental data are only available over a limited temperature range it is assumed that the uncertainty of the v_g values in table 12 is 0.1% over the whole range.

A.5. Saturated Vapor Enthalpies

In the absence of calorific data the uncertainty in saturation vapor enthalpy depends mainly on the uncertainty in the saturation vapor volumes. Using the Clausius-Clapeyron equation it may be shown that

$$\delta h_g \simeq v_g T \frac{dP_{\text{sat}}}{dT} \frac{\delta v_g}{v_g}.$$

Assuming $\delta v_g/v_g = 0.001$ and the information in tables 5 and 12 yields $\delta h_g = 2.2$ J/g at 30 °C and 1.3 J/g at 300 °C. Given also the uncertainty in the saturated liquid enthalpy, the uncertainty in saturation vapor enthalpy may be expected to range from 2 to 4 J/g as one proceeds from the triple point temperature to 300 °C.

Appendix B

Derivation of equation (6).

We first write

$$\begin{aligned} dh &= \left(\frac{\partial h}{\partial T}\right)_P dT + \left(\frac{\partial h}{\partial P}\right)_T dP \\ &= C_p dT + \left[\frac{\partial (v\tau)}{\partial \tau}\right]_P dP \end{aligned}$$

in which

$$\tau = 1/T.$$

Then we write

$$d(v\tau) = \left[\frac{\partial (v\tau)}{\partial \tau}\right]_P d\tau + \left[\frac{\partial (v\tau)}{\partial P}\right]_T dP$$

so that

$$\left(\frac{d(v\tau)}{d\tau}\right)_{\text{sat}} = \left[\frac{\partial (v\tau)}{\partial \tau}\right]_P + \left[\frac{\partial (v\tau)}{\partial P}\right]_T \frac{dP_{\text{sat}}}{d\tau}.$$

Thus

$$\begin{aligned} dh &= C_p dT + \left\{\left(\frac{d(v\tau)}{d\tau}\right)_{\text{sat}} - \left[\frac{\partial (v\tau)}{\partial P}\right]_T \frac{dP_{\text{sat}}}{d\tau}\right\} dP \\ &= C_p dT + \left\{\left(\frac{d(v\tau)}{d\tau}\right)_{\text{sat}} + \left(\frac{\partial v}{\partial P}\right)_T T \frac{dP_{\text{sat}}}{dT}\right\} dP \end{aligned}$$

and

$$\left(\frac{dh}{dT}\right)_{\text{sat}} = C_{pf} + \left[\left(\frac{d(v\tau)}{d\tau}\right)_{\text{sat}} + \left(\frac{\partial v}{\partial P}\right)_T T \frac{dP_{\text{sat}}}{dT}\right] \frac{dP_{\text{sat}}}{dT}$$

or,

$$\frac{dh_f}{dT} = C_{pf} + \left[\left(\frac{d(v_f\tau)}{d\tau}\right) + \left(\frac{\partial v}{\partial P}\right)_T T \frac{dP_{\text{sat}}}{dT}\right] \frac{dP_{\text{sat}}}{dT}.$$

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