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THE *PVT* PROPERTIES OF WATER
VI. DEUTERIUM OXIDE IN THE RANGE 150–500 °C AND 0–100 MPa

By G. S. KELL†, G. E. McLAURIN and E. WHALLEY
Division of Chemistry, National Research Council of Canada, Ottawa, Canada K1A 0R6

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CONTENTS

The density of heavy water has been measured at 11 temperatures from 150 to 500 °C, usually at intervals of 6 MPa but sometimes less, from near saturation to 100 MPa and to a precision of *ca.* 0.01 %. The H:D and $^{18}O:^{16}O$ ratios of the water are 0.00033 and 0.00590 ± 0.00003 respectively.

1. INTRODUCTION

Accurate thermodynamic properties of deuterium oxide (heavy water) are needed because it is widely used as a moderator and heat-transfer agent in nuclear reactors. A survey done some years ago (Whalley 1957) was the basis for the first D_2O steam tables intended for use in power generation. Since then, the use of heavy water in power generation has greatly increased and more accurate data are needed to make more accurate tables. A number of measurements have been reported in the meantime by Kirillin & Ulybin (1959), Rivkin (1959), Rivkin & Akhundov (1962, 1963), Tsederberg *et al.* (1972) and Tsederberg *et al.* (1973).

The density of ordinary water has been measured in this laboratory in the range 0–500 °C and 0–1000 bar‡ (Kell *et al.* 1984, cited as part V) and earlier papers. These measurements have now been extended to deuterium oxide of accurately known isotopic composition in the range 150–500 °C and 0–1 kbar.

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† Died March 1983.
‡ 1 bar = 10^5 Pa.

The measurements were made in the apparatus used earlier for light water (part V). Measurements had also been made on a larger sample of light water in a similar apparatus (Kell *et al.* 1978*a*) and so, because some systematic errors are similar in the various measurements, the accuracy of the measurements on heavy relative to light water should be somewhat greater than their separate accuracies. As the molar volume of water varies slowly with isotopic composition (Kell 1977), the effect of errors in the isotopic abundances has been minimized by reporting the results as molar densities. A preliminary report of the work was given at the 9th International Conference on the Properties of Steam (McLaurin & Kell 1980).

2. METHOD AND APPARATUS

2.1. *General features of the method*

The apparatus and experimental procedures were as described by Kell & Whalley (1965) and subsequently adapted for vapour measurements by Kell *et al.* (1968*a*). This work used the same experimental vessel and tried to parallel as closely as possible the techniques used for light water in part V. Briefly, the amount of water in a 35 cm^3 vessel containing the sample under investigation was changed by the displacement of water by the piston of a measuring screw injector that was maintained at room temperature. Both the experimental vessel and the cylinder of the screw injector were jacketed by outer pressure vessels, and the pressures inside and out were kept equal. The design incorporated many details (Kell & Whalley 1965; Kell *et al.* 1968*a*) to increase the sensitivity and accuracy and reduce the scatter of the measurements.

As in part V, new water was used for each run and each run was started with the vessel containing only water vapour and evacuated to well below the lowest measurement pressure. Each run was therefore made on an independent sample. Observations were made of the mass of water in the vessel at a series of fixed pressures, the lowest of which was much higher than the evacuation pressure. Eight to ten observations were made in the vapour region to determine the mass in the screw injector at zero pressure, and observations were then made at higher densities. At the end of each run, the sample was withdrawn from the vessel and examined for bubbles or discoloration. None was found.

The measurements on the vapour were analysed by using the virial equation in the form

$$p_i/RT = \rho_i + B_2\rho_i^2 + B_3\rho_i^3 \ldots, \tag{1}$$

where p_i is the pressure of the ith observation, R the gas constant, T the temperature, B_2 and B_3 the second and third virial coefficients respectively and ρ the density. The density in units of moles per unit volume was determined from the equation

$$\rho_i = \frac{m_0 - (m_\mathrm{i} + \delta m)}{M(V_\mathrm{v} - \delta V)\,(1 - \kappa p_i)}, \tag{2}$$

where m_i is the mass of liquid in the screw injector and the part of the connecting tubing that is at 25 °C, δm allows for the change of mass in the injector because the position of the meniscus in the temperature gradient changes with pressure, δV allows for the change in the volume available to the vapour because of the volume occupied by the mass δm, m_0 is the extrapolated value of the mass in the screw injector at zero pressure, found by fitting the measurements of one run in the low-density vapour to (1), M the molecular mass, V_v the volume of the vessel at the temperature of the experiment and zero pressure and κ is the compressibility of the vessel.

