A Fundamental Equation of State for Heavy Water

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A fundamental equation of state has been formulated for heavy water in the form

$$\Psi = \Psi(\rho, T)$$

in which Ψ = Helmholtz free energy

ρ = density

T = thermodynamic temperature

The complete range of single phase states in the range up to 100 MPa and 600 °C is covered by a single equation which is fitted both to PVT values, for saturated and unsaturated states, and to enthalpy values for saturation states only. The equation is constrained to fit the critical point conditions determined by Blank. It represents all thermodynamic properties of D_2O, in the above range of states.

Key words: equation of state; enthalpy; Helmholtz function; heavy water; PVT; specific heats; speed of sound; thermodynamic properties; vapor pressure

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1. Introduction

This paper describes the development of a fundamental equation for heavy water. The equation has the form

$$\Psi = \Psi(\rho, T)$$

in which Ψ is the specific Helmholtz free energy, ρ is the density, and T is the thermodynamic temperature. The equation represents a continuity of single phase states covering both liquid and vapor regions to about 100 MPa in pressure and 600 °C in temperature. From this equation all thermodynamic properties can be derived, including the saturation properties, within the experimental uncertainty.

It is only in recent years that sufficient data on the thermodynamic properties of D_2O have been acquired to permit a comprehensive formulation of this type. Vapor pressure data can now be said to be plentiful and the uncertainty in the vapor pressure is now less than 0.1%, except at low temperatures. PVT data for liquid states are also relatively abundant, but uncertainties in isotopic content mean that liquid volumes are not generally known within 0.01%, even at low temperatures. Experimentally determined virial coefficients are now available as well as critical-region and supercritical-region PVT data.

Considerable uncertainty still attaches to determination of saturation volumes (particularly on the vapor side at relatively high subcritical temperatures), and to determination of saturation enthalpies. Critical point parameters are also uncertain. The range of disagreement between reported values is as large as 1 °C, 0.1 MPa and 0.2 cm³/g, though Blank's determination of the critical temperature (by meniscus observation) differs by not more than 0.1 °C from the critical temperature one would infer from the critical region PVT data of Rivkin.

With these uncertainties in mind, it is clear that the accuracy of the best heavy water equation which it is possible to formulate at the present time will be less than that of existing light water equations of this type (see Keenan, Keyes, Hill and Moore[1][1] and Pollak [2]). However the level of accuracy now attainable will be, in almost all respects, well within engineering requirements.

Previous tables and equations of state for D_2O properties are described in Kirschenbaum [3], Kesselman [4], Baker [5], Mamedov [6], Plank [7], Suvorov [8], Elliot [9], Kirrillin [10], Lundquist and Persson [11], Rosta [12], Ivey and Tarasuk [13], Scheffler, Nitsche and Straub [14], Ikeda, Kageyama, and Nagashima [15], and Juza and Mares [16]. A comprehensive bibliography of papers on D_2O has been compiled by Uematsu and Watanabe [17].

The great advantage of the fundamental equation formulation is that it guarantees complete consistency of PVT and ener-gy, enthalpy, and entropy calculations. Moreover it contains the vapor pressure relationship (when used in conjunction with the two-phase equilibrium requirement). The equation also provides a calculation of all other thermodynamic variables including virial coefficients, Joule-Thomson coefficient, compressibility, and speed of sound. In principle all of the existing data on these variables can be used in the formulation process. The great contribution of high speed computing to the formulation process is in the possibility of fitting a single equation over the entire range of liquid and vapor states and over all kinds of available data. In practice, of course, it is wise to be selective, to include the highest quality data with appropriate weight, rather than including all data indiscriminately. Although experimental PVT measurements are now available to cover a broad temperature and pressure range, saturation values of liquid volume (v_f), vapor volume (v_g), liquid enthalpy (h_f), vapor enthalpy (h_g), and saturation pressure have been determined before the global fitting process begins. Previous papers (Hill and MacMillan [18] and [19]), describe a new vapor pressure formulation and the determination of saturation properties of D_2O.

2. The Equation of State

The equation of state has the following form:

$$\Psi = \Psi_o(T) + RT\,[\ln\rho + \rho Q(\rho, T)] \tag{1}$$

in which

$$Q = (\tau - \tau_c)\sum_{j=1}^{7}(\tau - \tau_{aj})^{j-2}\left[\sum_{i=1}^{8}A_{ij}(\rho - \rho_{aj})^{i-1} + e^{-E\rho}\sum_{i=9}^{10}A_{ij}\rho^{i-9}\right] \tag{2}$$

and

$$\Psi_o(T) = \sum_{i=1}^{6}C_i\left(\frac{T}{1000}\right)^{i-1} + C_7\ln T + \frac{C_8 T\ln T}{1000}. \tag{3}$$

$$R = 0.41515 \text{ kJ/kg K.}$$

The units are as follows:

Ψ, Ψ_o Specific Helmholtz free energy, kJ/kg

T Absolute thermodynamic temperature, K

τ $1000/T$, K^{-1}

ρ Density, 10^3kg/m³, i.e., g/cm³

The constants in the double series expansion of Q are:

τ_c	$= 1.553$	E	$= 4.3$
τ_{aj}	$= 1.553$ $(j = 1)$	ρ_{aj}	$= 0.7$ $(j = 1)$
τ_{aj}	$= 2.53$ $(j > 1)$	ρ_{aj}	$= 1.1$ $(j > 1)$

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

The coefficients C_j are given as follows:

$$C_1 = 1866.81 \qquad C_5 = 100.1333$$
$$C_2 = 4661.5 \qquad C_6 = -13.135$$
$$C_3 = 64.605 \qquad C_7 = 0.32684$$
$$C_4 = -284.8833 \qquad C_8 = -1211.253$$

and the coefficients A_{ij} are given in table 1. The coefficients C_1 and C_2 have been chosen so that the internal energy and Helmholtz free energy are both zero in the triple point liquid state, as shown in Appendix A.

From the fundamental equation the following properties are obtained by differentiation:

Pressure:

MPa

$$P = \rho^2 \left(\frac{\partial \Psi}{\partial \rho} \right)_\tau$$

$$P = \rho R T \left[1 + \rho Q + \rho^2 \left(\frac{\partial Q}{\partial \rho} \right)_\tau \right] \tag{4}$$

Specific Internal Energy:

kJ/kg

$$u = \left[\frac{\partial (\Psi \tau)}{\partial \tau} \right]_\rho$$

$$u = \frac{d}{d\tau} (\Psi_0 \tau) + R T \rho \tau \left(\frac{\partial Q}{\partial \tau} \right)_\rho \tag{5}$$

Specific Entropy:

kJ/kg K

$$s = -\left(\frac{\partial \Psi}{\partial T} \right)_\rho$$

$$s = -R \left[\ln \rho + \rho Q + \rho T \frac{\partial Q}{\partial T} \right] - \frac{d\psi_0}{dT} \tag{6}$$

Specific Enthalpy:

kJ/kg

$$h = u + P / \rho$$

$$h = RT \left[1 + \rho Q - \rho T \frac{\partial Q}{\partial T} + \rho^2 \frac{\partial Q}{\partial \rho} \right] + \frac{d(\psi_0 \tau)}{d\tau} \tag{7}$$

Other properties are obtained as follows:

Specific Heats:

kJ/kg K

$$C_P = \left(\frac{\partial h}{\partial T} \right)_P$$

$$C_P = \left(\frac{\partial h}{\partial T} \right)_\rho - \frac{\left(\frac{\partial h}{\partial \rho} \right)_T \left(\frac{\partial P}{\partial T} \right)_\rho}{\left(\frac{\partial P}{\partial \rho} \right)_T} \tag{8}$$

$$C_v = \left(\frac{\partial u}{\partial T} \right)_\rho$$

Second Virial Coefficient:

$(10^3 \text{kg/m}^3)^{-1}$

$$B = (Q)_{\rho \to 0} \tag{9}$$

Third Virial Coefficient:

$(10^3 \text{kg/m}^3)^{-2}$

$$C = \left(\frac{\partial Q}{\partial \rho} \right)_{\rho \to 0} \tag{10}$$

Joule-Thomson Coefficient:

