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Specific Volume of Liquid Water from (253 to 323) K and Pressures up to 350 MPa by Volumetric Measurements

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Water science is fundamental to investigate physical and biological phenomena. The volumetric properties of liquid water have been studied for different pressure and temperature conditions covering the whole domain of water in the liquid state. Nevertheless, the uncertainty of the existing data should be reduced. In this work, the specific volume v of water was determined by measuring the volume change Δv with pressure from a reference state v_{ref} at a given temperature, that is: $v = v_{\text{ref}} + \Delta v$. The purpose was to provide new v values to enrich the water properties database. A variable-volume piezometer with a solid-piston volumometer based on a linear variable differential transformer was employed. About 200 pvT points were determined between (253 and 323) K for pressures up to 350 MPa; the initial reference for the specific volume v_{ref} was calculated from the equation of state of the International Association for the Properties of Water and Steam (IAPWS-95 formulation). The relative combined uncertainty (confidence level of 95 %) was evaluated for each pvT value and was at most 0.07 % above 273 K and 0.2 % below 273 K at the maximal pressure investigated of 350 MPa.

Introduction

High-pressure studies are performed in many different fields: astrophysics, energy, biology, food, and so on. Water is often used as a reference in those studies to explain the behavior of matter under high pressure, for comparison purposes or for device calibration; this is because its physical properties are known over a wide range of conditions.[1] For instance, density and its reciprocal, specific volume, are useful to describe a great variety of phenomena from convection in the oceans to heat and mass transfers during food high-pressure processing.

Since Amagat at the end of the 19th century, many scientists have determined the pvT properties of liquid water.[2] While densities of liquids are measured in a routine manner at atmospheric pressure, it is not the case at high pressure. High-pressure piezometers used to be custom-made devices designed to measure in a specific pressure−temperature range according to the objectives of the study. As a result, the existing database for water specific volume is constituted by a variety of contributions, presenting data on different pressure and/or temperature ranges.[3] When the published data sets do not overlap, they are hard to compare between them, and some inconsistencies may appear. This was pointed out by Wagner and Pruss[1] when comparing the data of Kell and Whalley[4] (available up to 100 MPa) with those of Grindley and Lind[5] (available at successive pressures up to 800 MPa) for different temperatures above 273 K. Thus, it should be interesting to have some new data covering this pressure−temperature range.

Besides, it can be observed that the low temperature region ($T < 273$ K) has been much less investigated than the high temperature one ($T \geq 273$ K) under high pressure. The existence of two phases (solid and liquid) in that region as a function of pressure and temperature represents an added difficulty to the usual pvT measurements under pressure. In fact, the low temperature region at high pressure includes liquid water, different ice modifications, amorphous states, and metastable zones. The relative uncertainty of the existing data in that region is on the order of (0.1 to 0.2) %, while it is from (0.001 to 0.05) % at higher temperatures depending on the pressure range considered.[1] Thus, new data with a lower uncertainty at low temperatures are desirable.

In this work, the specific volume of water is determined between (253.15 and 323.15) K and at pressures up to 350 MPa. The volumetric device used for this purpose is presented in detail. The objective is to provide a new data set for water specific volume covering a relatively wide range of pressure and temperature, including the low temperature region.

Materials and Experimental Procedure

Experimental Setup. There is a high number of techniques to determine the pvT properties for liquids.[2] In this study, the specific volume of the sample was obtained by directly measuring the volume changes as a function of temperature and pressure from a reference condition. The device used here may be classified as a variable-volume piezometer with a solid-piston volumometer (Figure 1). It was designed and constructed at the Institute of High Pressure Physics in Warsaw (Poland). It consisted of a cylindrical stainless steel sample holder closed by a brass piston (24 mm internal diameter, 18 mL max. capacity). A rod, ended by a ferromagnetic core, was screwed to the piston and introduced inside a capillary tube. Volume changes of the liquid sample moved the piston and were thus transferred to the ferromagnetic core. The movement of this ferromagnetic core was detected by changes in the voltages induced in the solenoidal coils located around the capillary tube (linear variable differential transformer (LVDT), Peltron. Ldt. System, Poland). An O-ring in a groove around the piston ensured good tightness as well as low friction (nominal squeeze

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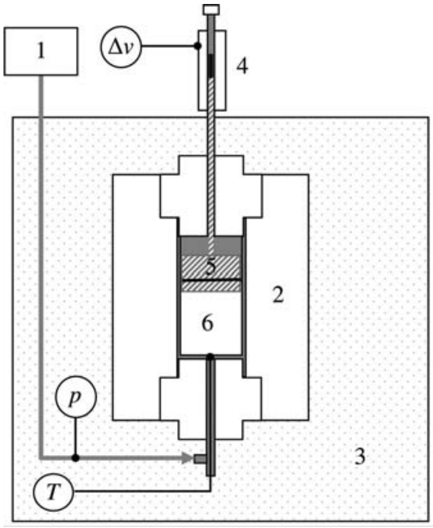

Figure 1. Volumetric device: 1, high pressure hydraulic pump; 2, high pressure vessel; 3, thermostatic bath; 4, LVDT; 5, solid piston; 6, sample.

10 %). Both the sample holder and the LVDT system were mounted on the upper plug of a high pressure vessel. Silicone oil was used as the pressure transmitting fluid. Any pressure gradient between the sample and the outside was prevented as the piezometer and the solid-piston volumometer were surrounded by this fluid. The working interval was (0.1 to 350) MPa for pressure and (253.15 to 323.15) K for temperature. The high pressure vessel and its connection to the hydraulic pump (high pressure pump 700 MPa type U111, Poland) were immersed in a water or ethanol bath (for high or for low temperatures, respectively). A full description of the high pressure equipment has already been given elsewhere.[6] The temperature of the bath was regulated by a cryostat (Haake K, Karlsruhe, Germany). A T-type thermocouple in contact with the bottom part of the sample holder allowed for checking temperature stability during experiments. The temperature stability achieved with this cryostat was better than 0.05 K. The pressure was measured in the capillary connection with the vessel by a strain gauge transducer (type EBM 6045 V-0-10 GmbH, KGT Kramer, Dortmund, Germany). The temperature, pressure, and position of the piston were recorded every 0.5 s by using a data acquisition system (DC100 Data Collector Yokogawa, Tokyo, Japan). The uncertainties of these measurements are given in the Results and Discussion section.