The quantities δm and δV were estimated, as described in part V, by assuming a linear temperature gradient in the capillary tubing between the molten salt of the thermostat bath and the water at 25 °C in the cooler.

The temperature and pressure were measured as before; the thermostat bath was controlled to *ca.* 2 mK, and the pressure measured to *ca.* 1 mbar. At the start of the present work the volume of the vessel at 0.53 MPa was redetermined as 35.3467 $\mathrm{cm^3}$ by filling it at 150 °C and 0.53 MPa with liquid ordinary water from the screw injector. This corresponds to 35.3468 $\mathrm{cm^3}$ at zero pressure, so it had contracted to the value reported in part V before the imbalances of the pressure, no doubt because the stresses induced by the deformation relaxed.

The thermal expansion of the vessel was taken as the value determined by two-temperature helium gas expansions in the range 0–500 °C (Kell *et al.* 1978*b*) and was described by equation (6) of part V, i.e.

$$V(t)/V(150) = 0.992\,371 + 49.17\times 10^{-6}\,t + 11.28\times 10^{-9}\,t^2, \tag{3}$$

with an error of *ca.* $100/10^6$, where $V(t)$ and $V(150)$ are the volumes of the vessel at temperature t and 150 °C respectively. The compressibility of the vessel was taken to be

$$\kappa_V/\mathrm{TPa}^{-1} = 5.96 + 0.0017\,t, \tag{4}$$

which was determined by Kell & Whalley (1975) for another vessel of the same material at temperatures in the range 0–150 °C from measurements of the relative compression of the vessel and water. The compression of water was taken as that calculated from the speed of sound (Kell & Whalley 1975). For the present work, (4) was extrapolated to 500 °C and the compressibilities are accurate to less than 1 $\mathrm{TPa^{-1}}$, which causes an error in the density at 0.1 GPa of not more than 1 in 10^4.

As in previous work on light water described in part V, the equation for the mass, m, in the screw injector was taken as

$$m = m_0 + A(p') + v[\rho_0 + B(p')], \tag{5}$$

where m_0 is the mass of water in the screw injector at scale reading zero and 1 atm† pressure, $A(p)$ and $B(p)$ are empirically determined third-degree polynomials in the pressure, which are zero at zero pressure, v the volume of water delivered by the injector at 1 atm pressure when the scale reading changes from zero to r, which is defined as

$$v = rc + \delta(r) \tag{6}$$

and

$$p' = p - 1\ \mathrm{atm},$$

where c is the mean volume delivered per scale unit at 1 atm, $\delta(r)$, which is zero at $r = 0$, is the small departure from linearity in the delivery at 1 atm and ρ_0 the density of the fluid at 1 atm. Both the elastic deformation of the screw injector and the compression of the fluid contained in it contribute to the coefficients A and B.

On changing the experimental fluid from light water, as was used in part V, to heavy water for this work, quantities c and $\delta(r)$ of (6) do not change as they are purely geometric. When (5) is used directly, A and B may be determined by a calibration for heavy water without reference to their values for light water. However, it is clear that if m_0 is known, (5) can be factored to give

$$m = \phi(r, p')\,\rho(p'), \tag{7}$$

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† 1 atm = 101325 Pa.

where ϕ includes all terms relating to the volume and deformation of the screw injector itself and none relating to the fluid contained and ρ is the density of the fluid. The analysis reported in the appendix to this paper leads to explicit expressions for (7) which fit the calibration data with the same goodness of fit as (5).