K/MPa

$$\mu = \left(\frac{\partial T}{\partial P} \right)_h$$

$$\mu = -\left(\frac{\partial h}{\partial P} \right)_T \frac{1}{C_P} = \frac{1}{\rho C_P} \left[\frac{T \left(\frac{\partial P}{\partial T} \right)_\rho}{\rho \left(\frac{\partial P}{\partial \rho} \right)_T} - 1 \right] \tag{11}$$

Compressibility (Isothermal):

$(\text{MPa})^{-1}$

$$K_T = \left[\rho \left(\frac{\partial P}{\partial \rho} \right)_T \right]^{-1} \tag{12}$$

Speed of Sound:

m/s

$$a = \left[\frac{1}{\left(\frac{\partial P}{\partial \rho} \right)_T} - \frac{T}{C_P \rho^2} \frac{\left(\frac{\partial P}{\partial T} \right)_\rho^2}{\left(\frac{\partial P}{\partial \rho} \right)_T} \right]^{-1/2} \tag{13}$$

The vapor pressure is obtained from the equation of state by satisfying the condition

$$(\Psi + P / \rho)_f = (\psi + P / \rho)_g, \tag{14}$$

TABLE 1. The coefficients A_{ij}

i	j	A_{ij}	i	j	A_{ij}
1	1	73.13848592	1	5	-6.73408249
2	1	-285.20415917	2	5	24.03602093
3	1	535.71659288	3	5	-41.08079830
4	1	-649.81000614	4	5	45.39111005
5	1	574.63280680	9	5	139.21659329
6	1	-387.92157774	10	5	566.02305152
7	1	206.34569512	1	6	-5.24802962
8	1	-79.89428513	2	6	18.52690633
9	1	-996.36169097	3	6	-31.42397369
10	1	-766.27290006	4	6	26.43208802
1	2	24.74108348	9	6	96.31411481
2	2	-105.57317181	10	6	453.20280933
3	2	200.87302906	1	7	-1.17583447
4	2	-235.18776440	2	7	4.13816432
5	2	224.56976938	3	7	-6.55842224
6	2	-40.09924297	4	7	4.75774631
7	2	128.77154771	9	7	19.39184297
8	2	-28.40907978	10	7	103.56819758
9	2	-1389.08003142			
10	2	-1672.09705556			
1	3	11.64775625			
2	3	-42.51820251			
3	3	72.45541064			
4	3	-82.55391089			
9	3	-267.85482520			
10	3	-998.64982710			
1	4	2.66566642			
2	4	-9.19657655			
3	4	15.13096920			
4	4	-7.24860975			
9	4	-46.83904320			
10	4	-227.34793319			

where f and g denote the saturated liquid and vapor phases, respectively.

3. The Fitting Procedure

The fitting procedure determines the coefficients A_{ij} by minimizing the quantity

$$D = \sum_{i=1}^{N} \left[\frac{P_{obs} - P_{calc}}{\Delta P} \right]^2 + \sum_{i=1}^{M} \left[\frac{h_{obs} - h_{calc}}{\Delta h} \right]^2$$

$$+ \sum_{i=1}^{K} \left[\frac{\zeta_g - \zeta_g}{\Delta \zeta} \right]^2 + \sum_{i=1}^{L} \lambda_i G_i \quad (15)$$

in which the first summation includes all PVT data points included in the fitting procedure and the second summation includes the enthalpy data points. The subscripts "obs" and "calc" refer to data points and calculated values, respectively. The third summation includes a weighted least squares fit to the saturation equilibrium condition (ζ_f and ζ_g being the chemical potential of saturated liquid and saturated vapor, respectively). This summation extends over a number (about 20) of the subcritical isotherms. The coefficients λ_i in the fourth summation are the Lagrange multipliers corresponding to the constraints G_i.

The terms ΔP, Δh and $\Delta \zeta$, which provide the weighting for the least squares summations, are the r.m.s. uncertainties of the dependent variable for each data point. For the PVT data

$$\frac{\Delta P}{P} = \left[\left(\frac{\delta P}{P} \right)^2 + \left(\frac{V}{P} \frac{\partial P}{\partial V} \frac{\delta V}{V} \right)^2 + \left(\frac{T}{P} \frac{\partial P}{\partial T} \frac{\delta T}{T} \right)^2 \right]^{1/2} \quad (16)$$
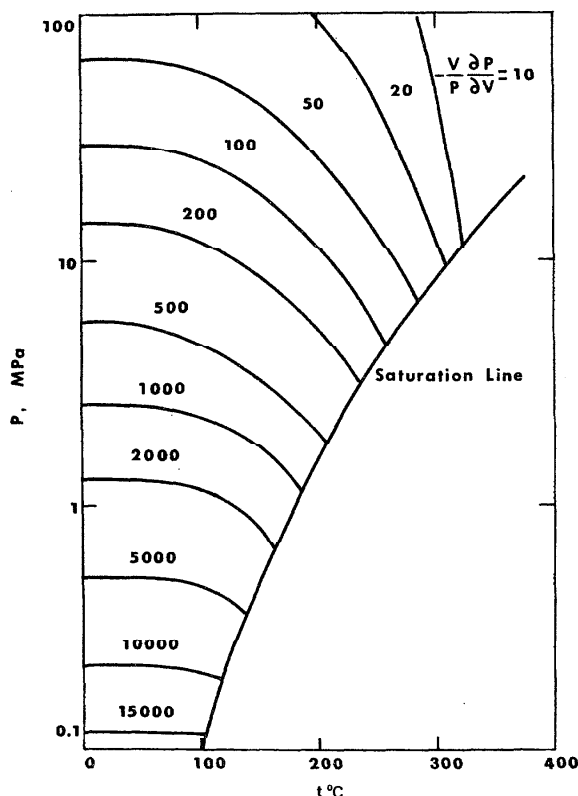

FIGURE 1. $(V/P)(\partial P/\partial V)$ for D_2O liquid states.

in which δP, δV and δT are the experimental uncertainties in pressure, volume, and temperature measurements, respectively. Nominal values, corresponding to best experimental technique are

$$\frac{\delta P}{P} = 10^{-3},$$

$$\frac{\delta V}{V} = 10^{-4},$$

$$\frac{\delta T}{T} = 2 \times 10^{-5} \text{ to } 5 \times 10^{-5}.$$

With H_2O data $\delta P/P$ and $\delta V/V$ can be as low as 10^{-4} and 10^{-5}, respectively, but for D_2O measurements the effect of H_2O and other isotopic content (with some uncertainty in composition) means that $\delta P/P$ and $\delta V/V$ are an order of magnitude larger even after attempts are made to correct the isotopic content. With the difference in specific volumes of H_2O and D_2O of the order of 10% and the uncertainty of actual H_2O content in experimental samples approaching 0.1%, the volume uncertainty is of the order of 10^{-4}.

The evaluation of ΔP with eq (16) depends strongly on the term $V/P \, \partial P/\partial V$ which reaches large values for low temperature liquid states. Figure 1 indicates the variation of this parameter throughout the liquid region as determined by the resulting equation of state for D_2O. With the previously stated values for $\delta P/P$, $\delta V/V$, $\delta T/T$, the dominant contribution to ΔP will come from the volume term, for $V/P \, \partial P/\partial V > 10$, i.e., for virtually all of the compressed liquid states. For low temperature liquid states

$$\Delta P \simeq V \frac{\partial P}{\partial V} \frac{\delta V}{V} = \frac{-1}{K_T} \frac{\delta V}{V}$$

in which K_T is the compressibility, and is of the order of 10^{-4} bar^{-1}. This means that ΔP will nominally be of the order of 1 bar in the low temperature liquid region. The values for ΔP are set with reference to eq (16) and any evidence of systematic errors are revealed by incompatibilities between overlapping data sets. For the vapor states the terms $V/P \, \partial P/\partial V$ and $T/P \, \partial P/\partial T$ are small enough that the dominant contribution to $\Delta P/P$ is the term $\delta P/P$ which means that $\Delta P/P$ is of the order 10^{-3} (a value of 2×10^{-3} is generally used for specific volumes greater than 1.4 cm^3/g).

