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THE *PVT* PROPERTIES OF WATER
V*. THE FLUID TO 1 KBAR AT 350–500 °C AND ALONG THE SATURATION LINE FROM 150 TO 350 °C

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CONTENTS

The density of water has been measured from low pressures to 1 kbar (1 bar = 10^5 Pa) at 25 K intervals from 350 to 500 °C and the density change on condensation has been measured from 150 to 350 °C by injecting water into a 35 cm^3 high-temperature vessel that can be completely filled in a single delivery from the screw injector used in earlier work. The thermal expansion of the vessel was determined by a gas-expansion method. The estimated uncertainty caused by the uncertainty of the volume of the vessel at low pressure is 0.02 kg m^{-3} at 150 °C and 0.08 kg m^{-3} at all other temperatures, and the uncertainty arising from the uncertainty in the compression of the vessel is 0.10 kg m^{-3} kbar^{-1}.

1. INTRODUCTION

Previous papers have reported measurements of the density of liquid water in the range 0–350 °C, 0–1 kbar‡ (Kell & Whalley 1965, 1975; Kell *et al.* 1978*a*) and virial coefficients of both H_2O (Kell *et al.* 1968*a*) and D_2O (Kell *et al.* 1968*b*) vapour. This paper reports measurements of the saturation densities of the liquid and vapour in the range 150–350 °C and densities in the range 350–500 °C and 0–1 kbar. Measurements were not made close to the critical point because the pressure vessel is too tall for accurate measurements there.

In the earlier work, below 350 °C, the compression of water was small and it could be measured accurately by injecting known amounts of water into a filled pressure vessel. At the higher temperatures used in this paper the compression is high and it is better to inject known amounts of water into an initially empty vessel. A 35 cm^3 vessel that could be filled in a single travel of the screw injector was therefore used.

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† Died March 1983.

‡ 1 bar = 10^5 Pa.

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2. APPARATUS AND CALIBRATION

2.1. *The apparatus*

The apparatus was that described for measurements on the liquid below 350 °C (Kell *et al.* 1978*a*). Briefly, the amount of fluid in a vessel at the experimental temperature was changed by the displacement of a screw injector at room temperature that had been calibrated as described by Kell & Whalley (1965) and whose working parts were kept as free as possible from non-hydrostatic stresses.

The pressure was measured with a pressure balance that had been calibrated to 1 kbar against a 17 m differential mercury column (Kell & Whalley 1965) to *ca.* $100/10^6$, and was adjusted for the various heads to the centre of the pressure vessel when the density was measured and to the meniscus when the vapour pressure was measured. As in the earlier work, measurements were made at 27 pressures in the range 5.30–1026.39 bar at intervals that ranged from 7 bar at the lowest pressures to 58 bar at the highest. Measurements were also made on the vapour at low pressures to extrapolate the volumometer readings to zero pressure so that the mass, m_0, of water in the system could be found, and in both the liquid and the vapour near saturation so that the density could be extrapolated to saturation. The pressures were generated by fixed weights on the pressure balance and the reported densities were adjusted to fixed pressures for the (small) changes in atmospheric pressure and the heads of fluid without introducing significant error. The screw injector was calibrated to 1 mg and was reproducible at each balance point to 0.2–0.5 mg. The temperature was measured with platinum resistance thermometers of our own design and manufacture and calibrated on the IPTS-48 in the earlier measurements and later on the IPTS-68, by R. J. Berry of the Division of Physics, National Research Council. The IPTS-48 temperatures were converted to the IPTS-68 as described by Kell *et al.* (1978*a*).

The pressure vessel had a double wall and is illustrated in figure 1. The inner vessel had an internal volume of *ca.* 35 cm³, so that it could be filled with a single pass of the screw injector, and was jacketed by the outer vessel to enable the pressures inside and out to be kept equal. It had a tube passing to the bottom, through which soluble impurities were removed every time water was removed. All parts were of 304 stainless steel and all parts that came in contact with the sample were made of the low-carbon form, 304L, to reduce corrosion due to the precipitation of carbide during welding. The several parts of the inner vessel were carefully cleaned before welding, welded without flux, annealed before the outer vessel was welded in place, and pickled in 10% (by volume) nitric acid.

The balancing pressure was seriously less than the working pressure on two occasions: once in December 1970 as the measurements were starting and once in November 1972 during a run at 475 °C, as they were nearly finished. The wall of the inner vessel was too thin to support 1 kbar without yielding and on both occasions the volume changed permanently.

The water used was laboratory conductivity water that had been boiled, twice distilled in vacuum, and subsequently handled under vacuum. At the end of each run the sample was removed from the vessel through the capillary tube, and was examined to make sure that it was not discoloured by corrosion, that it contained no trace of mercury from the W-tube and that there where no bubbles of gas. The vessel was then evacuated to a pressure lower than the first pressure of the next run.