2.2. *The heavy water*

Heavy water of high quality was supplied by Atomic Energy of Canada Limited (A.E.C.L.). It was transported and stored under a helium atmosphere at a gauge pressure of 0.05 MPa in a stainless-steel can of a design known to provide stable long-term storage. The water in the can had a pH of 6.1 and a specific conductance of 3 μS cm^{-1}. The mole fractions of hydrogen were given by A.E.C.L. as ^{1}H 0.00033; ^{2}H 0.99967 ± 0.00005 and ^{3}H 4×10^{-14}. The ^{18}O:^{16}O ratio had been measured for A.E.C.L. by Dr P. Fritz of the University of Waterloo as 2.96 times that for standard mean ocean water (s.m.o.w.) as given by Baertschi (1976). The concentration of ^{17}O was not measured, but can be calculated by using the plausible assumption that the enrichment of ^{17}O is a mean of the enrichments of ^{16}O and ^{18}O. One such relation is that used by Kell (1977),

$$\mathrm{d}y_{17}/y_{17} = \mathrm{d}y_{16}/2y_{16} + \mathrm{d}y_{18}/2y_{18}, \tag{8}$$

where y_{16}, y_{17} and y_{18} are the mole fractions of the isotopes ^{16}O, ^{17}O and ^{18}O. With the substitutions $y_{16} = 1 - y_{17} - y_{18}$ and $\mathrm{d}y_{16} = -\mathrm{d}y_{17} - \mathrm{d}y_{18}$, (8) becomes

$$\mathrm{d}\ln y_{17} = [(1 - y_{17} - 2y_{18})/(2 - y_{17} - 2y_{18})]\,\mathrm{d}\ln y_{18}. \tag{9}$$

In the approximation that y_{17} and y_{18} are small, the factor of $\mathrm{d}\ln y_{18}$ in (9) is $\frac{1}{2}$ and y_{17} is given by

$$y_{17}(\text{sample}) = y_{17}(\text{s.m.o.w.})\ [y_{18}(\text{sample})/y_{18}(\text{s.m.o.w.})]^{\frac{1}{2}}, \tag{10}$$

so that ^{17}O will be enriched to about $(2.96)^{\frac{1}{2}} = 1.72$ times its mole fraction of 0.00037 in s.m.o.w.

Two slightly different calculations of the molecular mass may be made; they agree well, which shows that the uncertainty is small. If we follow Kell (1977) and take the composition of s.m.o.w. to be $y_{16} = 0.997640$, $y_{17} = 0.000371$ and $y_{18} = 0.001989$, then the composition of the sample, using (10) to determine the concentration of ^{17}O, is $y_{16} = 0.99350$, $y_{17} = 0.00064$, $y_{18} = 0.00586 \pm 0.00003$ and the molecular mass is 20.0348 ± 0.0001. The uncertainty of the molecular mass arises chiefly from the uncertainty of the hydrogen-isotope concentration. By using Kell's (1977) correlation at 23.8 °C, which is the temperature of the screw injector, the molar volume is 18.1291 ± 0.0006 cm^3 mol^{-1} and its reciprocal, the molar density, is 55.160 ± 0.002 kmol m^{-3}.

Baertschi's (1976) measurements for ^{18}O lead to a composition for s.m.o.w. of $y_{16} = 0.997629$, $y_{17} = 0.000371$, $y_{18} = 0.002000$ and these values lead to a composition of our sample of $y_{16} = 0.99347$, $y_{17} = 0.00064$, $y_{18} = 0.00598 \pm 0.00003$, and a molecular mass of 20.0349 g mol^{-1}. This value was used in the calculations. The estimate of the molar volume in the preceding paragraph was used, because the correlation from which it derives was based on the quoted composition of s.m.o.w.