For the second summation in eq (15), only the enthalpy values for liquid saturation states have been used. The nominal uncertainty of the saturated liquid enthalpies has been taken as proportional to the enthalpy; it is 0 at the triple point and 2 J/g at 300 °C.

Determination of the coefficients A_{ij} by a least squares procedure, subject to a number of fixed constraints which are specified in section 5, follows a standard procedure (see McCarty [20]) except that the adjustment of the expansion points (ρ_{aj}, τ_{aj}), and use of high precision arithmetic are necessary to assure successful matrix inversion.

4. The Data Base
4.1. The Ideal Gas States

The molecular weight of 100 per cent D_2O (with the same relative abundance of oxygen isotopes as in standard mean ocean water) is given by Kell [21] as 20.027048. The difference
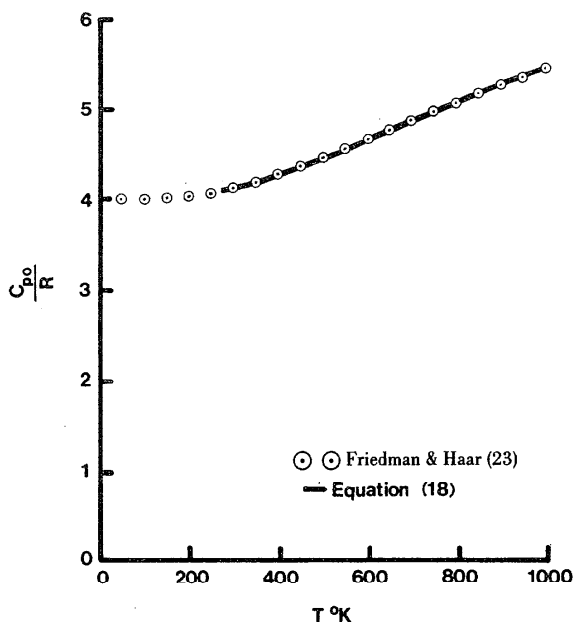
FIGURE 2. Specific heat of D_2O at low pressure.

between this value and the value 20.0284 (International Atomic Weights 1955) used by Whalley [22] and others will have negligible effect on the fitting process. The corresponding gas constant is 8.31434 kJ/(kg mol K) or 0.41515 kJ/(kg K).

Specific heat values are provided by Friedman and Haar [23] for the temperature range 50–5000 K. Figure 2 shows their values of specific heat of D_2O in the range of 270–1250 K in comparison with the following derivation from eq (1) for $\rho \rightarrow 0$.

$$\frac{C_{po}}{R} = \sum_{i=1}^{6} \frac{C_i(2-i)(i-1)}{RT}\left(\frac{T}{1000}\right)^{i-1}$$
$$+ \frac{C_7}{RT} + 1 - \frac{C_8}{1000R} \tag{17}$$

in which C_i values are given under eq (3). This equation fits the values of Friedman and Haar within 0.05%.

The corresponding zero pressure enthalpy equation is

$$h_0 = \sum_{i=1}^{6} \frac{C_i(2-i)T^{i-1}}{1000^{i-1}} + C_7(\ln T - 1) + \left[R - \frac{C_8}{1000}\right]T \tag{18}$$

TABLE 2. Differences between second virial coefficients of H_2O and D_2O

t (°C)	$B_{H_2O} - B_{D_2O}$ cm^3/mol Kell, McLaurin & Whalley [24]	cm^3/mol McLaurin & Kell [25]
150		0.60
200	3	0.41
225	2.8	0.35
250	1.1	0.30
275	0.77	0.27
300	0.70	0.24
325	0.38	
350	0.22	
375	0	
400	0.08	
425	0.03	
450	0.05	

4.2. Virial Coefficients

Values of the second and third virial coefficients of D_2O have been provided by Kell, McLaurin and Whalley [24]; table 2 provides the differences $B_{H_2O} - B_{D_2O}$ obtained in their paper.

Recent data of Kell [25] on the vapor volumes of both H_2O and D_2O in the range 150–350° permit direct determination of the differences between the second virial coefficients. The method and the results of these calculations are provided in reference [26]; table 2 indicates that these differences are small, of the order of 0.2% of the second virial coefficient for D_2O.

4.3. Joule-Thomson Coefficients

The main indication of gas imperfection for the low temperature vapor states is the Joule-Thomson coefficient data presented by Juza, Kmonicek, Sifner and Schovanec [27], which are limited to a small range of pressure and temperature.

4.4. Vapor Pressures

The vapor pressure of D_2O was formulated by Tanishita, Watanabe, Uematsu and Eguchi [28]. Since publication of their equation in 1974, no new data has appeared. However, in this work we rely on a new formulation (Hill and MacMillan [18]) which followed a reconsideration of unsmoothed experimental data. This proved to be particularly important for temperatures below 100 °C, the range in which smoothed data of various experimentalists show wide disagreement. Inspection of unsmoothed data was necessary to establish the apparent experimental uncertainty for each data set, after appropriate corrections had been made for H_2O concentration in the D_2O samples.
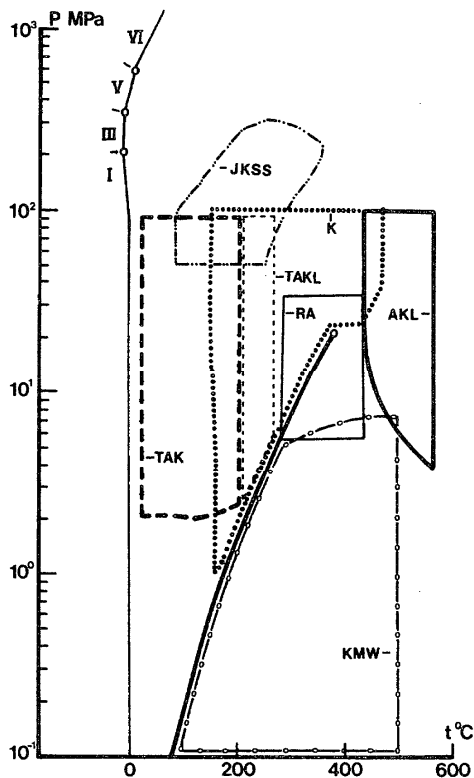

FIGURE 3. D_2O PVT data sources used in formulation. TAK: Tsederberg et al. (32); TAKL: Tsederberg et al. (33); JKSS: Juza et al. (27); K: Kell et al. (25), RA: Rivkin and Ahkundov (31); AKL: Alexandrov (35); KMW: Kell et al. (24).

TABLE 3. Sources of *PVT* data

Author	Ref	Data	Page/ table	Temp range (°C)	Press range (MPa)	Purity %
Rivkin & Akhundov	[31]	(1962)	62/2	275–425	5–34[a]	99.87
Juza et al.	[27]	(1966)	369/3	80–350	50–350[b]	99.86
Tsederberg et al.	[32]	(1972)	68/2	20–200	14–100	99.66
Tsederberg et al.	[33]	(1973)	14/1	200–425	2–100[a]	99.8
Emmet & Millero	[34]	(1975)	352/2	2–40	0.1–100[a]	>99.8
Alexandrov et al.	[35]	(1976)	4/2	400–550	4–100	99.7– 99.8
Kell	[25]	(1979)	/1	150–450	.5–100	~100

[a]Some data omitted (where isotherms are very close together).
[b]Data at 500 bar omitted.