The mass m_0 of water in the system, i.e. the mass that would be in the screw injector if all

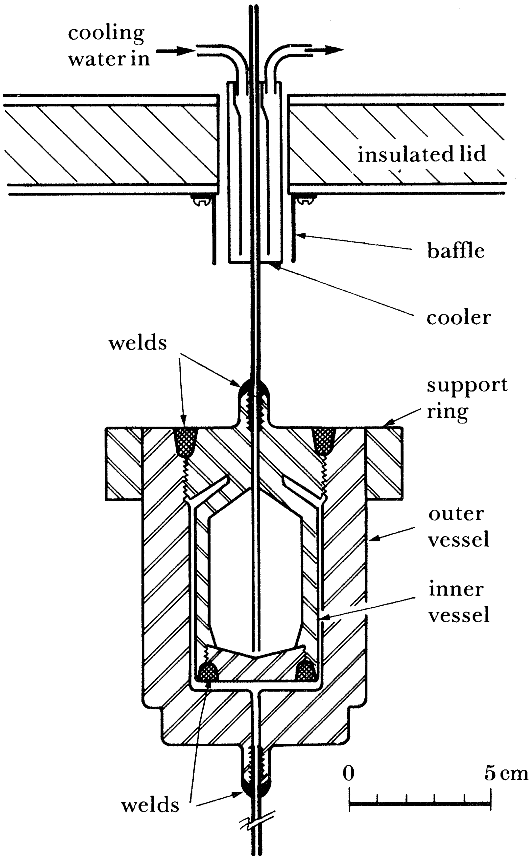

FIGURE 1. Cross-sectional view of the pressure vessel.

the water in the vessel were condensed into it, was determined by measuring the masses in the injector at several pressures when the vessel contained vapour, and fitting them by a least squares method to the equation (Kell *et al.* 1968*a*)

$$\frac{p_i}{T_i} = \frac{m_0 - m_i}{W(1-\kappa p_i)} + \frac{B_2}{R}\left(\frac{m_0 - m_i}{W(1-\kappa p_i)}\right)^2 + \frac{B_3}{R^2}\left(\frac{m_0 - m_i}{W(1-\kappa p_i)}\right)^3 + \dots, \tag{1}$$

where p_i is the pressure of measurement i, T_i its Kelvin temperature, m_i the mass contained in the screw injector, κ the compressibility of the vessel, B_2 and B_3 the second and third virial coefficients of the vapour, and $W = V_\mathrm{v}^0 M/R$, where V_v^0 is the volume of the pressure vessel at zero pressure and the temperature of the isotherm, M the molecular mass of the water, and R the gas constant. The values of B_2 were taken from Kell *et al.* (1968*a*), V_v^0 was determined by the thermal expansion measurements described in §2.2, and m_0 and B_3 were determined by the least-squares fit of p_i and m_i to (1). It was always verified that the values of V_v^0 and B_2 were consistent with the data.

The compressibility, κ, of the stainless-steel vessel at Celsius temperature t in the range 350–500 °C was taken as

$$\kappa/(\mathrm{Mbar}^{-1}) = 0.596 + 0.00017t, \tag{2}$$

as determined for another vessel of the same material in the range 0–150 °C (Kell & Whalley 1965, 1975). As the temperature range is $\frac{1}{5}$–$\frac{1}{6}$ of the melting point of the steel, the extrapolated values are probably accurate to *ca.* 0.04 and *ca.* 0.1 $\mathrm{Mbar^{-1}}$ at 350 and 500 °C respectively. These uncertainties correspond to *ca.* ±0.04 and *ca.* 0.1 $\mathrm{kg\ m^{-3}}$ in the density of water.

The density, ρ, of the water was calculated directly from the equation

$$\rho = \frac{m_0 - (m_i^* + \delta m)}{(V_v^0 - \delta V)\,(1 - \kappa p_i)}, \tag{3}$$

where m_i^* is the mass in the screw injector and the tubing between the injector and the bottom of the cooler in figure 1, and δm and δV are variations respectively in the mass of the liquid water and in the volume available to the vapour due to the variable location of the meniscus.

The values of δm and δV were evaluated as follows. When the water vapour was below the critical point, there was a meniscus in the capillary tube between the bottom of the cooler and the surface of the bath. The tube was assumed to have a uniform temperature gradient of length L between the temperature in the cooler, of 23.8 °C for measurements with water and 25 °C for gas expansions, and the temperature, t, of the bath immediately below the cooler. At the meniscus, the pressure is equal to the vapour pressure, and the temperature t_m at which this was so was calculated without significant error from the Antoine equation,

$$t_m = \{-2080/[\lg(p/\mathrm{bar}) - 5.58] - 273.15\}\ ^\circ\mathrm{C}. \tag{4}$$

The fractional length, x, of the tube filled with liquid is

$$x = (25 - t_m)/(25 - t). \tag{5}$$

Then

$$\delta V = AxL,$$

where A is the cross-sectional area of the bore, and δm can be obtained from δV and the mean density of the liquid, which was approximated as the density at 25 °C without significant error. The pressure was corrected for the pressure drop δp_1 across the meniscus of $2\sigma/r$ where σ is the surface tension and r the radius, and for the head δp_2 of liquid. The real length of the temperature gradient is unknown but is unlikely to exceed 1 cm, and for that value $\delta V < 2\ \mathrm{mm^3}$, $\delta m < 2$ mg, and $\delta p_2 < 1$ mbar. Also, $\delta p_1 < 4$ mbar. The uncertainty of the corrections therefore does not contribute significantly to the uncertainty of the experiment, as was also true in the earlier work (Kell *et al.* 1968*a*, *b*).