The only purification needed was removal of the helium. This was done by a method based on that described by Battino *et al.* (1971). Before using the method with heavy water we practised with light water to ensure mastery of the technique. Briefly, 400 cm^3 of heavy water was transferred from the storage can without contact with air, (by using a hollow needle to pierce the rubber septum of the can) to a 2 l conical glass flask containing a magnetic stirring bar. A valve at the top of the flask led to two condensers followed by a vacuum system. To degas the sample, the condensers were filled with liquid nitrogen. The stirrer kept the water in vigorous motion to speed equilibration with the vapour. The valve at the top of the flask was opened for two or three seconds, long enough to sweep out most of the vapour above the liquid without giving much time for more to evaporate. The water condensed in the first condenser but the second remained clear, showing that no water vapour was carried over. The helium passed through both condensers. After waiting three minutes for the remaining helium to equilibrate between liquid and vapour, the valve was opened again. Tests were made with a Tesla coil at the second condenser and evacuations of up to ten seconds continued until no helium was detected by the Tesla discharge; the total time for degassing was about 20 min. The stopcock above the first condenser was then closed, the liquid nitrogen drained from the condenser and the liquid water from the melting condensate was run back into the flask. In our earlier degassings, because of surface-tension effects, between 0.1 and 0.25 cm^3 water did not run back, but this loss would change the isotopic composition of the liquid remaining behind by less than the uncertainties of the composition given above. In later runs the condenser was dried by heating with an electric blower, and in this case the liquid was degassed without significant loss of water. The degassed water was then transferred under its own vapour pressure to a 500 cm^3 flask that was used to fill the screw injector.

Evidence of the freedom of the water from nucleating impurities was provided by the observation that after run 3 at 200 °C, where the vapour pressure is 1.5 MPa, the pressure on the liquid was reduced to atmospheric and persisted in this metastable condition for some minutes before nucleation occurred.

3. EXPERIMENTAL DENSITIES OF HEAVY WATER

3.1. *Experimental results*

The observed densities are listed in table 1, which contains the main series of measurements at the same pressures as used in earlier measurements, and table 2, which lists additional measurements at pressures other than those used for the measurements in table 1. The additional measurements were made either to obtain data near saturation or to have more nearly even increments of density. The run numbers are in the order in which the runs were made, run 1 being made in November 1976, and run 24 in October 1977. Run 9 was faulty and is omitted. Calibrations of the screw injector were made before and during the measurements and they agreed within the precision of the measurements.

Observations were made near 25 or 50 K intervals on the IPTS-68 from 150–500 °C and near the pressures used previously (Kell & Whalley 1965, 1975). Variations in atmospheric pressure and the temperature of the thermostat were allowed for and the observed masses in the screw injector were adjusted to the exact target pressures and temperatures without significant error (because the adjustments were small) by using the '1968 I.F.C. Formulation for Scientific and General Use' of the International Association of the Properties of Steam, assuming for the adjustments that the compressibilities and thermal expansivities of light and heavy water are the same.

TABLE 1. EXPERIMENTAL DENSITIES OF HEAVY WATER

t/°C(IPTS68)	150			200		250	
run no.	1	4	24	2	3	5	6
p/MPa				ρ/(kmol m^{-3})			
0.530	50.796	50.798	50.796	—	—	—	—
1.260	50.820	50.821	50.819	—	—	—	—
2.000	50.843	50.844	50.843	47.864	47.865	—	—
2.740	50.867	50.867	50.866	47.896	47.895	—	—
4.211	50.913	50.914	50.913	47.959	47.958	44.141	44.140
5.681	50.959	50.960	50.959	48.020	48.021	44.238	44.237
7.151	51.005	51.006	51.004	48.082	48.082	44.333	44.332
8.631	51.050	51.052	51.050	48.143	48.142	44.427	44.426
10.101	51.096	51.097	51.095	48.203	48.203	44.519	44.518
11.571	51.140	51.142	51.140	48.263	48.262	44.609	44.609
13.052	51.185	51.187	51.184	48.322	48.322	44.699	44.698
15.189	51.250	51.251	51.249	48.408	48.406	44.826	44.825
21.028	51.423	51.423	51.423	48.633	48.633	45.159	45.158
26.857	51.593	51.594	51.591	48.853	48.853	45.474	45.474
32.695	51.761	51.760	51.758	49.066	49.065	45.775	45.774
38.522	51.922	51.923	51.920	49.272	49.272	46.061	46.059
44.349	52.081	52.082	52.079	49.472	49.473	46.334	46.334
50.185	52.238	52.238	52.235	49.669	49.668	46.598	46.596
56.011	52.391	52.391	52.388	49.859	49.859	46.849	46.850
61.847	52.542	52.542	52.539	50.045	50.044	47.095	47.093
67.671	52.690	52.691	52.686	50.226	50.225	47.330	47.329
73.506	52.837	52.837	52.832	50.404	50.403	47.558	47.558
79.329	52.980	52.980	52.976	50.577	50.576	47.779	47.779
85.163	53.121	53.121	53.117	50.746	50.746	47.994	47.994
90.985	53.260	53.260	53.256	50.912	50.912	48.202	48.202
96.808	53.397	53.396	53.392	51.074	51.074	48.405	48.404
102.639	53.532	53.531	53.527	51.234	51.234	48.603	48.603