Procedure. The cylindrical sample holder was filled with about 17 mL of deionized water type I (Millipore, Billerica, MA, USA) and closed by the solid piston. The greatest part of air enclosed was evacuated by opening a screw designed for that purpose at the bottom of the sample holder and by pressing the piston until water went out. The remaining air was degassed by heating. The bleed screw was then closed and the sample let cool down. The sample holder was weighed (the tare being made before filling with water). The rod was screwed to the piston and introduced inside the volumometer capillary tube. The sample holder was screwed to the high-pressure upper plug. This assembly was placed in the vessel, and the upper plug was screwed to close the vessel; the vessel was immersed in the thermostatic bath. It took roughly between half an hour to two hours to bring the sample to the required temperature. Then pressure was slowly increased to 70 MPa, then to 100 MPa, and then by 50 MPa steps up to 350 MPa. The sample temperature was let equilibrate during around ten minutes between each pressure increase. This waiting time was necessary to dissipate the adiabatic heat generated during compression; it had been previously determined by observing the temperature evolution at the sample holder center during an independent similar experiment in which the volumometer was substituted by a thermocouple. The measurements taken during 1 min after temperature equilibration at each pressure were averaged to obtain the final result. The repeatability found between these measurements (p, T, position of piston) was about $\pm$ 0.04 K for temperature, $\pm$ 0.7 MPa for pressure, and $\pm 1 \cdot 10^{-5}$ m (i.e., $\pm 3 \cdot 10^{-7}\ \mathrm{m^3 \cdot kg^{-1}}$) for piston position. When 350 MPa was reached, the pressure was released, and the cell was reweighed to check that there was neither leak of sample nor contamination of it with the pressure transmitting fluid. The complete procedure was repeated at least three times at each temperature.

The specific volume at pressure p was:

$$v(p) = v_{\mathrm{ref}} + \Delta v(p) \tag{1}$$

where v_{ref} is the specific volume of the sample at the reference conditions (atmospheric pressure at temperatures above 273 K and high pressure at temperatures below 273 K). v_{ref} is calculated at the temperature of measurement with the International Scientific Standard equation of state from the International Association for the Properties of Water and Steam, called IAPWS-95 formulation;[1] $\Delta v(p)$ is the sample specific volume change due to the pressure increase:

$$\Delta v(p) = \frac{k \cdot (U_0 - U(p)) \cdot \pi \cdot r^2}{m} \tag{2}$$

where k is the constant of calibration of the LVDT, U_0 and $U(p)$ are respectively the initial and final voltage, r is the radius of the sample holder, and m is the sample mass.

U_0 is the voltage value from which the volume changes have to be computed, but it is not exactly the initial voltage at atmospheric pressure. In fact, during the initial pressure build-up from atmospheric pressure to 2 MPa, there was an apparent volume reduction about 10 times higher than between 2 MPa and the successive pressures. This was attributed to air entrapped in the O-ring groove that could not be removed and to a slight deformation of the O-ring. This effect became negligible at pressures higher than 2 MPa (the volume of liquid was much higher than that of the compressed remaining air or of the O-ring and so were their respective volume changes). Thus, a method was developed to obtain the starting voltage value for volume change computation. An iterative algorithm was employed to determine U_0. It consisted in looking for the voltage above its initial value that gave the best correlation coefficient when representing the secant bulk modulus as a linear function of pressure, at pressures below 200 MPa. This is because water secant bulk modulus is known to vary linearly with pressure in this pressure range. This procedure for specific volume measurements was elaborated, taking into account Hayward's recommendations.[7]

When measurements were performed at temperatures below 273 K, the procedure described above was different: the sample was pressurized as soon as the vessel was immersed in the bath to avoid freezing. The initial pressure was chosen, according to the water phase diagram and melting curve,[1] in the liquid region (about (2 to 8) MPa higher than the melting pressure): 70 MPa at 268 K, 115 MPa at 263 K, 160 MPa at 258 K, and 200 MPa at 253 K. Thus, the specific volume at pressure p was determined from the specific volume of water calculated at that

Table 1. Uncertainty Budget on Temperature, Pressure, and Specific Volume Measurements at (69.1 and 349.4) MPa and for the Studied Temperature of 273 K

	standard uncertainties from random effects in the determination process		standard uncertainties from systematic effects in the determination process			
source of uncertainty[a]	type A evaluation	type B evaluation	type A evaluation	type B evaluation	combined standard uncertainty	expanded uncertainty[b]
			$p = 69.1$ MPa			
temperature					0.09 K	0.09 K
$u(T_s)$/K		0.003				
$u(T_{cal})$/K		0.09				
$u(T_{rep})$/K	0.004					
pressure					0.4 MPa	0.4 MPa
$u(p_s)$/MPa		0.03				
$u(p_{cal})$/MPa		0.4				
$u(p_{rep})$/MPa	0.06					
specific volume					$1.1 \cdot 10^{-7}$ m$^3 \cdot$kg^{-1}	$2.2 \cdot 10^{-7}$ m$^3 \cdot$kg^{-1}
$u(\upsilon_{ref})$/m$^3 \cdot$kg^{-1}				$0.5 \cdot 10^{-9}$		
$u_c(\Delta\upsilon)$/m$^3 \cdot$kg^{-1}			$7.16 \cdot 10^{-8}$			
$u(\upsilon_{uT})$/m$^3 \cdot$kg^{-1}				$2.31 \cdot 10^{-8}$		
$u(\upsilon_{up})$/m$^3 \cdot$kg^{-1}				$7.36 \cdot 10^{-8}$		
			$p = 349.4$ MPa			
temperature					0.09 K	0.09 K
$u(T_s)$/K		0.003				
$u(T_{cal})$/K		0.09				
$u(T_{rep})$/K	0.003					
pressure					1.7 MPa	1.7 MPa
$u(p_s)$/MPa		0.03				
$u(p_{cal})$/MPa		1.7				
$u(p_{rep})$/MPa	0.09					
specific volume					$3.0 \cdot 10^{-7}$ m$^3 \cdot$kg^{-1}	$6.0 \cdot 10^{-7}$ m$^3 \cdot$kg^{-1}
$u(\upsilon_{ref})$/m$^3 \cdot$kg^{-1}				$0.5 \cdot 10^{-9}$		
$u_c(\Delta\upsilon)$/m$^3 \cdot$kg^{-1}			$2.29 \cdot 10^{-7}$			
$u(\upsilon_{uT})$/m$^3 \cdot$kg^{-1}				$2.31 \cdot 10^{-8}$		
$u(\upsilon_{up})$/m$^3 \cdot$kg^{-1}				$1.95 \cdot 10^{-7}$		