2.2. *Volume of the vessel*

The volume of the vessel was determined in two ways. In the first, which was used at 150 °C only, it was filled with water from the screw injector to 5.3 bar, and the density at this temperature and pressure was taken as 0.91707 $\mathrm{g\ cm^{-3}}$, with an estimated uncertainty of *ca.* $12/10^6$ from Kell's (1975) correlation of Kell & Whalley's (1965) measurements and reanalysis (Kell & Whalley 1975). The vessel was not thoroughly evacuated of water vapour before making the measurements, and so the mass m_0 in it at the start was determined from the measured pressure and compression measurements on the vapour by using (1), as described by Kell *et al.* (1968*a*).

Four measurements were made by this method between the two imbalances of the inside and outside pressures described in §2.1 and the volumes obtained are listed as those for runs 5, 6, 21, and 31 in table 1. The apparent drift of the volume at the rate of about $4/10^6$ per month is well within the uncertainty and is probably coincidental. The standard deviation of the mean is $50/10^6$. Nevertheless, the apparent drift in volume was taken account of in the final densities.

Table 1. Volume of the 35 cm³ vessel as determined by filling with liquid water at 150 °C and 5.3 bar

run no.	volume/cm³	date
5	35.3506	1971 Mar.
6	35.3495	1971 May
21	35.3478	1971 Oct.
31	35.3469	1972 Aug.
mean	35.3487 ± 0.0020	
36	35.3567	1973 Feb.

After each of these measurements, a series of compression measurements as made to a pressure of 1 kbar to test the apparatus. The results are also summarized under runs 5, 6, 21, 31 and 36 of table 4.

The standard error at each pressure is 0.00–0.02 kg m^{-3}, and the mean values at each pressure agree very well with the earlier measurements (Kell & Whalley 1975), which are more accurate because the pressure vessel was almost ten times larger. It was concluded that the apparatus works very well.

The volume of the vessel was also determined in the range 0–150 °C by filling it with water and measuring the apparent thermal expansion of the water at 5.30 bar by means of the screw injector. The specific volume of the water at 5.30 bar and 0–150 °C was taken from Kell & Whalley (1975) and Kell *et al.* (1978*a*). Two series of measurements were made with different fillings of water, and the deviations of the volume ratio from (6) are plotted in figure 2 as open triangles and open squares for the two series.

The second method of determining the volume of the vessel consisted of expanding helium

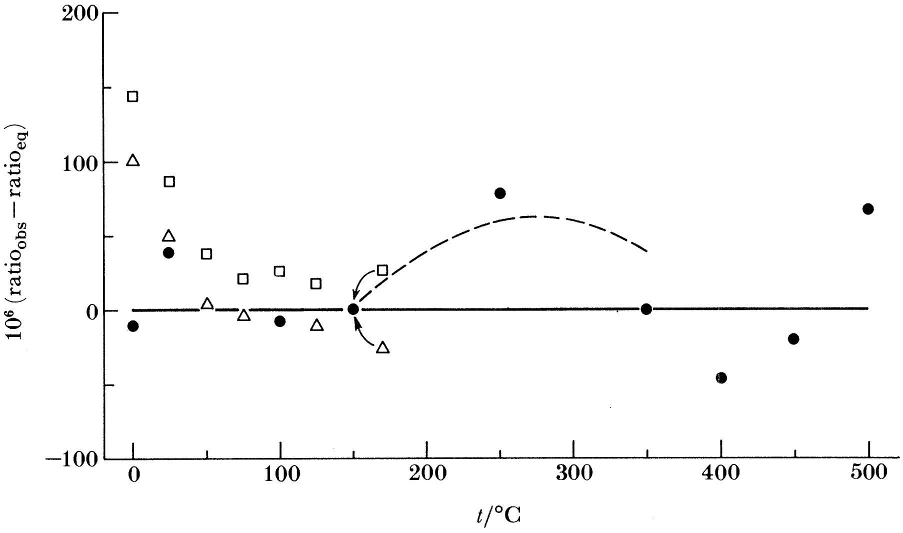

Figure 2. The ratio of the volume of the vessel at temperature t and 150.00 °C less the ratio described by (6). Each symbol represents a different series of measurement; ●, gas expansion measurements from this work; – – –, calculated by (12) of Kell *et al.* (1978*a*); △, measurements relative to liquid water, series 1, this work; □, measurements relative to liquid water, series 2, this work. The data have been treated so that both lines and all three series of points coincide at 150 °C.