t/°C(IPTS68)	275		300		325	
run no.	18	19	7	8	20	21
p/MPa			ρ/(kmol m^{-3})			
7.151	41.964	41.964	—	—	—	—
8.631	42.093	42.093	—	—	—	—
10.101	42.217	42.217	39.370	39.371	—	—
11.571	42.339	42.338	39.554	39.554	—	—
13.052	42.458	42.458	39.731	39.732	36.041	36.040
15.189	42.626	42.626	39.975	39.976	36.488	36.486
21.028	43.058	43.059	40.585	40.585	37.498	37.498
26.857	43.460	43.458	41.128	41.128	38.318	38.316
32.695	43.835	43.833	41.619	41.619	39.019	39.019
38.522	44.185	44.184	42.069	42.071	39.632	39.631
44.349	44.518	44.516	42.488	42.487	40.182	40.181
50.185	44.834	44.831	42.879	42.878	40.685	40.683
56.011	45.134	45.132	43.246	43.245	41.146	41.145
61.847	45.420	45.419	43.593	43.592	41.575	41.573
67.671	45.696	45.695	43.921	43.921	41.977	41.976
73.506	45.960	45.959	44.235	44.235	42.353	42.353
79.329	46.216	46.214	44.534	44.534	42.710	42.709
85.163	46.462	46.460	44.821	44.821	43.049	43.048
90.985	46.699	46.698	45.096	45.096	43.371	43.370
96.808	46.930	46.928	45.361	45.361	43.679	43.679
102.639	47.154	47.152	45.617	45.617	43.976	43.975

TABLE 1 (*cont.*)

t/°C(IPTS68)	350		375		400	
run no.	10	11	14	15	12	13
p/MPa			ρ/(kmol m^{-3})			
21.028	33.031	33.029	—	—	—	—
26.857	34.634	34.632	28.498	28.502	—	—
32.695	35.787	35.786	31.321	31.323	23.160	23.161
38.522	36.710	36.709	32.992	32.994	27.683	27.683
44.349	37.490	37.490	34.225	34.226	30.016	30.018
50.185	38.171	38.169	35.219	35.221	31.624	31.623
56.011	38.777	38.777	36.057	36.058	32.863	32.865
61.847	39.326	39.326	36.789	36.790	33.884	33.884
67.671	39.829	39.828	37.440	37.441	34.754	34.754
73.506	40.295	40.294	38.028	38.030	35.516	35.517
79.329	40.729	40.728	38.566	38.567	36.197	36.197
85.163	41.136	41.134	39.063	39.064	36.814	36.813
90.985	41.520	41.518	39.525	39.527	37.377	37.377
96.808	41.883	41.881	39.958	39.958	37.898	37.898
102.639	42.228	42.226	40.365	40.366	38.383	38.383

t/°C(IPTS68)	450		500	
run no.	16	17	22	23
p/MPa		ρ/(kmol m^{-3})		
44.349	18.062	18.062	—	—
50.185	—	—	14.163	14.163
56.011	24.654	24.654	16.781	16.780
61.847	26.728	26.727	19.232	19.230
67.671	28.347	28.347	21.393	21.390
73.506	29.671	29.671	23.251	23.249
79.329	30.787	30.788	24.840	24.838
85.163	31.755	31.755	26.213	26.212
90.985	32.608	32.608	27.411	27.411
96.808	33.372	33.372	28.469	28.467
102.639	34.066	34.065	29.415	29.413