[a] Subscripts meaning: s stands for sensor specification, cal stands for calibration, rep stands for repeatability, ref stands for reference, u*T* stands for uncertainty in temperature, u*p* stands for uncertainty in pressure. [b] Expanded uncertainty is given with a coverage factor of 1 for *p* and *T* (confidence level about 68 %) and of 2 for υ (confidence level about 95 %).

initial pressure and from the measured specific volume changes. The specific volume of water under pressure (υ_{ref}) at temperatures below 273 K was calculated in the same way than at atmospheric pressure and at temperatures above 273 K, that is to say, with the IAPWS-95 formulation.[1]

Calibrations. The thermocouple was calibrated with a DBC 150-TS temperature calibrator (Druck, Rho, Italy) ($T \geq 273.15$ K) or with a reference thermometer Pt100 (TESTO, model 735-2, Germany) ($T < 273.15$ K). The standard uncertainty of calibration was at most 0.09 K except at 253 K where it was 0.15 K. The pressure transducer was calibrated by the provider (KGT Kramer, Dortmund, Germany). Its relative uncertainty of calibration was 0.05 %.

The calibration of the high pressure piezometer consisted in two parts. First, the LVDT constant of calibration was determined. To do that, the upper plug of the high pressure vessel with the LVDT was placed on a support. Metal pieces of known thickness (measured with an electronic calliper) were used to change the piston position. The electric voltage observed at each piston position was recorded. Then, the slope of the straight line obtained when plotting piston position versus voltage gave the calibration constant *k*. Second, the correction related with the deformation of the volumetric device with pressure was determined. For that purpose, the volumetric device was used under pressure without any sample. The piston, bathed by the pressure transmitting fluid, was let at rest, free (without O-ring), at the bottom of the sample holder. Pressure was increased by 50 MPa steps, and the voltage from the LVDT was recorded at each pressure increase under constant temperature conditions of (253.15, 273.15, 293.15, and 313.15) K. The voltage ($U_{apparent}$) increased linearly with pressure due to the deformation of the volumetric device (piston could not float). These tests pointed out that the piston position changed but only apparently and thus that the volume changes were overestimated during the measurements with sample. For instance, there was an apparent volume change of $5.5 \cdot 10^{-8}$ m$^3 \cdot$kg^{-1} between (0.1 and 350) MPa. The following correlation was used to correct the recorded voltages and in this way to calibrate measurements as a function of pressure:

$$U_{real} = U_{apparent} - (0.000181 \cdot p/\text{MPa} + 0.000289) \tag{3}$$

Results and Discussion

Uncertainties of the Results. The combined standard uncertainties in the temperature and pressure were calculated, respectively, as follows:

$$u_c(T) = \sqrt{u^2(T_s) + u^2(T_{cal}) + u^2(T_{rep})} \tag{4}$$

$$u_c(p) = \sqrt{u^2(p_s) + u^2(p_{cal}) + u^2(p_{rep})} \tag{5}$$

The considered contributing terms were, in order of appearance, the uncertainty according to sensor specification, the uncertainty of calibration, and the uncertainty of repeatability. This gave at most $u_c(T) = 0.09$ K for temperatures above 253 K and $u_c(T) = 0.15$ at 253 K. Regarding pressure, the calculation gave $u_c(p) = 0.005 \cdot p$. An example of uncertainties calculation is given in

Table 1. Since it may be assumed that the possible estimated values of T and p are approximately normally distributed with the approximate standard deviation u_c, the unknown value of T and p are believed to lie in the defined intervals ($u_c(T)$ and $u_c(p)$) with a level of confidence of about 68 %.

The combined standard uncertainty in the specific volume was evaluated as follows:

$$u_c(v) = \sqrt{u^2(v_{\text{ref}}) + u_c^2(\Delta v) + u^2(v_{uT}) + u^2(v_{up})} \qquad (6)$$

where $u(v_{\text{ref}})$ is the uncertainty of the calculated initial specific volume of reference. $u_c(\Delta v)$ is the combined standard uncertainty in volume change measurements. $u(v_{uT})$ and $u(v_{up})$ are respectively the uncertainties in v due to the uncertainty in the temperature and in the pressure measurements.

The uncertainty $u(v_{\text{ref}})$ was estimated from the tolerance given by Wagner and Pruss[1] for the use of the IAPWS-95 formulation to calculate the initial specific volume of reference. It is 0.0001 % of v_{ref} at atmospheric pressure and 0.2 % of v_{ref} at temperatures below 273 K and at the selected experimental initial pressures. This tolerance is defined as the range of possible values that can take the density as judged by IAPWS, and it has no statistical significance.[1] At atmospheric pressure and temperatures above 273 K, Harvey et al.[8] have examined the compatibility of CIPM (International Committee for Weights and Measures) and IAPWS standards for water density. From this comparison, it appears that the tolerance given by Wagner and Pruss[1] is of the same order of magnitude than the expanded uncertainty (with coverage factor of 2) assigned to the CIPM standard. Thus, it can be considered that the uncertainty $u(v_{\text{ref}})$ is 0.00005 % of v_{ref} at atmospheric pressure. At high pressures and temperatures below 273 K, the relative deviation between the experimental data employed to fit the IAPWS-95 formulation and the values calculated from IAPWS-95 tend to increase with pressure up to 0.2 % for the isotherm 268 K (see ref 1, pp 446−447). At the reference conditions for v_{ref} calculation (i.e., 70 MPa at 268 K, 115 MPa at 263 K, 160 MPa at 258 K, and 200 MPa at 253 K), this deviation is below 0.1 %. Thus, it can be reasonably considered that the uncertainty $u(v_{\text{ref}})$ in the low temperature region is 0.1 % of v_{ref}.