from another vessel at 25 °C having a volume of 75 cm^3 into the experimental vessel at the required temperature and was used at nine temperatures in the range 0–500 °C. Second and third virial coefficients of helium were obtained during this work, and full details of these and measurements with other vessels are described by Kell *et al.* (1978*b*). The standard error of the volumes is about $50/10^6$. The volume at 150 °C as determined by injecting water into the vessel at 5.30 bar is more accurate than the volume determined by gas expansion and has been adopted. The volumes from gas expansion were then used only to determine the ratio R of the volume at various temperatures to the volume at 150 °C; these ratios are listed in table 2.

TABLE 2. THE RATIO R OF THE VOLUME OF THE VESSEL AT TEMPERATURES t AND 150 °C AND THE SECOND VIRIAL COEFFICIENT B_2 OF HELIUM DETERMINED BY GAS-EXPANSION MEASUREMENTS WITH THE 35 cm^3 VESSEL[1]

$t/°\text{C}$	ratio of volumes 35 cm^3 vessel	 250 cm^3 vessel	$B_2/(\text{cm}^3\ \text{mol}^{-1})$
0	0.99236 ± 0.00006	—	12.23 ± 0.02
25	0.99365 ± 0.00006	—	12.13 ± 0.02
100	0.99739 ± 0.00004	—	11.80 ± 0.02
150	1.00000 ± 0.00006	1.00000	11.56 ± 0.05
250	1.00545 ± 0.00004	1.00543 ± 0.00006	11.19 ± 0.02
350	1.01096 ± 0.00005	1.01100 ± 0.00005	10.79 ± 0.04
400	1.01380 ± 0.00005	—	10.61 ± 0.05
450	1.01676 ± 0.00005	—	10.53 ± 0.04
500	1.01984 ± 0.00004	—	10.26 ± 0.07

[1] The values of B_2 in Kell *et al.* (1978*b*) were derived in part from these values.

The ratios were fitted to a polynomial in the Celsius temperature, t, by least squares with equal weights to give

$$R = 0.992384 + 49.17 \times 10^{-6}\, t + 11.28 \times 10^{-9}\, t^2,$$

with a standard deviation of 0.00004. The value of 150 °C predicted by this equation is 1.000013, whereas by definition it should be 1 exactly. The value 0.000013 has, therefore, been subtracted from all values of R to ensure that this is true. The constant term in this equation was then replaced by the value 0.992371. The final equation used to calculate the volume ratios was

$$R = 0.992371 + 49.17 \times 10^{-6}\, t + 11.28 \times 10^{-9}\, t^2. \tag{6}$$

The deviations of the measured values from this equation are plotted as filled circles in figure 2. The deviations of a similar equation, (12) of Kell *et al.* (1978*a*), used in the range 150–350 °C, are plotted as a broken line.

The values of the ratio, R, of volumes in the range 0–100 °C measured with a gas and with a liquid differ significantly in that the difference of volume at 0 °C is about $100/10^6$ greater for the gas measurements than for the liquid, and decreases to about zero at 100 °C. The gas measurements measure the difference of the quantity $(V/T)\,T_{68}$, where T is the thermodynamic temperature and T_{68} is the temperature on the IPTS-68 scale, whereas the liquid measurements measure the difference of the volume on the IPTS-68 scale. The difference of the values of R would be explained if 100 °C on the IPTS-68 scale were about 0.04 K greater than 373.16 K. Guildner & Edsinger (1973, 1976) have reported on the basis of gas thermometric measurements that it is in fact 0.03 K greater. The measurements reported here, therefore, support Guildner and Edsinger's conclusion.

In November 1972 the balancing pressure failed and caused the vessel to grow. Soon after the accident a compression run on water at 475 °C showed that the volume of vessel had increased by the factor 1.000 56 ± 0.000 01. A second set of runs at 150 °C in February 1973 showed that the ratio had decreased to 1.000 28 ± 0.000 02 and a gas expansion run also at 150 °C gave the ratio as 1.000 20 ± 0.000 05. The volume of the vessel had, therefore, relaxed about half-way towards its original volume. The volume used for reducing the observations at 500 °C was the volume measured by filling with water at 150 °C (run 36) multiplied by the thermal expansion factor R of 1.019 775 as calculated by (6).

3. Experimental results

3.1. *Saturation pressures*

The saturation pressures were measured at intervals of 25 K between 150 and 350 °C at several degrees of filling of the pressure vessel. The final pressures were taken when the vessel was about half full.