3.2. *Uncertainty of the results*

The additive and multiplicative errors of measurement are roughly comparable. The principal additive error is the scatter of the readings of the screw injector, which is primarily a result of variations in the shape of the meniscus in the mercury U-tube and is *ca.* 5×10^{-8} kmol in magnitude. The largest contribution to the multiplicative errors is the error of the volume of the vessel, which is about 10^{-4} of its volume. These values combine in the expression for the density to give

$$\rho = (m \pm 5\times10^{-8})/[MV(1\pm10^{-4})],$$

where m is the mass of water in the vessel and V the volume of the vessel, which is about 36 cm^3 and at zero pressure is described by (3). As the additive and multiplicative errors are not correlated, a measurement of density may be considered as taken from a population of variance σ^2 given by

$$(\sigma/\rho)^2 = 10^{-8} + 1.9\times10^{-6}/\rho^2. \qquad (12)$$

Above the critical temperature, the lower limit of the measurements has been such that the fractional error arising from the measurement of mass is less than 10^{-4}. Thus, to a good approximation, the estimated error of the values in tables 1 and 2 is $100/10^6$. The difference between replicate measurements is nowhere as great as this.

TABLE 2. ADDITIONAL EXPERIMENTAL DENSITIES OF HEAVY WATER FOR THE RUNS REPORTED IN TABLE 1

t/°C(IPTS68)	p/MPa	run no.	ρ/(kmol m^{-3})
250	4.954	5	44.190
250	4.954	6	44.189
275	6.060	18	41.865
275	6.060	19	41.866
275	6.133	18	41.872
275	6.133	19	41.873
275	6.428	18	41.899
275	6.428	19	41.899
300	9.370	7	39.275
300	9.370	8	39.275
325	12.688	20	35.958
325	12.688	21	35.958
325	13.792	20	36.201
325	13.792	21	36.200
325	18.109	21	37.023
350	17.524	10	31.540
350	17.524	11	31.539
350	18.107	10	31.844
350	18.107	11	31.842
350	18.691	10	32.121
350	18.691	11	32.118
350	19.857	10	32.607
350	19.857	11	32.604
350	23.941	10	33.914
350	23.941	11	33.912
375	23.357	14	23.390
375	23.357	15	23.396
375	23.941	14	25.116
375	23.941	15	25.121
375	24.524	14	26.159
375	24.524	15	26.160
375	25.690	14	27.534
375	25.690	15	27.538
375	29.191	14	29.879
375	29.191	15	29.882
400	28.608	12	14.978
400	28.608	13	14.975
400	30.940	12	20.430
400	30.940	13	20.429
400	35.607	12	25.919
400	35.607	13	25.919
450	39.690	16	14.446
450	39.690	17	14.448
450	42.022	16	16.276
450	42.022	17	16.276
450	46.687	16	19.716
450	46.687	17	19.717
450	49.602	16	21.538
450	49.602	17	21.539
450	52.518	16	23.092
450	52.518	17	23.092

3.3. *Comparison with previous work*

Ours and previous densities are compared in figure 1 by plotting deviations from the formulation of Hill *et al.* (1982), which was used in preparing steam tables for heavy water (1981). It is not always clear what molecular mass previous authors considered appropriate for their samples, but these uncertainties appear minor.