The combined standard uncertainty of the volumetric device $u_c(\Delta v)$ was calculated according to the following formula and by using eq 2:

$$u_c(\Delta v) = \sqrt{\left(\frac{\partial(\Delta v)}{\partial k}\right)^2 \cdot u^2(k) + \left(\frac{\partial(\Delta v)}{\partial U_0}\right)^2 \cdot u^2(U_0) + \left(\frac{\partial(\Delta v)}{\partial U(p)}\right)^2 \cdot u^2(U(p)) + \left(\frac{\partial(\Delta v)}{\partial r}\right)^2 \cdot u^2(r) + \left(\frac{\partial(\Delta v)}{\partial m}\right)^2 \cdot u^2(m)} \qquad (7)$$

The evaluation of the uncertainties $u(k)$, $u(U_0)$, $u(U(p))$, $u(r)$, and $u(m)$ is detailed below.

The uncertainty in the determination of k was evaluated from three individual calibrations:

$$u(k) = \frac{\sigma_k}{\sqrt{3}} = 1.5 \cdot 10^{-6} \qquad (8)$$

where σ_k is the standard deviation between the three values obtained for k.

The uncertainty in the determination of U_0 was evaluated from the maximal interval ($a = 0.001$) separating two successively tested U_0 values according to the procedure explained in the previous section:

$$u(U_0) = \frac{a}{\sqrt{3}} = 0.06 \cdot 10^{-2} \qquad (9)$$

The uncertainty in the determination of $U(p)$ was evaluated from different contributions. One contribution comes from the LVDT voltage reading (manufacturer's specification $b = 0.001$), another from the maximal standard deviation ($\sigma_U = 0.005$) observed from 120 measurements under pressure (during 1 min every 0.5 s, repeatability), and another from the correction applied from eq 3 ($c = 0.000181$).

$$u(U(p)) = \sqrt{\left(\frac{b}{2\sqrt{3}}\right)^2 + \left(\frac{\sigma_U}{\sqrt{120}}\right)^2 + \left(\sqrt{c^2 \cdot u_c^2(p) + (p/\text{MPa})^2 \cdot u^2(c)}\right)^2} \qquad (10)$$

$u(c)$ was evaluated to be about 0.00001.

The uncertainty in the determination of r was evaluated by combining the uncertainty of the electronic calliper used to measure r at atmospheric pressure ($d = 0.01 \cdot 10^{-3}$) with the uncertainty (e) due to the compression of sample holder wall at the pressure p ($e = 0.0015p \cdot (1 - 2\mu)/E$, with $\mu = 0.272$ and $E = 197\,000$ MPa).

$$u(r) = \sqrt{\left(\frac{d}{2\sqrt{3}}\right)^2 + \left(\frac{e}{\sqrt{3}}\right)^2} \qquad (11)$$

The uncertainty in the determination of the mass sample was evaluated from uncertainty specification of the balance ($f = 0.00001$):

$$u(m) = \sqrt{\left(\frac{f}{2\sqrt{3}}\right)^2} \qquad (12)$$

Thus, the combined standard uncertainty of volume change $u_c(\Delta v)$ was:

$$u_c(\Delta v) = \frac{\pi r^2 k (U_0 - U(p))}{m} \times \sqrt{\frac{2.24 \cdot 10^{-12}}{k^2} + \frac{6.25 \cdot 10^{-7} + 10^{-10} \cdot (p/\text{MPa})^2}{(U_0 - U(p))^2} + \frac{3.33 \cdot 10^{-11} + 1.61 \cdot 10^{-17} \cdot (p/\text{MPa})^2}{r^2} + \frac{8.33 \cdot 10^{-12}}{m^2}} \qquad (13)$$

This gave at most $2.4 \cdot 10^{-7}$ $\text{m}^3 \cdot \text{kg}^{-1}$.

The uncertainty in the temperature measurement $u_c(T)$ can cause a change of v value of up to $dv_{uT} = 4.0 \cdot 10^{-8}$ $\text{m}^3 \cdot \text{kg}^{-1}$. The uncertainty in the pressure measurements $u_c(p)$ can cause a change of v value of up to $dv_{up} = (-3.13 \cdot 10^{-12} \cdot p^2/\text{MPa}^2 + 2.07 \cdot 10^{-9} \cdot p/\text{MPa})$ $\text{m}^3 \cdot \text{kg}^{-1}$. Thus, the corresponding uncertainty contributions are:

Table 2. Experimental Specific Volume Changes and Calculated Specific Volumes of Water above 273 K with Their Corresponding Combined Uncertainties