The equation formulated is similar to the equations which Pollak [2] and Wagner [29] have shown to be successful in correlating H_2O vapor pressure data. The equation was developed using a statistical criterion for retaining only the most significant terms. It satisfies the critical point pressure and temperature determined by Blank [30], and also incorporates the critical point singularity

$$\frac{d^2P}{dT^2} \rightarrow (T_c - T)^{-\theta} \quad \theta = 0.1$$

The new D_2O vapor pressure equation is as follows:

$$\ln\frac{P}{P_c} = \frac{T_c}{T}(\alpha_1\tau + \alpha_2\tau^{1.9} + \alpha_4\tau^2 + \alpha_{11}\tau^{5.5} + \alpha_{20}\tau^{10})$$

(19)

in which

$$\tau = 1 - \frac{T}{T_c}$$

$$T_c = 643.89 \text{ K (IPTS 68)}$$

$$P_c = 21.66 \text{ MPa}$$

and

$$\alpha_1 = -7.81583 \quad \alpha_{11} = -3.92488$$
$$\alpha_2 = 17.6012 \quad \alpha_{20} = 4.19174$$
$$\alpha_4 = -18.1747$$

4.5. *PVT* Data

The *PVT* data used in the fitting process were obtained from Rivkin and Akhundov [31], Juza, Kmonicek, Sifner and Scholvanec [27], Tsederberg, Alexandrov and Khasanshin [32], Tsederberg, Alexandrov, Khasanshin and Larkin [33], Emmet and Millero [34], Alexandrov, Khasanshin and Larkin [35], and Kell [25]. Some data on closely neighbouring isotherms were omitted, as were data for volumes greater than 0.010 m³/kg at subcritical temperatures. The tolerances were assumed to depend only on (P, T), not on the data set. The pressure and temperature ranges for these data are shown in figure 3.

Data omitted in the fitting process included the measurements of Bridgman [36], Rivkin [37], Kirillin and Ulybin [38], Rivkin and Akhundov [39], Steckel and Szapiro [40], Alexandrov, Khasanshin and Larkin [41], and various measurements at saturation and atmospheric pressure (see Kirillin [10], Uematsu and Watanabe [17] and Kell [42]).

In addition, Rivkin and Akhundov [31] and Kell [25] and Alexandrov et al. [35] adequately cover the region above 300 °C, and so the data of Tsederberg, Alexandrov, Khasanshin and Larkin [33] in that region were omitted.

All volumes were corrected to 100% D_2O using the following correction formula (which assumes zero "volume of mixing")

$$v_{D_2O} = \frac{v_{obs} - v_{H_2O}Y}{1 - Y}$$

in which v_{obs} is the observed specific volume, v_{H_2O} is the specific volume of H_2O at the same pressure and temperature and Y is the mass fraction of H_2O in the experimental sample. The quantity v_{H_2O} was determined by use of the equation of Keenan, Keyes, Hill and Moore [1]. In the region very near the critical, the results of this method of correction for H_2O impurity were found to differ somewhat from those of the method of Hastings, Levelt Sengers and Balfour [43] which utilizes the corresponding states principle. Given these differences, data in the region $362 < \theta < 380$ °C and $200 < \rho < 500$ kg/m³ were excluded from the fitting process.

TABLE 4. Saturation States of D_2O

t °C (IPTS 68)	P_{sat} MPa	v_f cm³/g	v_g	h_f J/g	h_g
3.8	.000660	.90464	174115	0.0	2324.0
6.0	.000774	.90439	149645	9.3	2327.7
10.0	.001026	.90419	114461	26.4	2334.6
15.0	.001442	.90428	82893	47.4	2342.9
20.0	.001999	.90472	60818	68.6	2351.3
25.0	.002737	.90545	45175	89.8	2359.7
30.0	.003702	.90645	33949	110.8	2367.8
35.0	.004950	.90771	25796	131.8	2376.0
40.0	.006549	.90918	19807	152.8	2384.1
49.99	.011115	.91274	12030	194.7	2400.3
100.0	.096252	.94057	1585.8	404.0	2479.0
111.02	.141942	.94866	1102.1	450.1	2495.2
150.0	.465323	.98296	361.22	613.7	2546.3
200.0	1.546004	1.04354	114.87	825.0	2588.7
250.0	3.995293	1.13149	44.61	1046.8	2596.3
275.0	5.997285	1.19270	28.99	1167.5	2583.4
300.0	8.688479	1.2740	19.03		
325.0	12.267	1.3917	12.34		
350.127	16.845	1.6044	7.493		
360.057	19.028	1.7709	5.792		

FIGURE 4. Liquid saturation volumes: comparison of values.
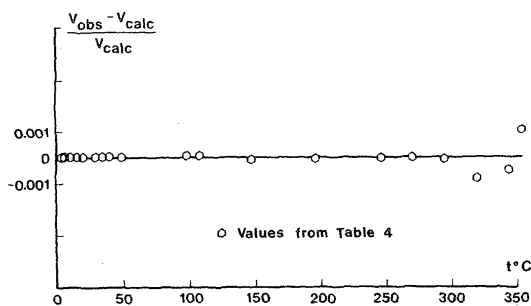

FIGURE 6. Pressures at 200 °C: comparison of values.

Values of percent D_2O composition are listed in table 3. A value of 99.87% was inferred for the Emmet and Millero data from comparison with the data of Steckel and Szapiro. Kell [42] indicates that the values of Steckel and Szapiro may be low by as much as 0.00003 cm^3/g at 20 °C, and cites recent atmospheric pressure measurements which differ by $\pm$ 0.00005 cm^3/g from the data of Steckel and Szapiro at 20 °C. (The value 0.9043546 cm^3/g for 98.78% D_2O at 11.22 °C$_{48}$ was used to obtain absolute densities from the Steckel and Szapiro paper). Kell [42] considers that a standard D_2O sample has an oxygen isotopic composition identical to that of standard mean ocean water, and shows that control of oxygen isotope composition is necessary for accurate measurements.

Tsederberg et al. [32], [33] do not mention a temperature scale; the temperatures are assumed to be IPTS-48. The data of Emmet and Millero [34] are reported in "bars applied pressure"; one standard atmosphere (0.101325 MPa) is therefore added to these pressures. Where possible, unsmoothed data were used. The data of Juza et al. [27] are published in smoothed form only.

4.6. Saturation States

Hill and MacMillan [19] determined a set of saturation states for D_2O by extrapolating liquid volume and specific heat data and using a vapor virial equation and the Clapeyron equation. Table 4 presents a revision of this set of states, resulting from use of recent data and an improved calculation.

From 150 °C to 325 °C saturated liquid volumes have been determined from the recent measurements of Kell [25] of compressed liquid volumes.
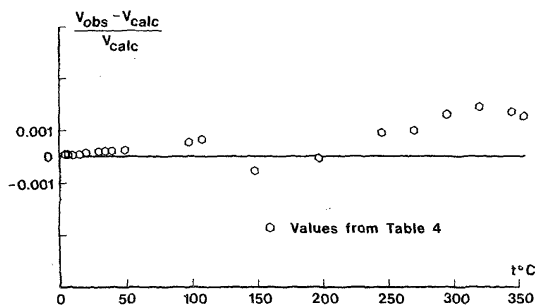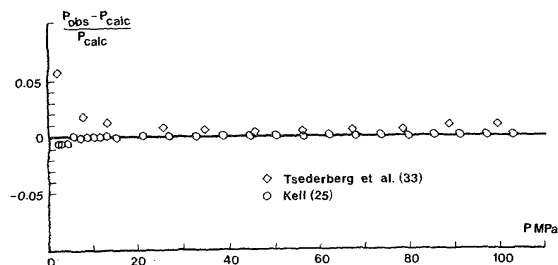
The saturated vapor volumes up to 275 °C have been recalculated after deriving new virial equations for H_2O and D_2O [26], using well known vapor data for H_2O and the recent Kell volume measurements for both H_2O and D_2O vapor.

Above 150 °C the saturated liquid enthalpy values have been revised to be consistent with saturated vapor enthalpies (derived from the virial equation) and the saturated liquid and vapor volumes. From 3.8 to 150 °C the saturated liquid enthalpies are the same as in [19], integrated from the triple point with extrapolated specific heat values (corrected for compressibility effect). In this temperature range the saturated vapor enthalpy values have been determined from the virial equation and the saturated vapor volumes have been adjusted for thermodynamic consistency with the h_g, h_f, and v_f values. From 200 to 275 °C the saturated vapor enthalpies have been determined from the virial equation.

4.7. Specific Heats

Specific heats at constant pressure for D_2O have been reviewed by Rosta [12], who has analyzed the data of Rivkin and Egorov [44], [45], Cockett and Ferguson [46], and Eucken and Eigen [47].