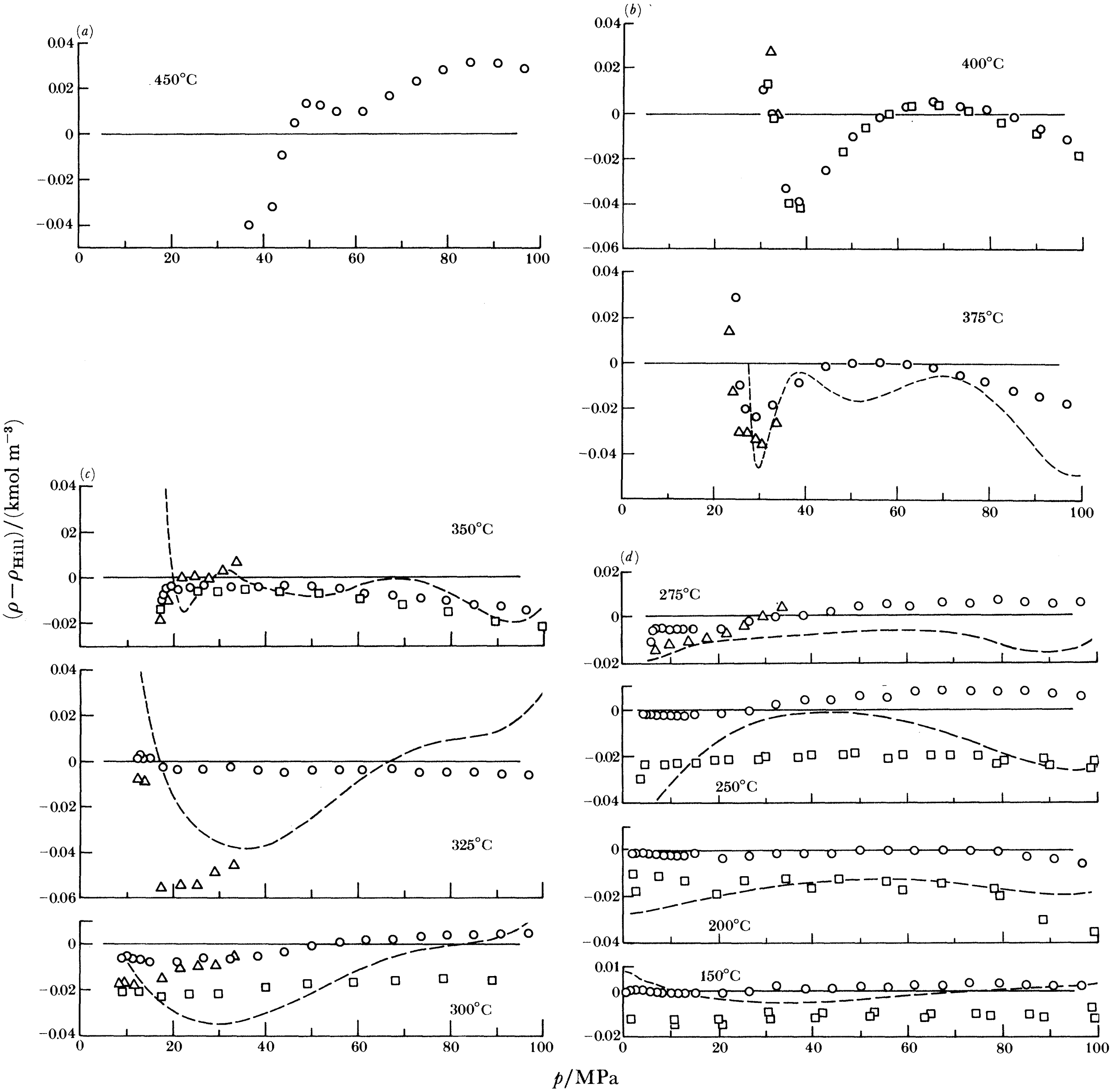

FIGURE 1. Deviations of the density, ρ, of D_2O from the density ρ_{Hill} predicted by the equation of Hill *et al.* (1982). ○, present work; □, Tsederberg *et al.* (1972, 1973); △, Rivkin & Akhundov (1962); ---, Ikeda *et al.* (1977). Parts (*a*), (*b*), (*c*) and (*d*) contain the data for different temperatures.

There are two data sets of sufficient precision that they may be shown conveniently with the present values. Tsederberg *et al.* (1972, 1973), who claim an error of $100/10^6$ report measurements on different samples in their two papers. Each paper reports values at 200 °C, and the results differ systematically by *ca.* $100/10^6$. Their values are mostly lower than ours by up to $600/10^6$.