p / MPa	T / K	$\Delta v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(\Delta v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$	p / MPa	T / K	$\Delta v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(\Delta v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$
323 K											
0.1	323.29	0	0	1.01218	0.00002	198.3	323.34	−0.06759	0.00015	0.94463	0.00022
68.3	323.35	−0.02760	0.00007	0.98458	0.00010	248.7	323.04	−0.08047	0.00018	0.93175	0.00026
99.6	323.37	−0.03861	0.00008	0.97357	0.00013	298.4	323.26	−0.09196	0.00021	0.92026	0.00029
149.0	323.35	−0.05434	0.00011	0.95784	0.00018	349.0	323.21	−0.10269	0.00024	0.90953	0.00031
198.8	323.09	−0.06864	0.00014	0.94354	0.00022	0.1	323.31	0	0	1.01218	0.00002
249.0	323.17	−0.08147	0.00017	0.93071	0.00025	69.2	323.33	−0.02793	0.00007	0.98425	0.00010
299.1	323.18	−0.09308	0.00020	0.91910	0.00028	99.1	323.31	−0.03848	0.00008	0.97370	0.00013
349.3	323.34	−0.10368	0.00022	0.90850	0.00030	149.3	323.30	−0.05439	0.00011	0.95779	0.00018
0.1	323.38	0	0	1.01222	0.00002	199.0	323.28	−0.06836	0.00014	0.94382	0.00022
68.8	323.46	−0.02738	0.00007	0.98484	0.00010	248.9	323.25	−0.08096	0.00017	0.93122	0.00025
99.2	323.43	−0.03800	0.00009	0.97422	0.00013	299.2	323.13	−0.09257	0.00020	0.91961	0.00028
149.2	323.41	−0.05382	0.00012	0.95840	0.00018	349.4	323.17	−0.10310	0.00023	0.90908	0.00030
313 K											
0.1	313.20	0	0	1.00786	0.00002	199.2	313.40	−0.06918	0.00014	0.93872	0.00022
69.1	313.39	−0.02769	0.00007	0.98017	0.00010	249.2	313.46	−0.08185	0.00017	0.92605	0.00025
99.0	313.41	−0.03818	0.00009	0.96968	0.00013	299.7	313.48	−0.09344	0.00020	0.91446	0.00028
149.0	313.42	−0.05399	0.00011	0.95387	0.00018	348.9	313.44	−0.10376	0.00022	0.90414	0.00030
199.1	313.46	−0.06809	0.00014	0.93977	0.00022	0.1	313.35	0	0	1.00792	0.00002
248.9	313.45	−0.08065	0.00017	0.92721	0.00025	69.1	313.40	−0.02793	0.00007	0.97999	0.00010
299.6	313.44	−0.09225	0.00021	0.91561	0.00028	98.6	313.40	−0.03836	0.00008	0.96956	0.00013
349.3	313.38	−0.10269	0.00024	0.90517	0.00031	148.8	313.39	−0.05438	0.00011	0.95354	0.00018
0.1	313.30	0	0	1.00790	0.00002	198.9	313.42	−0.06855	0.00014	0.93937	0.00022
69.0	313.43	−0.02820	0.00007	0.97970	0.00010	249.3	313.43	−0.08130	0.00017	0.92662	0.00025
98.8	313.39	−0.03883	0.00008	0.96907	0.00013	299.4	313.45	−0.09274	0.00020	0.91518	0.00028
149.3	313.38	−0.05499	0.00011	0.95291	0.00018	349.5	313.46	−0.10322	0.00023	0.90470	0.00030
303 K											
0.1	303.43	0	0	1.00446	0.00002	198.8	303.57	−0.06897	0.00015	0.93551	0.00022
69.2	303.37	−0.02849	0.00007	0.97597	0.00010	248.8	303.57	−0.08171	0.00018	0.92277	0.00026
98.9	303.40	−0.03917	0.00009	0.96529	0.00013	299.1	303.55	−0.09330	0.00021	0.91118	0.00029
148.9	303.40	−0.05528	0.00011	0.94918	0.00018	349.2	303.63	−0.10387	0.00024	0.90061	0.00031
198.9	303.41	−0.06955	0.00014	0.93491	0.00022	0.1	303.41	0	0	1.00445	0.00002
248.9	303.43	−0.08229	0.00017	0.92217	0.00025	69.8	303.42	−0.02852	0.00007	0.97593	0.00010
299.1	303.49	−0.09384	0.00020	0.91062	0.00028	98.5	303.35	−0.03879	0.00008	0.96566	0.00013
349.3	303.52	−0.10435	0.00023	0.90011	0.00030	149.0	303.48	−0.05505	0.00011	0.94940	0.00018
0.1	303.51	0	0	1.00448	0.00002	199.0	303.56	−0.06927	0.00014	0.93518	0.00022
68.9	303.42	−0.02822	0.00007	0.97626	0.00011	249.3	303.57	−0.08207	0.00017	0.92238	0.00025
99.2	303.48	−0.03894	0.00009	0.96554	0.00014	299.2	303.61	−0.09351	0.00020	0.91094	0.00028
149.1	303.51	−0.05487	0.00012	0.94961	0.00018	349.1	303.72	−0.10397	0.00023	0.90048	0.00030
293 K											
0.1	293.55	0	0	1.00188	0.00002	199.0	293.25	−0.06914	0.00014	0.93186	0.00022
69.2	293.60	−0.02839	0.00007	0.97349	0.00011	249.0	293.20	−0.08192	0.00017	0.91908	0.00025
99.2	293.47	−0.03912	0.00009	0.96276	0.00014	299.0	293.22	−0.09344	0.00020	0.90756	0.00028
148.8	293.49	−0.05509	0.00012	0.94679	0.00018	349.3	293.34	−0.10390	0.00023	0.89710	0.00030
199.1	293.46	−0.06940	0.00015	0.93248	0.00022	0.1	293.53	0	0	1.00188	0.00002
248.9	293.52	−0.08207	0.00018	0.91981	0.00026	68.9	293.42	−0.02870	0.00007	0.97318	0.00010
299.0	293.54	−0.09363	0.00021	0.90825	0.00029	99.1	293.40	−0.03960	0.00009	0.96228	0.00013
349.2	293.53	−0.10427	0.00024	0.89761	0.00031	149.1	293.41	−0.05578	0.00011	0.94610	0.00018
0.1	293.50	0	0	1.00100	0.00002	199.4	293.39	−0.07011	0.00014	0.93177	0.00022
69.3	293.35	−0.02794	0.00007	0.97306	0.00010	249.0	293.38	−0.08274	0.00017	0.91914	0.00025
99.3	293.28	−0.03881	0.00008	0.96219	0.00013	299.4	293.38	−0.09429	0.00020	0.90759	0.00028
149.2	293.23	−0.05494	0.00011	0.94606	0.00018	349.2	293.31	−0.10467	0.00023	0.89721	0.00030
283 K											
0.1	283.55	0	0	1.00033	0.00002	198.9	283.53	−0.07205	0.00014	0.92827	0.00022
69.0	283.54	−0.02973	0.00007	0.97060	0.00010	249.1	283.54	−0.08523	0.00017	0.91509	0.00025
98.9	283.51	−0.04089	0.00009	0.95944	0.00013	299.3	283.56	−0.09685	0.00020	0.90347	0.00028
148.8	283.52	−0.05739	0.00011	0.94294	0.00018	349.3	283.62	−0.10739	0.00023	0.89293	0.00030
199.0	283.47	−0.07198	0.00014	0.92835	0.00022	0.1	283.46	0	0	1.00033	0.00002
248.9	283.50	−0.08481	0.00017	0.91552	0.00025	69.0	283.36	−0.02964	0.00007	0.97069	0.00010
299.0	283.60	−0.09627	0.00020	0.90406	0.00028	99.0	283.70	−0.04083	0.00008	0.95950	0.00013
348.0	283.72	−0.10595	0.00023	0.89438	0.00030	149.1	283.48	−0.05751	0.00011	0.94282	0.00018
0.1	283.38	0	0	1.00032	0.00002	199.0	283.33	−0.07207	0.00014	0.92826	0.00022
69.2	283.50	−0.02981	0.00007	0.97051	0.00010	249.0	283.43	−0.08501	0.00017	0.91532	0.00025
99.0	283.51	−0.04098	0.00009	0.95934	0.00013	298.7	283.39	−0.09657	0.00020	0.90376	0.00028
149.3	283.49	−0.05773	0.00012	0.94259	0.00018	349.1	283.43	−0.10722	0.00023	0.89311	0.00030
273 K											
0.1	273.60	0	0	1.00013	0.00002	199.0	273.67	−0.07467	0.00014	0.92547	0.00022
69.1	273.52	−0.03168	0.00007	0.96845	0.00011	249.3	273.63	−0.08790	0.00017	0.91224	0.00026
99.1	273.53	−0.04344	0.00009	0.95669	0.00014	298.9	273.74	−0.09957	0.00020	0.90057	0.00028
149.0	273.52	−0.06070	0.00012	0.93943	0.00018	350.4	273.82	−0.11060	0.00024	0.88954	0.00031
198.9	273.55	−0.07570	0.00014	0.92443	0.00022	0.1	273.62	0	0	1.00013	0.00002
248.9	273.52	−0.08896	0.00017	0.91117	0.00025	69.1	273.32	−0.03127	0.00007	0.96886	0.00010
298.8	273.38	−0.10074	0.00020	0.89939	0.00028	99.3	273.46	−0.04300	0.00009	0.95713	0.00013
349.4	273.40	−0.11223	0.00023	0.88790	0.00030	149.1	273.44	−0.06010	0.00012	0.94003	0.00018
0.1	273.50	0	0	1.00014	0.00002	199.0	273.51	−0.07500	0.00015	0.92513	0.00022
69.1	273.48	−0.03102	0.00007	0.96912	0.00010	249.1	273.57	−0.08820	0.00018	0.91193	0.00026
98.6	273.56	−0.04249	0.00009	0.95765	0.00013	298.9	273.65	−0.09995	0.00021	0.90018	0.00028
149.1	273.57	−0.05983	0.00011	0.94031	0.00018	348.8	273.68	−0.11095	0.00024	0.88918	0.00031