The measured balancing pressure was adjusted to the pressure at the surface of the liquid by allowing for the various heads. The vessel has two equilibrium states at saturation, according to whether the capillary inside the vessel and above the level of the fluid is filled with liquid or with vapour. The liquid in the capillary is, of course, metastable relative to the vapour. The capillary was undoubtedly filled initially with cool liquid from the screw injector. If, after some time, a vapour bubble were to nucleate and the capillary become filled with vapour, the balancing pressure would increase by the difference in heads of liquid and vapour, which is a maximum of 15 mbar. This was never observed in this work, so the capillary was always filled with liquid.

Table 3. Observed saturation pressures p_s and the values adjusted to rounded temperatures on the IPTS-68 and IPTS-48 temperature scales

	observed		adjusted			
run	t_{68}/°C	p_s/bar	t_{68}/°C t_{48}/°C	p_s/bar	t_{48}/°C t_{68}/°C	p_s/bar
5	150.019	4.759 ± 0.001	$150 = 149.980$	4.757	$150 = 150.020$	4.759
6	150.020	4.759 ± 0.001	$150 = 149.980$	4.756	$150 = 150.020$	4.759
21	150.019	4.758 ± 0.001	$150 = 149.980$	4.756	$150 = 150.020$	4.758
31	149.994	$4.752 \pm 0.000_5$	$150 = 149.980$	4.753	$150 = 150.020$	4.755
36	149.998	4.757 ± 0.001	$150 = 149.980$	4.757	$150 = 150.020$	4.760
7	175.003	8.918 ± 0.002	$175 = 174.968$	8.917	$175 = 175.032$	8.924
8	175.003	8.918 ± 0.001	$175 = 174.968$	8.917	$175 = 175.032$	8.924
9	199.999	15.536 ± 0.001	$200 = 199.957$	15.536	$200 = 200.043$	15.550
10	199.999	15.535 ± 0.001	$200 = 199.957$	15.535	$200 = 200.043$	15.549
11	224.997	25.474 ± 0.001	$225 = 224.947$	25.475	$225 = 225.053$	25.501
12	225.008	25.479 ± 0.002	$225 = 224.947$	25.475	$225 = 225.053$	25.500
3	250.058	39.780 ± 0.002	$250 = 249.939$	39.741	$250 = 250.061$	39.782
4	250.058	39.772 ± 0.004	$250 = 249.939$	39.733	$250 = 250.061$	39.774
13	274.997	59.416 ± 0.002	$275 = 274.932$	59.419	$275 = 275.068$	59.481
14	274.997	59.416 ± 0.002	$275 = 274.932$	59.419	$275 = 275.068$	59.481
15	300.000	85.821 ± 0.002	$300 = 299.927$	85.821	$300 = 300.073$	85.909
16	299.999	85.822 ± 0.003	$300 = 299.927$	85.823	$300 = 300.073$	85.911
17	324.999	$120.44_6 \pm 0.005$	$325 = 324.924$	120.44_8	$325 = 325.076$	120.56_7
18	325.000	$120.44_3 \pm 0.005$	$325 = 324.924$	120.44_3	$325 = 325.076$	120.56_3
1	350.074	165.37 ± 0.02	$350 = 349.923$	165.22	$350 = 350.077$	165.38
2	350.074	165.37 ± 0.01	$350 = 349.923$	165.22	$350 = 350.077$	165.38
19	350.000	$165.19_6 \pm 0.01_0$	$350 = 349.923$	165.19_6	$350 = 350.077$	165.35_2