Specific heats at constant volume for a number of isochores in the vicinity of the critical point have been reported by Amirkhanov, Stepanov and Mursalov [48].

5. Constraints

The following conditions are fixed in the least squares procedure by use of Lagrangian multipliers: triple point tempera-

FIGURE 5. Vapor saturation volumes: comparison of values.
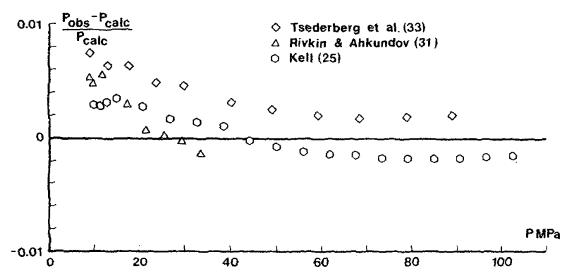
FIGURE 7. Pressure at 300 °C: comparison of values.

FIGURE 8. Pressures at 371/375 °C: comparison of values.
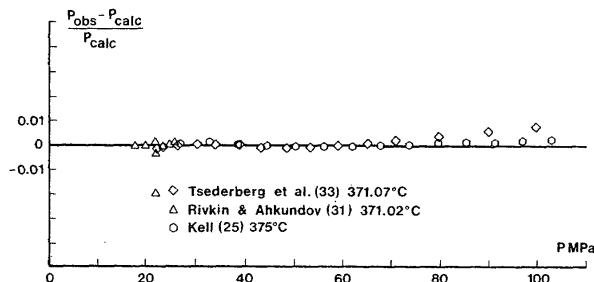

FIGURE 10. Pressures at 500 °C: comparison of values.

ture, pressure and energy, critical point temperature and volume, two values of the second virial coefficient B at high temperature, and one point along the line of maximum density. The introduction of a constraint requires the least squares equation to satisfy exactly the constraint condition.

5.1. Critical Conditions

The critical pressure and temperature above were determined by Blank [30]. This determination (unlike others in earlier literature) is in close agreement with the near critical isotherms of Rivkin and Akhundov [31] (see reference [19]).

$$P_c = 21.66 \text{ MPa}$$

$$T_c = 370.66 \text{ °C (IPTS 48)}$$

$$= 370.74 \text{ °C (IPTS 68)}$$

$$\rho_c = 358 \text{ kg/m}^3$$

The critical pressure was not constrained in the fitting process but the first and second derivatives were set equal to zero. The critical pressure determined by the equation was 21.679 MPa, which agrees with the Blank value within what is believed to be the experimental uncertainty.

5.2. Triple Point

At $\theta = 3.8 \text{ °C}_{48} = 3.8 \text{ °C}_{68}$

and

$$\rho_f = 1.1054 \text{ g/cm}^3$$

we arbitrarily set

$$u_f = 0$$

$$\Psi_f = 0.$$

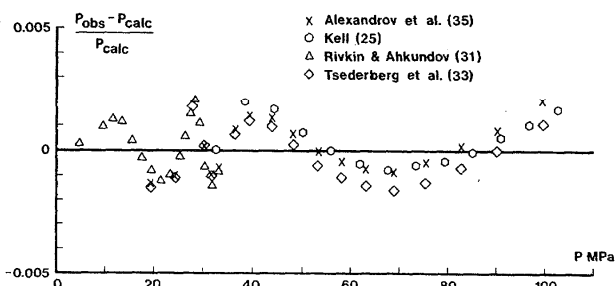### 5.3. Maximum Density Point

At $\theta = 11.2 \text{ °C}$

and

$$\rho = 1.106 \text{ g/cm}^3$$

$$\left(\frac{\partial P}{\partial T}\right)_\rho = \left(\frac{\partial \rho}{\partial T}\right)_P = 0.$$

We also set

$$B = -0.75 \text{ cm}^3/\text{g} \quad \text{at } T = 840 \text{ °C (IPTS 68)}$$

$$B = 0 \quad \text{at } T = 1265.5 \text{ °C (IPTS 68)}.$$

6. The Temperature Scale

Data in which the temperatures are reported in IPTS 48 are converted to IPTS 68 using the equations given by Bedford and Kirby [49]. Between 0 °C and 630.74 °C we have

$$t_{68} = t_{48} + w(t) + z(t)$$

where t is the Celsius temperature, and

$$w(t) = 0.00045t \, (t/100 - 1) \times (t/419.58 - 1)$$

$$\times (t/630.74 - 1)$$

and

$$z(t) = \frac{4.9035 \times 10^{-5} t \, (t/100 - 1)}{1 - 2.94855 \times 10^{-4} t}.$$

The arguments of w and z may be either t_{68} or t_{48} without loss of precision.

7. PVT Data

Figures 4 and 5 compare the saturation PVT values used as input to the fitting process (from table 4), and those calculated
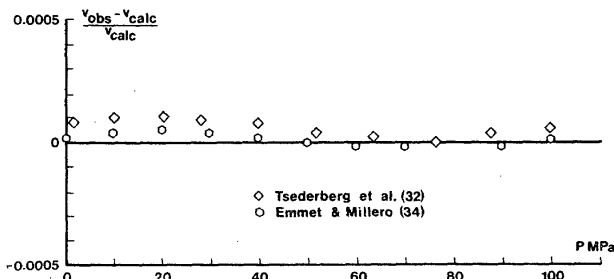

FIGURE 9. Pressures at 400 °C: comparison of values.

FIGURE 11. Volumes at 20 °C: comparison of values.

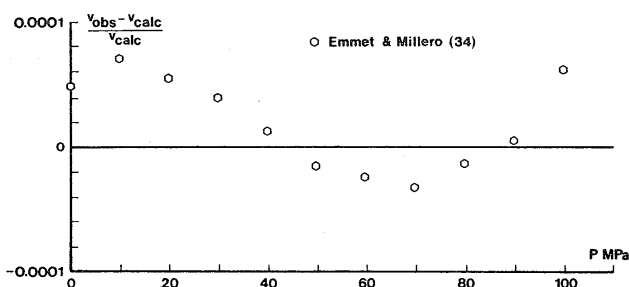FIGURE 12. Volumes at 40 °C: comparison of values.

FIGURE 14. Volumes at 150 °C: comparison of values.

by the resulting equations. Figure 4 shows the differences below 300° between fitted and "data" values of saturated liquid volumes to be generally less than 1 in 10^4, i.e., within experimental accuracy. Figure 5 indicates the discrepancy between the equation and the table 4 values of saturated vapor volumes to be less than 1 part in 10^3 up to 250 °C. At 325 °C extrapolations to saturation of existing vapor volumes are difficult so that the uncertainty in this volume is about 0.2%, i.e. about the same as the difference between the equation value and the one from table 4.

Figures 6, 7, 8, 9 and 10 show the comparisons between measured and calculated pressures. In figure 6 the agreement with the Kell [25] data is within 2% except for lower pressures where the volume uncertainty of 0.01% necessarily means a pressure uncertainty greater than 2%. Consider for example the large discrepancy with the Tsederberg data shown at 200 °C and 2 MPa (fig. 6), which is somewhat over 5%. Figure 1 would suggest that for these conditions

$$\frac{V}{P} \frac{\partial P}{\partial V} = 0 \quad (500)$$

so that a volume discrepancy of 0.01% could be equivalent to a pressure uncertainty of as much as 5%. In the light of this, figures 6 and 7 show good agreement between calculated and experimental pressures.

Figure 8 indicates close agreement with the Rivkin near-critical isotherm ($371.02 \, °C_{68}$, the critical temperature being taken to be $370.74 \, °C_{68}$), but a large discrepancy with the Tsederberg data at high pressures. In this region the agreement with Kell [25] is within 0.27%.