Table 3. Experimental Specific Volume Changes and Calculated Specific Volumes of Water below 273 K with Their Corresponding Combined Uncertainties[a]

p / MPa	T / K	$\Delta v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(\Delta v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$	p / MPa	T / K	$\Delta v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(\Delta v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$v \cdot 10^3$ / $m^3 \cdot kg^{-1}$	$u_c(v) \cdot 10^3$ / $m^3 \cdot kg^{-1}$
					268 K						
69.6	268.30	0	0	0.96794	0.00097	249.1	268.51	−0.05861	0.00017	0.90988	0.00100
99.5	268.42	−0.01185	0.00008	0.95609	0.00098	298.4	268.48	−0.07052	0.00020	0.89797	0.00101
149.2	268.47	−0.02924	0.00011	0.93870	0.00098	348.9	268.47	−0.08149	0.00023	0.88700	0.00101
198.8	268.51	−0.04431	0.00014	0.92363	0.00099	70.0	268.78	0	0	0.96782	0.00097
249.0	268.52	−0.05801	0.00017	0.90993	0.00100	99.8	268.58	−0.01185	0.00008	0.95597	0.00098
298.9	268.55	−0.07015	0.00020	0.89779	0.00101	149.7	268.51	−0.02936	0.00011	0.93846	0.00098
348.9	268.60	−0.08108	0.00023	0.88686	0.00101	199.3	268.48	−0.04450	0.00014	0.92332	0.00099
68.4	268.60	0	0	0.96849	0.00097	248.7	268.47	−0.05807	0.00017	0.90975	0.00100
99.4	268.55	−0.01237	0.00008	0.95612	0.00098	300.2	268.47	−0.07059	0.00021	0.89723	0.00101
149.7	268.52	−0.03002	0.00011	0.93847	0.00098	349.1	268.48	−0.08149	0.00024	0.88633	0.00102
198.4	268.52	−0.04487	0.00013	0.92362	0.00099						
					263 K						
114.2	263.57	0	0	0.94972	0.00096	248.8	263.61	−0.04148	0.00017	0.90814	0.00098
149.5	263.62	−0.01225	0.00010	0.93747	0.00097	299.1	263.51	−0.05394	0.00020	0.89568	0.00099
198.4	263.65	−0.02746	0.00013	0.92226	0.00097	350.0	263.52	−0.06534	0.00023	0.88428	0.00100
249.8	263.60	−0.04153	0.00016	0.90819	0.00098	114.2	263.85	0	0	0.94976	0.00096
298.9	263.58	−0.05357	0.00020	0.89615	0.00099	149.2	263.75	−0.01237	0.00010	0.93739	0.00097
349.1	263.69	−0.06456	0.00023	0.88516	0.00100	198.6	263.69	−0.02771	0.00013	0.92205	0.00097
114.5	263.77	0	0	0.94962	0.00096	248.8	263.64	−0.04154	0.00016	0.90822	0.00098
149.4	263.69	−0.01229	0.00011	0.93733	0.00097	298.0	263.64	−0.05361	0.00020	0.89615	0.00099
198.7	263.64	−0.02762	0.00014	0.92200	0.00097	349.9	263.64	−0.06518	0.00023	0.88458	0.00100
					258 K						
159.6	258.62	0	0	0.93291	0.00094	273.3	258.60	−0.03328	0.00019	0.89995	0.00097
174.1	258.58	−0.00466	0.00012	0.92825	0.00095	299.2	258.61	−0.03963	0.00021	0.89360	0.00098
199.3	258.59	−0.01237	0.00014	0.92054	0.00096	323.4	258.60	−0.04517	0.00022	0.88806	0.00098
225.0	258.55	−0.01979	0.00015	0.91312	0.00096	349.5	258.58	−0.05096	0.00024	0.88227	0.00098
249.3	258.54	−0.02642	0.00017	0.90649	0.00097	158.5	258.37	0	0	0.93324	0.00094
275.3	258.53	−0.03304	0.00019	0.89987	0.00097	174.0	258.40	−0.00501	0.00011	0.92823	0.00095
298.5	258.54	−0.03863	0.00020	0.89428	0.00097	198.4	258.37	−0.01242	0.00013	0.92082	0.00096
323.3	258.52	−0.04437	0.00022	0.88854	0.00098	223.3	258.41	−0.01970	0.00014	0.91354	0.00096
348.9	258.46	−0.05004	0.00023	0.88287	0.00098	248.4	258.37	−0.02658	0.00016	0.90666	0.00096
158.7	258.73	0	0	0.93323	0.00094	274.9	258.38	−0.03321	0.00017	0.90003	0.00097
173.5	258.68	−0.00479	0.00012	0.92844	0.00095	299.6	258.45	−0.03912	0.00019	0.89412	0.00097
198.4	258.66	−0.01251	0.00014	0.92072	0.00096	324.1	258.52	−0.04453	0.00020	0.88871	0.00098
223.3	258.64	−0.01983	0.00016	0.91340	0.00096	348.8	258.60	−0.04960	0.00022	0.88364	0.00098
248.5	258.64	−0.02680	0.00017	0.90643	0.00097						
					253 K						
199.8	253.57	0	0	0.91938	0.00093	199.7	253.61	0	0	0.91942	0.00093
223.6	253.58	−0.00696	0.00014	0.91242	0.00095	223.7	253.58	−0.00694	0.00014	0.91248	0.00095
248.3	*253.64*	*−0.01376*	*0.00016*	*0.90562*	*0.00095*	*249.4*	*253.60*	*−0.01397*	*0.00016*	*0.90545*	*0.00095*
273.3	*253.68*	*−0.02036*	*0.00017*	*0.89902*	*0.00096*	*273.6*	*253.58*	*−0.02019*	*0.00017*	*0.89923*	*0.00096*
299.6	*253.65*	*−0.02682*	*0.00019*	*0.89256*	*0.00096*	*298.2*	*253.56*	*−0.02618*	*0.00019*	*0.89324*	*0.00096*
325.3	*253.69*	*−0.03261*	*0.00021*	*0.88677*	*0.00096*	*323.5*	*253.58*	*−0.03194*	*0.00020*	*0.88748*	*0.00096*
349.8	*253.67*	*−0.03786*	*0.00022*	*0.88152*	*0.00097*	*349.1*	*253.63*	*−0.03760*	*0.00022*	*0.88182*	*0.00097*
200.3	253.92	0	0	0.91929	0.00093	199.0	253.59	0	0	0.91963	0.00093
223.6	253.90	−0.00677	0.00015	0.91252	0.00095	223.7	253.64	−0.00710	0.00014	0.91253	0.00095
248.6	*253.87*	*−0.01364*	*0.00016*	*0.90565*	*0.00095*	*248.9*	*253.61*	*−0.01402*	*0.00016*	*0.90561*	*0.00095*
273.4	*253.86*	*−0.02014*	*0.00018*	*0.89915*	*0.00096*	*273.3*	*253.58*	*−0.02028*	*0.00017*	*0.89935*	*0.00096*
298.2	*253.86*	*−0.02602*	*0.00019*	*0.89327*	*0.00096*	*298.4*	*253.60*	*−0.02627*	*0.00019*	*0.89336*	*0.00096*
323.3	*253.83*	*−0.03175*	*0.00021*	*0.88754*	*0.00096*	*325.3*	*253.56*	*−0.03238*	*0.00021*	*0.88725*	*0.00096*
349.5	*253.83*	*−0.03750*	*0.00023*	*0.88179*	*0.00097*	*349.8*	*253.56*	*−0.03770*	*0.00022*	*0.88193*	*0.00097*