TABLE 4. DENSITY OF LIQUID WATER IN THE RANGE 150–500 °C AND 5.30–1026.39 bar

t_{68}/°C	150					175		200		225		250		275		300	
run	5	6	21	31	36	7	8	9	10	11	12	3	4	13	14	15	16
V/cm^3	35.3506	35.3495	35.3478	35.3469	35.3567	35.3962	35.3962	35.4434	35.4430	35.4907	35.4907	35.5404	35.5404	35.5875	35.5875	35.6363	35.6363
p_s/bar	4.757	4.756	4.756	4.753	4.757	8.917	8.917	15.536	15.535	25.475	25.475	39.741	39.733	59.419	59.419	85.821	85.823
Z_{sv}	0.952	0.953	0.951	0.951	0.951	0.932	0.932	0.901	0.901	0.8648	0.8695	0.8222	0.8223	0.7687	0.7687	0.7033	0.7029
ρ_{sv}/(kg m^{-3})	2.56	2.56	2.56	2.56	2.56	4.62	4.62	7.89	7.92	12.81	12.74	20.02	19.98	30.55	30.55	46.13	46.16
ρ_{sl}/(kg m^{-3})	917.04	917.04	917.04	917.04	917.04	892.36	892.35	864.75	864.77	833.89	833.89	799.03	799.03	759.21	759.24	712.44	712.44
p/bar	ρ/(kg m^{-3})																
5.30	917.07	917.07	917.07	917.07	917.07	—	—	—	—	—	—	—	—	—	—	—	—
12.60	917.50	917.49	917.51	917.49	917.49	892.60	892.59	—	—	—	—	—	—	—	—	—	—
20.00	917.92	917.91	917.93	917.91	917.92	893.10	893.06	865.10	865.10	—	—	—	—	—	—	—	—
27.40	918.33	918.33	918.35	918.34	918.33	893.56	893.56	865.65	865.65	834.07	834.07	12.77	12.76	11.88	11.88	11.18	11.14
42.11	919.18	919.16	919.19	919.18	—	894.52	894.51	866.76	866.76	835.43	835.42	799.30	799.31	19.48	19.47	18.04	18.01
56.81	919.99	920.00	920.01	919.99	—	895.46	895.43	867.86	867.86	836.76	836.75	801.02	801.03	28.66	28.64	25.79	25.81
71.51	920.79	920.81	920.82	920.80	—	896.37	896.37	868.97	868.97	838.09	838.07	802.68	802.70	761.10	761.13	34.98	34.95
86.31	921.64	921.63	921.64	921.64	—	—	—	870.04	870.04	839.39	839.38	804.35	804.36	763.34	763.35	712.53	712.54
101.01	922.43	922.43	922.46	922.44	—	—	—	—	—	840.70	840.66	—	805.97	765.51	765.52	715.80	715.81
115.71	923.23	923.23	923.25	923.23	—	—	—	—	—	841.97	841.95	—	—	767.64	767.64	718.96	718.95
130.52	924.06	924.05	924.07	924.06	—	—	—	—	—	—	—	—	—	769.72	769.74	722.01	722.01
151.89	925.20	925.24	925.22	925.21	—	—	—	—	—	—	—	—	—	—	—	726.24	726.24
210.28	928.31	928.32	928.32	928.30	—	—	—	—	—	—	—	—	—	—	—	736.80	736.79
268.57	931.36	931.36	931.36	931.35	—	—	—	—	—	—	—	—	—	—	—	—	—
326.95	934.30	934.35	934.33	934.31	—	—	—	—	—	—	—	—	—	—	—	—	—
385.22	937.22	937.24	937.24	937.19	—	—	—	—	—	—	—	—	—	—	—	—	—
443.49	940.06	940.10	940.08	940.04	—	—	—	—	—	—	—	—	—	—	—	—	—
501.85	942.83	942.83	942.88	942.82	—	—	—	—	—	—	—	—	—	—	—	—	—
560.11	945.60	945.58	945.61	945.55	—	—	—	—	—	—	—	—	—	—	—	—	—
618.47	948.29	948.25	948.30	948.26	—	—	—	—	—	—	—	—	—	—	—	—	—
676.71	950.93	950.89	950.94	950.90	—	—	—	—	—	—	—	—	—	—	—	—	—
735.06	953.53	953.49	953.54	953.50	—	—	—	—	—	—	—	—	—	—	—	—	—
793.29	956.08	956.06	956.09	956.05	—	—	—	—	—	—	—	—	—	—	—	—	—
851.63	958.60	958.59	958.61	958.58	—	—	—	—	—	—	—	—	—	—	—	—	—
909.85	961.08	961.08	961.10	961.05	—	—	—	—	—	—	—	—	—	—	—	—	—
968.08	963.52	963.52	963.54	963.48	—	—	—	—	—	—	—	—	—	—	—	—	—
1026.39	965.93	965.93	965.96	965.90	—	—	—	—	—	—	—	—	—	—	—	—	—