The data of Rivkin & Akhundov (1962), for which a scatter of not more than $200/10^6$ is claimed, overlap with the low-pressure end of our data and differ from it by up to $\pm 200/10^6$, but agree particularly well at 400 °C. The break in the data for the 325 °C isotherm at *ca.* 15 MPa shown in figure 1 suggests an experimental difficulty.

The data of Kirillin & Ulybin (1959), in the range 250–500 °C to 49 MPa, are of lower precision, having a claimed scatter within $100/10^6$ in the liquid phase. Their values do not show any systematic errors relative to the more precise data, and are not plotted in figure 1. Jůza *et al.* (1966) made measurements to about $1000/10^6$ over a narrow range of densities at temperatures from 80–350 °C and at pressures from 50–350 MPa; two of their points fall on the 200 °C isotherm within our pressure range, one above and one below our data.

Preliminary values of the present data for isotherms up to 400 °C were used by Hill *et al.* (1981) in establishing their correlating equation. At temperatures from 150–325 °C this formulation agrees with our data to $100/10^6$ almost everywhere, and furthermore agrees with our data rather than with those of Tsederberg *et al.* (1972, 1973). At 350 °C and above the different experimental data sets agree with one another in showing systematic errors in the Hill *et al.* formulation which increase with increasing temperature. At 500 °C, the highest pressure reported by Rivkin lies below our lowest pressure, and a graph has not been drawn; our values lie below the Hill *et al.* formulation at low pressures, and above it by $1000/10^6$ at higher pressures. In summary, the Hill *et al.* surface fits the density well at all but the highest temperatures but is of lower accuracy at our highest temperatures, and in the critical region, where only low-accuracy data were available previously.

The equation proposed by Ikeda *et al.* (1977) for the liquid region to 100 MPa deviates systematically from both the present data and the data of Tsederberg *et al.* (1972, 1973) in a way that the Hill *et al.* (1982) formulation does not, as is shown in figure 1. Accordingly, the Hill *et al.* formulation is preferred in our temperature range.

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APPENDIX

Calibration of the screw injector for different liquids

In our earlier work, the mass of liquid contained in the screw injector under isothermal conditions has been represented by (5) in the form

$$m = m_0 + a_1 p + a_2 p^2 + a_3 p^3 + v[\rho_0 + b_1 p + b_2 p^2 + b_3 p^3], \tag{A 1}$$

where a_1, a_2, a_3, b_1, b_2 and b_3 are constants. In principle, both the elastic deformation of the screw injector and the compression of the fluid contribute to the coefficients a_i and b_i. Both contribute significantly to a_1 and b_1, as the compressibility of water contributes 45 Mbar^{-1} to b_1, and the compressibility of steel, which determines a_1, is 0.6 Mbar^{-1} or 1 % of the total. The compressibility of the apparatus contributes negligibly to the terms a_2, a_3, b_2, and b_3. For example, the contribution of the compression of water to b_2 is 700 Mbar^{-2}, and that of steel is 2 Mbar^{-2}, which is 0.3 % of the contribution from water and can be neglected. Over the whole delivery of the volumometer and a pressure change of 1 kbar, the quadratic term in the compressibility of steel makes a contribution to m that is just less than the smallest difference that can be read. Allowance for the quadratic compressibility of the O-rings of the volumometer would increase this contribution negligibly and assuming the quadratic term to be due to the fluid alone produces no significant degradation of the fit of the calibration data.

By arguments similar to those used in the derivation of (A 1), (7) can be written as

$$\begin{aligned} m &= \phi(v,p)\,\rho(p), \\ &= [\phi_0+k_a p+v(1+k_b p)]\,\rho(p), \end{aligned} \tag{A 2}$$

where ϕ_0 is the volume of the screw injector plus its attached tubing when $p = 0$ and $r = 0$, k_a the elasticity of that volume, k_b the elasticity of the volume that can be displaced by the piston, and ρ the density of the liquid, which may be taken as

$$\rho = \rho_0+\rho_1 p+\rho_2 p^2+\rho_3 p^3. \tag{A 3}$$

Equation (A 2) with (A 3), when expanded, differs from (A 1) only in higher-order terms, which have just been shown to be unimportant.