[a] Values in italics are for the measurements performed in the metastable liquid region at 253 K.

$$u(v_T) = \frac{dv_{uT}}{\sqrt{3}} \quad \text{and} \quad u(v_p) = \frac{dv_{up}}{\sqrt{3}} \qquad (14)$$

Finally, taking into account all of the uncertainty components, the combined standard uncertainty in the specific volume measurements as a function of pressure was:

For $T \geq 273$ K,

$$u_c(v) = \sqrt{\begin{array}{c}(5 \cdot 10^{-8} \cdot v_{ref})^2 + u_c^{\,2}(\Delta v) + (2.3 \cdot 10^{-8})^2 + \\ (-1.81 \cdot 10^{-12} \cdot p^2 + 1.19 \cdot 10^{-9} \cdot p)^2\end{array}} \qquad (15)$$

For $T < 273$ K,

$$u_c(v) = \sqrt{\begin{array}{c}(1 \cdot 10^{-3} \cdot v_{ref})^2 + u_c^{\,2}(\Delta v) + (2.3 \cdot 10^{-8})^2 + \\ (-1.81 \cdot 10^{-12} \cdot p^2 + 1.19 \cdot 10^{-9} \cdot p)^2\end{array}} \qquad (16)$$

This gave a relative standard uncertainty between (0.01 and 0.03) % at temperatures above 273 K and around 0.1 % below 273 K. In Table 1, an example of the calculations is shown at 273 K at the lowest and at the highest studied pressure. The relative expanded uncertainty for the specific volume at high pressure was calculated with a coverage factor of 2. Then it was comprised between (0.02