t_{68}/°C	325		350			375		400		425		450		475			500	
run	17	18	1	2	19	20	22	23	24	25	26	27	28	29	32	33	34	35
V/cm³	35.6856	35.6856	35.7398	35.7392	35.7356	35.7862	35.7856	35.8368	35.8367	35.8883	35.8882	35.9403	35.9402	35.9929	35.9925	36.0130	36.0559	36.0559
p_s/bar	120.448	120.443	165.22	165.22	165.196	—	—	—	—	—	—	—	—	—	—	—	—	—
Z_{sv}	0.6177	0.6185	0.5033	0.5053	0.5055	—	—	—	—	—	—	—	—	—	—	—	—	—
ρ_{sv}/(kg m^{-3})	70.64	70.54	114.14	113.69	113.63	—	—	—	—	—	—	—	—	—	—	—	—	—
ρ_{sl}/(kg m^{-3})	654.61	654.60	574.46	574.69	574.65	—	—	—	—	—	—	—	—	—	—	—	—	—
p/bar									ρ/(kg m^{-3})									
5.30	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
12.60	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
20.00	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
27.40	10.55	10.57	10.03	10.03	10.04	—	—	—	—	—	—	—	—	—	—	—	—	—
42.11	16.86	16.88	15.88	15.94	15.91	15.13	15.09	14.40	14.40	13.77	13.75	13.18	13.21	12.69	12.68	12.68	12.20	12.20
56.81	23.78	23.82	22.21	22.27	22.23	20.98	20.97	19.88	19.86	18.92	18.94	18.11	18.09	17.34	17.34	17.36	16.67	16.70
71.51	31.52	31.53	29.08	29.18	29.09	27.23	27.22	25.68	25.64	24.32	24.32	23.17	23.18	22.18	22.17	22.19	21.28	21.26
86.31	40.50	40.52	36.70	36.72	36.73	34.00	33.96	31.84	31.79	30.00	30.02	28.50	28.51	27.17	27.18	27.19	26.04	26.04
101.01	51.18	51.17	45.15	45.26	45.18	41.32	41.29	38.36	38.33	35.96	35.95	34.01	34.00	32.33	32.34	32.33	30.89	30.88
115.71	64.93	64.93	54.92	55.01	54.97	49.31	49.32	45.30	45.29	42.22	42.21	39.72	39.74	37.65	37.63	37.65	35.85	35.87
130.52	658.40	658.38	66.65	66.69	66.68	58.31	58.25	52.87	52.88	48.88	48.89	45.76	45.78	43.20	43.21	43.22	41.05	41.05
151.89	665.84	665.82	89.71	89.74	89.74	73.49	73.47	65.03	65.00	59.28	59.27	55.00	55.02	51.62	51.61	51.61	48.78	48.82
210.28	682.95	682.94	606.65	606.68	606.74	155.53	155.51	110.58	110.59	94.22	94.25	84.34	84.37	77.37	77.37	77.34	72.00	72.05
268.57	696.99	696.97	633.04	633.08	633.12	530.53	530.58	214.67	214.69	146.40	146.41	122.50	122.43	108.46	108.48	108.48	98.85	98.81
326.95	709.10	709.06	652.59	652.64	652.68	575.60	575.61	438.07	438.07	239.03	239.20	175.36	175.32	147.31	147.29	147.30	130.38	130.41
385.22	719.76	—	668.42	668.51	668.53	603.61	603.60	511.81	511.77	368.44	368.62	249.43	249.24	196.13	196.12	196.04	167.60	167.63
443.49	—	—	681.96	681.96	682.00	624.71	624.65	551.06	551.04	450.67	450.80	334.45	334.28	254.93	254.95	254.87	210.90	210.82
501.85	—	—	693.75	693.77	693.85	641.85	641.80	578.56	578.54	499.06	499.16	404.03	403.82	317.10	317.09	317.09	258.76	258.76
560.11	—	—	704.46	704.34	704.42	656.38	656.37	600.01	599.94	532.49	532.57	453.62	453.38	372.63	372.63	372.64	307.28	307.29
618.47	—	—	713.98	713.95	714.04	669.15	669.11	617.72	617.65	558.16	558.22	490.20	490.04	417.90	417.88	417.88	352.42	352.41
676.71	—	—	722.81	722.81	722.85	680.51	680.51	632.89	632.83	579.01	579.02	518.70	518.54	454.04	454.02	454.00	391.82	391.80
735.06	—	—	731.02	730.98	731.06	690.79	690.84	646.25	646.18	596.62	596.66	542.02	541.88	483.53	483.48	483.47	425.46	425.42
793.29	—	—	738.63	738.60	738.68	700.24	700.29	658.18	658.12	611.93	611.96	561.68	561.56	508.07	508.04	508.12	454.05	454.06
851.63	—	—	745.78	745.79	745.85	708.98	709.04	669.01	668.95	625.52	625.56	578.75	578.61	529.09	529.06	529.10	478.69	478.67
909.85	—	—	752.56	752.51	752.62	717.13	717.17	—	678.87	637.73	637.77	593.78	593.66	547.36	—	547.38	500.09	500.07
968.08	—	—	759.02	758.96	759.04	724.75	724.86	—	688.05	648.87	648.90	607.28	607.15	563.55	—	563.57	518.99	518.97
1026.39	—	—	765.10	765.05	765.16	731.97	732.06	—	696.62	659.12	659.14	619.55	619.42	578.16	—	578.10	535.87	535.86

V is the vessel volume, measured at 150 °C as summarized in table 1 and as measured by gas expansion at other pressures; p_s is the saturation pressure; Z_{sv} is the ratio $pV = nRT$, where R is the gas constant and n the number of moles of water in the vessel extrapolated to the saturation pressure; ρ, ρ_{sv} and ρ_{sl} are the density, the saturated vapour density, and the saturated liquid density respectively.

The observed saturation temperatures and pressures are summarized in the first two columns of table 3. The observed pressures were adjusted to rounded IPTS-68 and IPTS-48 temperatures without significant error by using the Schmidt (1979) steam tables to calculate the small differences. The adjusted values are listed on the right-hand side of table 3.