At 400 °C, figure 9 indicates a close degree of agreement between Tsederberg et al. and Rivkin and Ahkundov data, and a fit to the equation of state within 0.2%. At these high tempera-
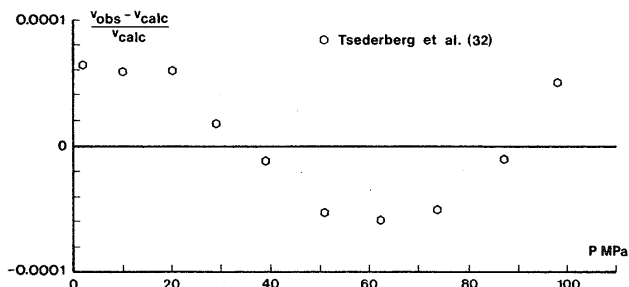
tures the effect of H_2O impurity corrections are not as significant as at lower temperatures.

Figure 10 shows that, at 500 °C, the equation differs from the data of Alexandrov, Khasanshin and Larkin [35] by as much as 0.4% at maximum pressure. This is the only data available in this region.

Figures 11, 12, 13 and 14 show volume discrepancies at lower temperatures. The discrepancies are within 0.01% except at 150 °C where the difference between Tsederberg and Kell data is about 0.02%.

At 70 °C, figure 15 shows the discrepancy between the equation and the 0.1 MPa data of Steckel and Szapiro (which were not used in the fitting process) to be less than 0.01%. The Steckel and Szapiro data were used to infer the purity of the Emmet and Millero data up to 40 °C.

7.1. Line of Maximum Density

Figure 16 compares the maximum density line calculated from the Ψ equation with the calculation of Alexandrov, Larkin, Matveev, Ershova [51] and the calculation of Alexandrov [52] from speed of sound data. It may be noted that the maximum density line was constrained to pass through 11.2 °C and 1.106 g/cm^3.

7.2. Vapor Pressure Equation

Figure 17 shows the comparison between the vapor pressure calculated from the Helmholtz equation and eq (19) which is a direct fit to the vapor pressure data. As shown, the discrepancy is less than 0.02% except within 4 or 5 degrees of the critical point where the discrepancy rises to 0.05%, which is of the order of the uncertainty of the critical pressure of heavy water.
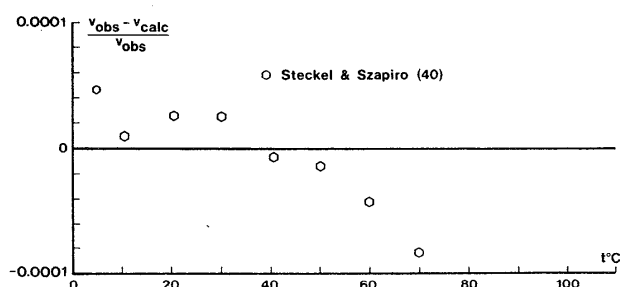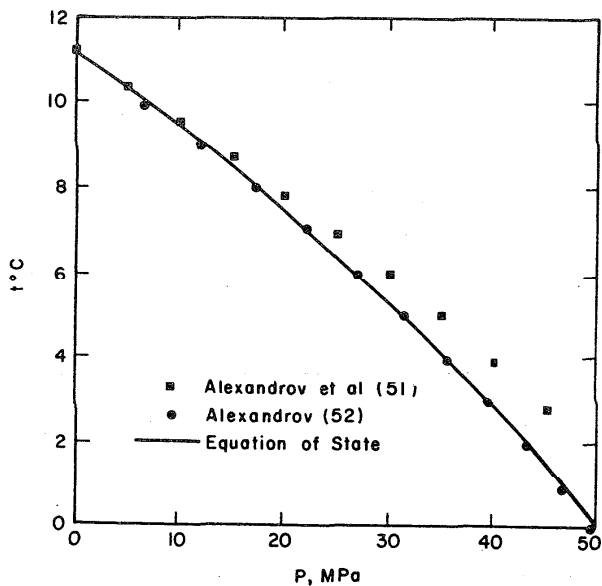

FIGURE 13. Volumes at 50 °C: comparison of values.

FIGURE 15. Volumes at 0.1 MPa: comparison of values.

FIGURE 16. Line of maximum density calculated from ψ equation.

7.3. Virial Coefficients

Figure 18 compares the virial coefficients calculated from the equation of state with the second virial coefficient of Kell, McLaurin and Whalley [24] and Kell [25].

7.4. Specific Heats at Constant Pressure

Figures 19, 20, 21, 22 and 23 indicate close agreement between the equation of state and the specific heat data of Rivkin and Egorov [44], [45], [53]. The agreement provides a strong check of the equation, since only the inferred saturation values of C_p were used in determining the liquid saturation line. None of the C_p values for the compressed liquid or superheated vapor states were included in the fit. Figures 22 and 23 show that the equation consistently underestimates the maximum value of C_p.

7.5. Specific Heats at Constant Volume

Figures 24 and 25 indicate reasonably good agreement between the equation and the experimental C_v values of Amirkhanov at low volumes, but a considerable discrepancy in the region of the critical volume ($v_c \approx 2.76$ cc/g). This discrepancy
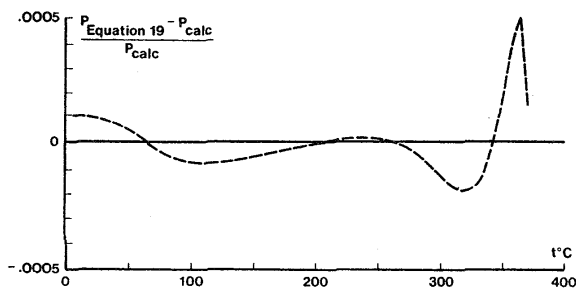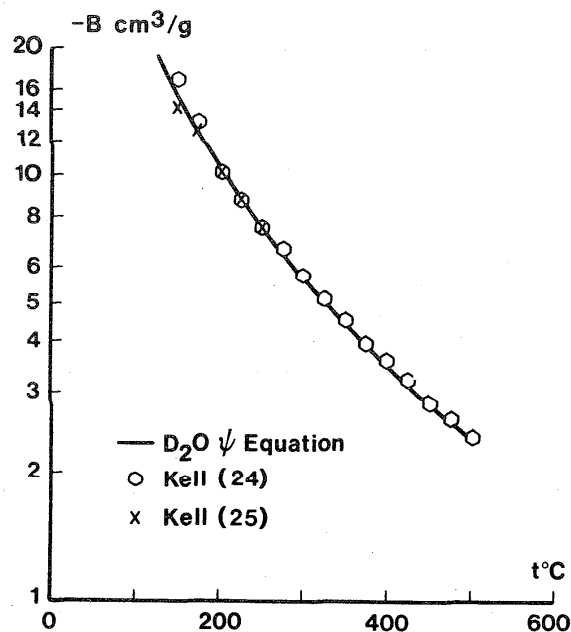

FIGURE 18. Virial coefficients: comparison of values 100–500 °C.

may be due to the attempt to use an analytic equation to represent the non-analytic character of the critical region. The analytic equation will show C_v undergoing a step change at the critical isochore, in crossing the saturation line. Non-analytic critical

FIGURE 17. Saturation vapor pressure calculated from ψ equation.
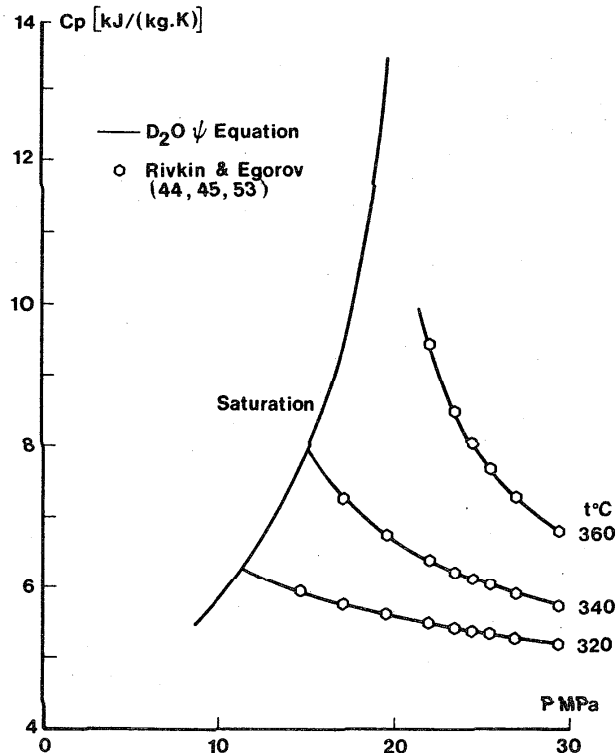