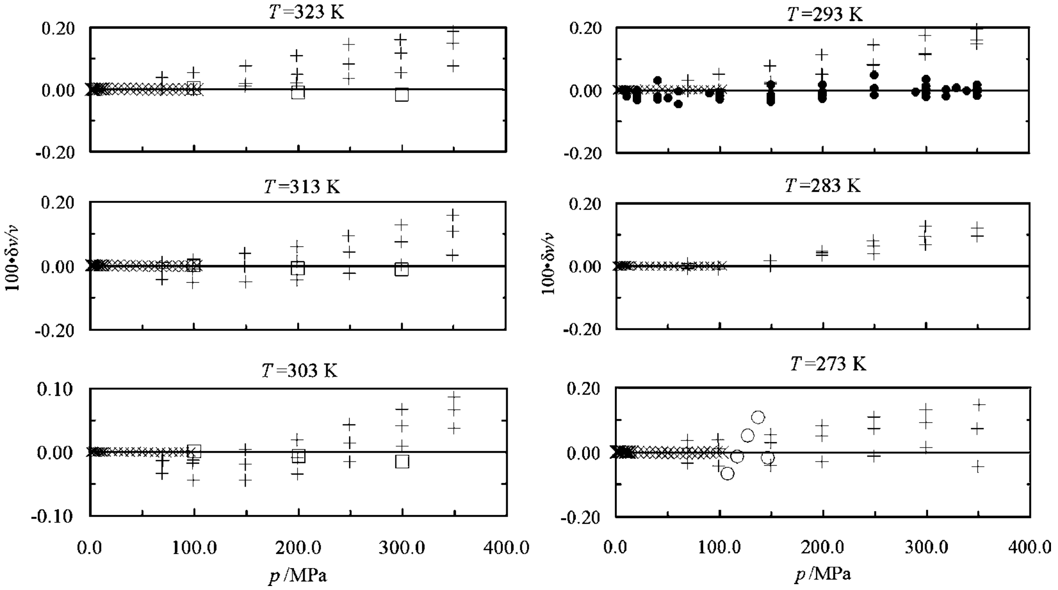

Figure 2. Relative deviations $\delta v = v(\text{expt}) - v(\text{calc})$ of the experimental specific volume v(expt) at different temperatures from values v(calc) calculated using the IAPWS-95 formulation, as a function of pressure at 273 K and above. +, this work; ×, Kell and Whalley, ref 4; ○, Tammann and Jellinghaus, ref 11; ●, Hilbert et al., ref 9; □, Grindley and Lind, ref 5.

and 0.07) % at temperatures above 273 K and around 0.2 % below 273 K. Since it can be assumed that the possible estimated values of v are approximately normally distributed with approximate standard deviation u_c, the unknown value of v is believed to lie in the intervals defined ($2u_c$) with a level of confidence of about 95 %.

Comparison with Previous Investigations. The specific volume of degassed pure water was determined at (253, 258, 263, 268, 273, 283, 293, 303, 313, and 323) K as a function of pressure. The corresponding results are shown in Table 2 for temperatures above and equal to 273 K and in Table 3 for temperatures below 273 K. The experimental data from Kell and Whalley,[4] from Grindley and Lind,[5] from Hilbert et al.,[9] from Bridgman,[10] and from Tammann and Jellinghaus[11] were selected for comparison with the data of Tables 2 and 3 among the different available sources, as they are commonly recognized as accurate. The International Association for the Properties of Water and Steam used these data among others to develop the international scientific standard equation of state for water, called the IAPWS-95 Formulation.[1] These data were also available from the web of IAPWS http://www.iapws.org/ in the “Main Thermodynamic Formulations” section. The relative deviation between the experimental data and the calculated values with the IAPWS-95 equation of state are plotted as a function of pressure at each studied temperature in Figure 2 for temperatures above 273 K and in Figure 3 for temperatures below 273 K. Data obtained for liquid water in metastable state, that is, at 253 K above 244 MPa, were also included. The usual proofs of ice nucleation (sudden volume and temperature change, pressure instability) were not observed. Moreover, ice III nucleation would have required lower supercooling temperatures than 253 K.[12] Thus, it is believed that water stayed in the liquid state during measurements in that region. The relative deviations between our data and the calculated values are from (−0.05 to 0.2) % at temperatures above 273 K and from (−0.14 to 0.04) % below 273 K. The relative deviations tend to increase with pressure, and the highest relative deviations are usually observed at (300 to 350) MPa. However, this tendency is not systematic; it depends on the considered temperature (see for instance data at (303, 273, or 268) K). The experimental data are in agreement with the selected experimental data from the literature, taking into account their respective experimental relative uncertainties and keeping in mind that the data sets do not exactly correspond to the same temperature (maximal difference between the near-isothermal sets is 0.8 K).

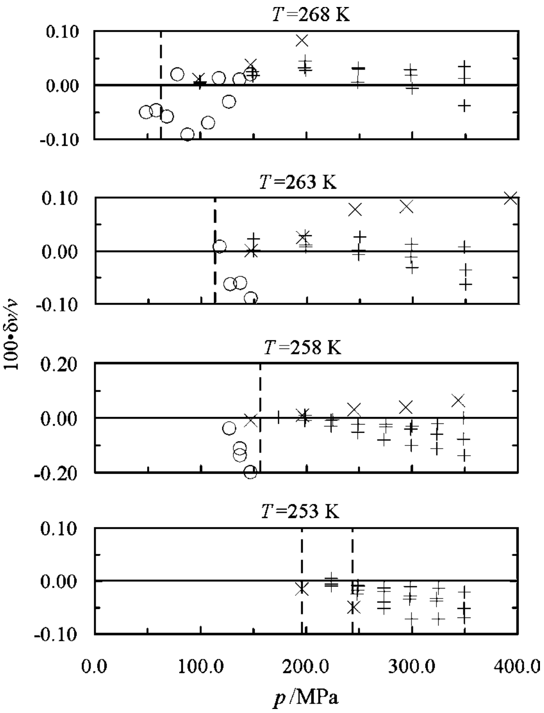

Figure 3. Relative deviations $\delta v = v(\text{expt}) - v(\text{calc})$ of the experimental specific volume v(expt) at different temperatures from values v(calc) calculated using the IAPWS-95 formulation, as a function of pressure below 273 K. Vertical dotted lines indicate the phase boundary. At 253 K, data above 240 MPa correspond to measurements performed in the metastable region of liquid−ice III. a. 268 K: +, this work; ×, Bridgman, ref 10; ○, Tammann and Jellinghaus, ref 11. b. 263 K: +, this work; ×, Bridgman, ref 10; ○, Tammann and Jellinghaus, ref 11. c. 258 K: +, this work; ×, Bridgman, ref 10; ○, Tammann and Jellinghaus, ref 11. d. 253 K: +, this work; ×, Bridgman, ref 10.

Conclusions

For 273 K and higher temperatures, the volumetric device presented in this work allowed for the determination of the specific volume with a relative expanded uncertainty from 0.02 % at 70 MPa to 0.07 % at 350 MPa (the coverage factor is 2, and the confidence level is about 95 %). Below 273 K, the relative expanded uncertainty was about 0.2 %. A new set of specific volume data at a temperature range from (253 to 323) K and for pressures up to 350 MPa is now available. These data represent a valuable contribution to the thermodynamic properties of liquid water for temperatures below 323 K and, in particular, below 273 K.

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