The mean of our five values at 150 °C (IPTS-68) is 4.7558 ± 0.0015 bar, which is lower by 1.6 mbar than the value given by Ambrose & Lawrenson's (1972) correlation. The corresponding value at 150 °C (IPTS-48), which is 4.7582 bar, is 0.9 mbar lower than the value of Osborne *et al.* (1933) of 4.7591 bar, whose precision is two or three times greater than that of this work. Our values agree with the value of Osborne *et al.* within the combined uncertainties except perhaps at 300 °C, where our value of 85.910 ± 0.003 bar at 300 °C (IPTS-48) is lower than their value of 85.9205 bar, although their smoothed value is 85.911 bar. The International Skeleton Tables (1963) of the Properties of Steam recommend the value 85.917 ± 0.024 bar, and Gibson & Bruges's (1967) correlation recommends 85.916 bar.

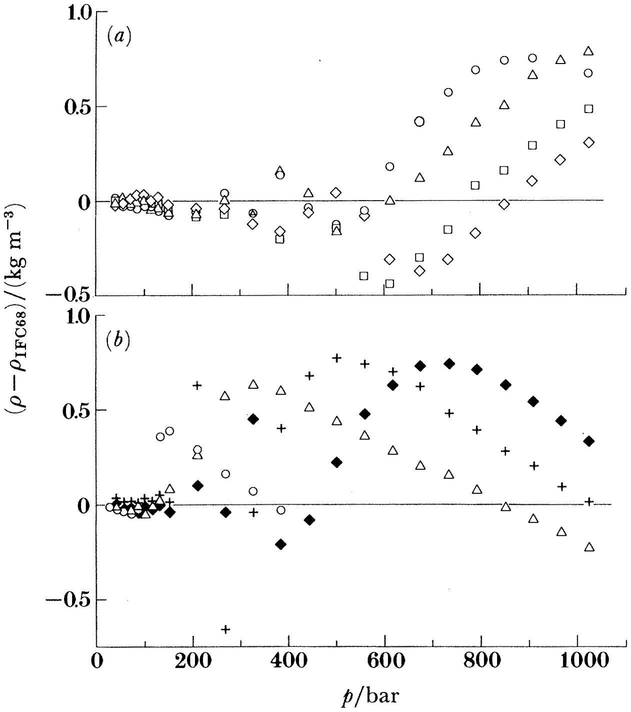

FIGURE 3. Differences of density between the results summarized in table 4 and the 1968 IFC Formulation for Scientific and General Use. The runs for which the differences are plotted are: (*a*) ◇, run 34, 500 °C; □, run 33, 475 °C; △, run 27, 450 °C; ○, run 25, 425 °C; (*b*) ◆, run 24, 400 °C; +, run 20, 375 °C; △, run 19, 350 °C; ○, run 17, 325 °C.

3.2. *Densities not at saturation*

The densities adjusted to rounded values of the IPTS-68 temperature and to the pressures used previously (Kell & Whalley 1965; Kell *et al.* 1968*a*, *b*, 1978*a*) are listed in the range 350–500 °C in table 4. The runs, which are identified by the number in the second row of the table, are independent of one another, and were made in the order of run number except that run 30 does not exist. The main purpose of the measurements in the range 175–325 °C was to determine the saturation density, and so only a small part of the pressure range was used.

The standard deviation of replicate determinations is *ca.* 0.030 kg m^{-3} far from the critical point and *ca.* 0.050 kg m^{-3} near it. These correspond to *ca.* 1 and *ca.* 1.8 mg in the pressure vessel, which are similar to the reproducibility of 1 mg from run to run of the screw injector. The uncertainty of the volume of the vessel at low pressures corresponds to an uncertainty of the density of *ca.* 0.08 kg m^{-3} at all temperatures except 150 °C, where it is *ca.* 0.02 kg m^{-3}. The uncertainty caused by the uncertainty of the compression of the vessel increases linearly from zero at zero pressure to 0.10 kg m^{-3} at 1 kbar.

3.3. *Saturation densities*

The saturated liquid densities in the range 150–300 °C were determined by extrapolating the liquid densities over a range of about 0.3–0.6 bar to the saturation pressure using a quadratic or cubic expansion in the pressure. At 325 and 350 °C, the densities deviated significantly from quadratic or cubic polynomial expansions, and the deviations were allowed for by extrapolating graphically.

The saturated vapour densities at 150 and 175 °C were calculated from the equation of state determined earlier (Kell *et al.* 1968*a*) extrapolated to the saturation pressures determined in this work. Between 200 and 350 °C, the densities reported in this paper were fitted by a low-order polynomial in the pressure, and the deviations were extrapolated graphically.

The uncertainties of the extrapolated liquid densities are the same as the uncertainties of the liquid densities they are based on, which are described in §3.2. The uncertainties of the extrapolated vapour densities at 150 and 175 °C are the uncertainties of the equation of state (Kell *et al.* 1968*a*) and are included in table 4.

The deviations of the liquid densities from the 1968 IFC Formulation for Scientific and General Use are plotted against temperature in figure 3. Other measurements have been compared with the same formulation by Watanabe & Uematsu (1975).

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