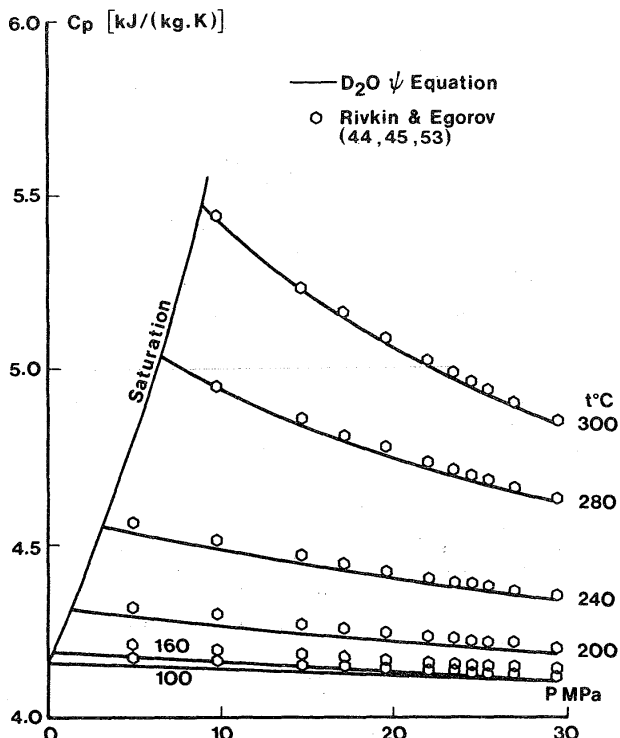FIGURE 19. Specific heats at constant pressure: 320–360 °C.

FIGURE 20. Specific heats at constant pressure: 100–300 °C.

region behaviour includes the specific heat singularity along the critical isochore:

$$C_v \sim (T_c - T)^{-\alpha}$$
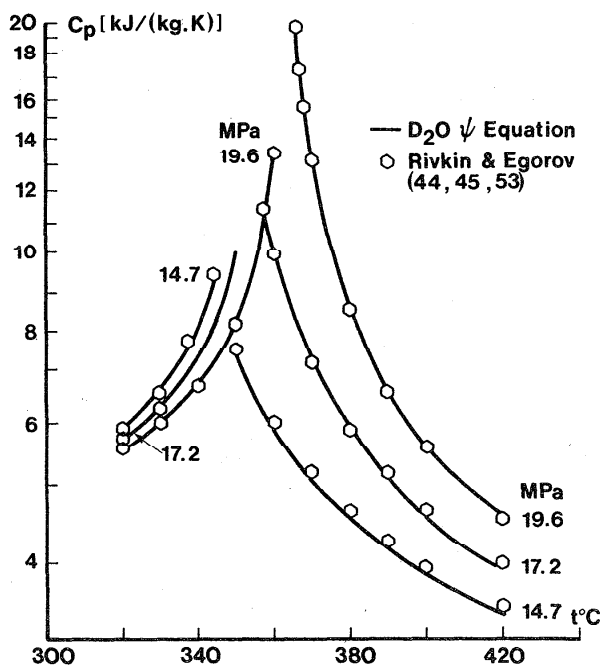
where

$$\alpha \approx 0.1.$$

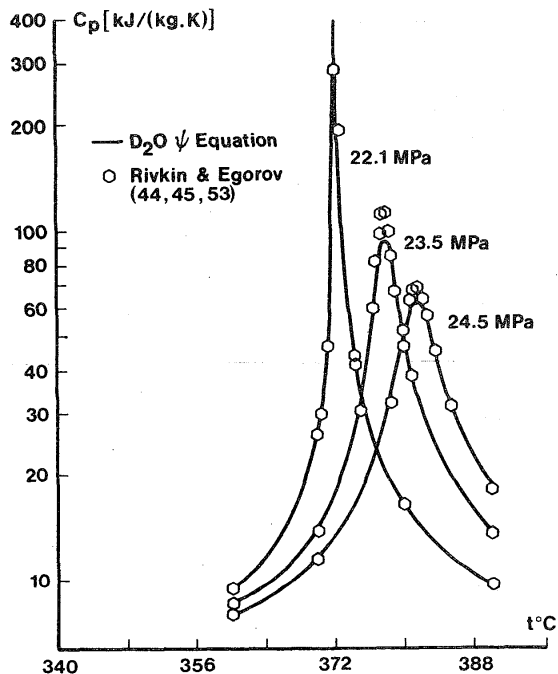FIGURE 21. Specific heats at constant pressure: 14.7, 17.2, 19.6 MPa.

FIGURE 22. Specific heats at constant pressure: 22.1, 23.5, 24.5 MPa.

7.6. Speed of Sound

Figure 26 indicates the agreement between the D_2O speed of sound measurements of Wilson [54] and Alexandrov and Larkin [55], and the calculated values. The values agree within 2 m/s, except at 97 MPa, where the difference is up to 10 m/s, and at 0.1 MPa, where the difference is up to 6 m/s. Alexandrov's measurements have been corrected for H_2O impurity, while the measurements of Wilson have not. However, for Wilson's data, the correction would be only of the order of about 0.2 m/s for 99.8% D_2O (see Wilson [54] and Mathieson and Conway [56]).
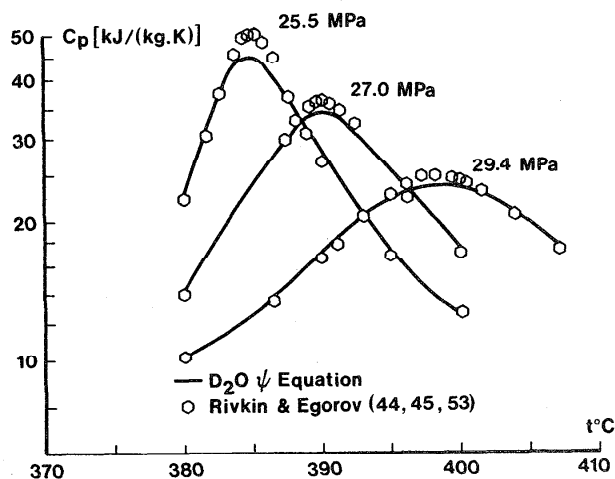

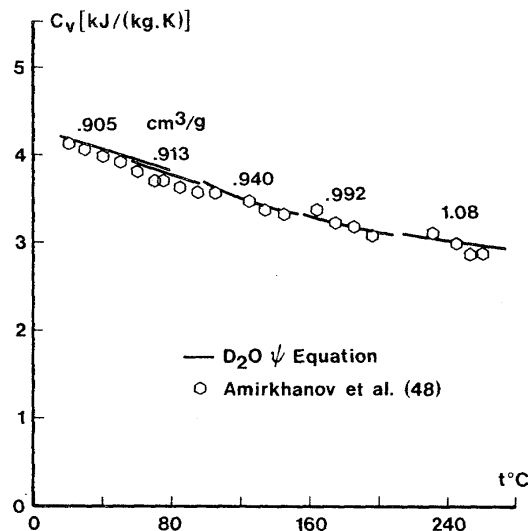FIGURE 23. Specific heats at constant pressure: 25.5, 27.0, 29.4 MPa.

FIGURE 24. Specific heats at constant volume: 0.9–1.1 cm³/g.

Figure 27 shows a comparison of the calculated and experimental values of the speed of sound provided by Alexandrov and Larkin [55] for the temperature range 150–371 °C.

7.7. Joule-Thomson Coefficient

Figure 28 compares observed and calculated Joule-Thomson coefficients. The calculated values differ from the limited experimental data of Juza, Kmonicek, Sifner and Schovanec. The apparent disagreement in the effect of temperature on μ_J is of the same order of magnitude as the Ertle correction of the

FIGURE 26. Speed of sound: comparison of values, 0–100 °C.

corresponding Juza data for H_2O [26]; Ertle uses the method of Hoxton. Thus, the discrepancy may be within the experimental uncertainty.

8. Conclusion

A fundamental equation of state has been developed for D_2O for the whole field of liquid and vapor states from the triple
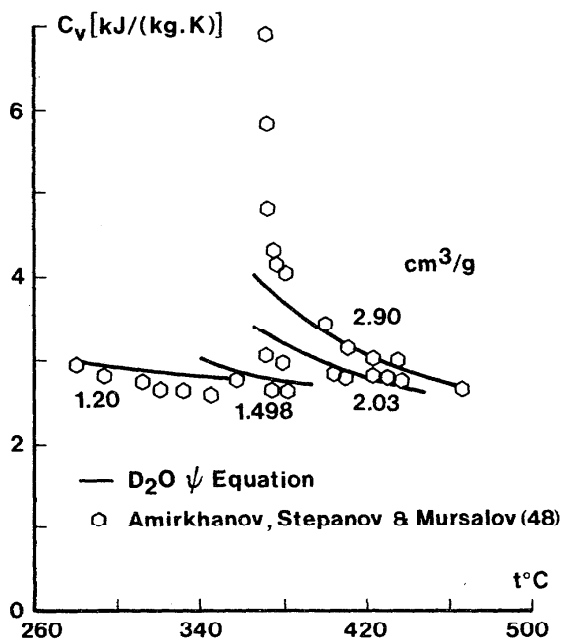

FIGURE 25. Specific heats at constant volume: 1.2–2.9 cm³/g.
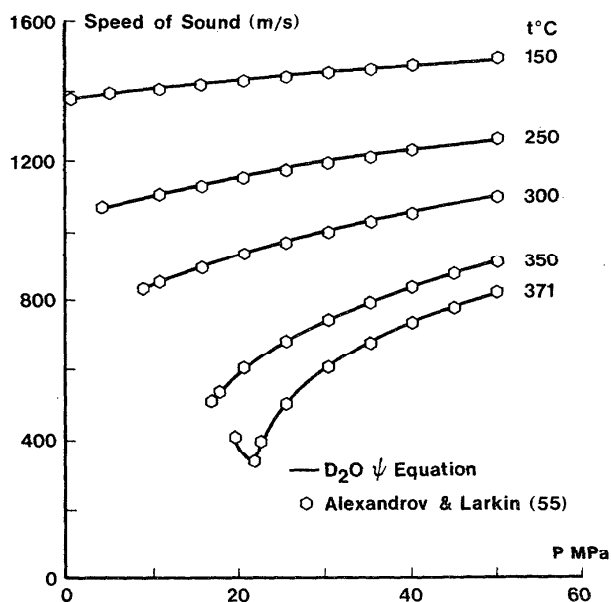
FIGURE 27. Speed of sound: comparison of values, 150–371 °C.
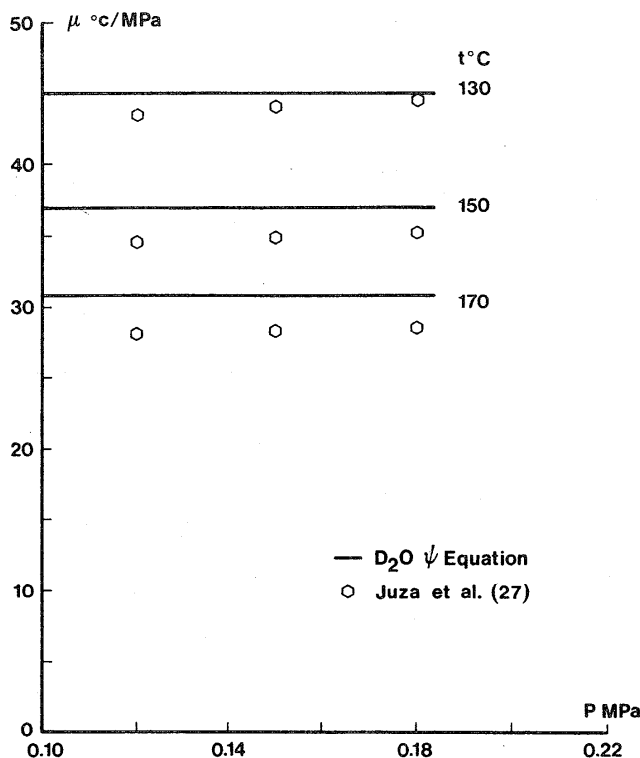
FIGURE 28. Joule Thomson coefficients: comparison of values, 130–170 °C.

point up to 600 °C and 100 MPa. *PVT*, specific heat, and speed of sound data are generally represented within the accuracy of the data, except possibly very close to the critical point and at maximum pressure and temperature where data are scarce. The equation is in agreement with a new formulation of the vapor pressure of D_2O within 0.01% except very close to the critical point, where it is still within experimental uncertainty.

Acknowledgment

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Appendix A
Evaluation of C_1 and C_2

At 3.8 °C $h = h_f$ is set equal to zero (within 0.001 J/g, $h_f = u_f$ at that point).

At the same temperature it may be shown that

$$h_o = C_1 + \sum_{i=3}^{6} (2-i)\left(\frac{T}{1000}\right)^{i-1} + C_7(\ln T - 1)$$

$$+ \left(R - \frac{C_8}{1000}\right)T = C_1 + 457.38.$$

But one can also write

$$h_o = h_o - h_g + h_{fg} + h_f$$

or

$$C_1 + 457.38 = 0.42 + 2323.7 + 0.0.$$

Whence

$$C_1 = 1866.81.$$

The constant C_2 is obtained by setting $\psi_f = 0$ at 3.8 °C. With $u_f = 0$, this is equivalent to $s_f = 0$.

Writing

$$s_f = s_o + s_g - s_o + s_f - s_g$$

we have

$$0 = -[R \ln \rho]_{P \to 0} - \frac{d\psi_0}{dT}$$

$$+ \int_0^{P_{sat}} \left(\frac{\partial s}{\partial P}\right)_T dP - \frac{h_{fg}}{T}.$$

For the low temperature vapor

$$\left(\frac{\partial s}{\partial P}\right)_T = \frac{1}{T}\left(\frac{\partial h}{\partial P}\right)_T - \frac{V}{T}$$

$$\approx R \frac{dB\tau}{d\tau}\left(\frac{\partial \rho}{\partial P}\right)_T - \frac{R}{P}\left(1 + \frac{B}{v}\right).$$

So

$$\int_0^{P_{sat}} \left(\frac{\partial s}{\partial P}\right)_T dP$$

$$\approx \frac{R}{v_g}\frac{dB\tau}{d\tau} - R \ln P_{sat} + R [\ln P]_{P \to 0} - \frac{B}{T}P_{sat}.$$

Hence, the entropy equation becomes

$$0 = -[R \ln \rho]_{P \to 0} - \frac{d\psi_0}{dT} - R \ln P_{sat}$$

$$+ [R \ln P]_{P \to 0} - \frac{h_{fg}}{T}$$

$$- \frac{B}{T}P_{sat} + \frac{R}{v_g}\frac{dB\tau}{d\tau}$$

which reduces to

$$C_2 = 1000\left[-R \ln\left(\frac{P_{sat}}{RT}\right) - \frac{h_{fg}}{T} - \frac{B}{T}P_{sat} + \frac{R}{v_g}\frac{dB\tau}{d\tau}\right]$$

$$- \sum_{i=3}^{6} C_i(i-1)\left(\frac{T}{1000}\right)^{i-2}$$

$$- C_7\frac{1000}{T} - C_8(\ln T + 1)$$

in which

T	$= 3.8 + 273.15$
P_{sat}	$= 0.00066005$ MPa
R	$= 0.41515$ kJ/kg·k
h_{fg}	$= 2323.7$ kJ/kg
B	$\simeq -.075$ m^3/kg
$\dfrac{dB\tau}{d\tau}$	$= -0.4$ m^3/kg
v_g	$= 174.1$ m^3/kg.

This yields approximately

$$C_2 = 4661.5.$$