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THE SPECIFIC VOLUME OF WATER IN THE RANGE 1000 TO 8900 BARS, 20° TO 900°C*

C. WAYNE BURNHAM, J. R. HOLLOWAY, and N. F. DAVIS

Department of Geochemistry and Mineralogy,
The Pennsylvania State University, University Park, Pennsylvania 16802

ABSTRACT. More than 1000 determinations have been made of the specific volume of water in the temperature range 20° to 925°C, at pressures up to 8500 bars. They were made in two interconnected argon-pressurized vessels, one of which was equipped with an internal heater. Water pressure within the volumometer system was balanced exactly by external argon pressure through use of a bellows as part of the volumometer system, thereby eliminating the uncertainty in volume associated with deformation of metals at high non-hydrostatic pressures.

The data, in terms of specific volume ($\bar{V}$) as a function of pressure and temperature, were fitted throughout most of the P-T region by a ninth degree polynomial in $P\bar{V}$ as a function of T and P. The data in the low pressure-high temperature region were fitted better by an eighth degree polynomial in $P\bar{V}$ as a function of T and 1/P. The overall fit of these equations, which were used to generate tables of specific volume on orthogonal coordinates from 1000 to 8900 bars and from 20° to 900°C, is within 0.1 percent (one standard deviation).

Comparisons reveal very good agreement with the work of Bridgman (1935) at high pressures and low temperatures and with the International Skeleton Tables (Bain, 1964) at 1000 bars and high temperatures. At higher pressures and elevated temperatures, however, previously published specific volumes generally are smaller than those presented here by amounts that increase with pressure. Most of these discrepancies probably are due to errors in corrections required, inherent in previous methods, for the deformational effects of high non-hydrostatic stresses on the water containers, especially at elevated temperatures.

INTRODUCTION

Extensive work has been done on the P-V-T properties of water up to 1400 bars pressure, but at the time this study was undertaken, very few reliable data had been obtained by static methods at higher pressures and temperatures in excess of 100°C. The need for these data at high temperatures and pressures has become increasingly apparent to those involved in research in several disciplines, especially to those working on the chemistry of aqueous solutions. Moreover, the availability of P-V-T data for water makes it experimentally feasible to determine the P-V-T properties of many substances by replacing part of the water in the P-V-T cell with the substance to be investigated, sealed in a flexible-walled container.

The specific volumes of water presented in table 1 were obtained entirely from the present investigation, except for those at 1000 bars. Data in the pressure region below 1000 bars were not included in table 1 because of: (1) incomplete coverage at higher temperatures, (2) the fact that more accurate data could be obtained at these low pressures by other methods, and (3) the ready availability of reliable data up to 1000 bars in the Natl. Engineering Lab. Steam Tables 1964 (Bain, 1964). An upper limit of 8500 bars was set as a precaution against damage to the

* Contribution No. 67-82, College of Earth and Mineral Sciences, The Pennsylvania State University, University Park, Pennsylvania 16802. The study was aided by a grant from the Office of Saline Water, U. S. Department of the Interior.

volumometer system that might result from the freezing of water in the bellows assembly.

The data in table 1, combined with those in the Natl. Engineering Lab. Steam Tables 1964, have been used to calculate values for the Gibbs free energy, entropy, enthalpy, fugacity, and fugacity coefficient of water at 20° intervals from 20°C to 1000° and 100 bar intervals from 1 bar to 10,000 bars. Tables of these thermodynamic properties are too extensive for inclusion here and therefore will be published elsewhere.

EXPERIMENTAL APPARATUS

Pressure system.—The pressure apparatus consists essentially of two interconnected pressure vessels plus auxiliary pressure generating and measuring equipment. Both vessels are essentially similar in design to that shown in figure 1. Thick-walled cylinders (30.5 cm OD by 5.1 cm ID) were fabricated from vacuum-melted (CVM) steel (modified SAE-4340) and heat treated to Rockwell C-40 to 42 in hardness. After final machining following heat treatment, the vessels were wrapped tightly with copper tubing (square cross-section), as shown in figure 1, through which coolant water could be circulated.

The bore of each vessel is sealed near the ends by closure plugs, through which fluids, electric power, and sheathed thermocouples enter the pressure chamber. The special feature of these closure plugs is the double O-ring seal, in which two rubber O-rings of different size seal against different diameters of a hardened steel collar. The collar is free to move and thereby exert a differential force on the larger of the O-rings that is proportional to the pressure in the vessel. In the absence of this differential force, which maintains radial pressure of the O-ring against the cylinder wall regardless of hydrostatic pressure, very high hydrostatic pressures would cause the O-ring to shrink away from the cylinder wall and allow gas to blow by. Both O-rings are confined by mild-steel anti-extrusion rings. In addition, the inner O-ring is supported by a lead washer which is sufficiently fluid to assume the sealing function at pressures where the O-ring shrinks enough to allow blow-by.

The vessels were pressurized by a two-stage pressure generating system which utilizes argon from commercial cylinder supplies. The first-stage intensifier (Hardwood, Model SA10-10-1.875B-50K) receives argon from the cylinder supply and compresses it hydraulically into both the second-stage intensifier (Hardwood, Model SA10-6-.875-200K) and the pressure vessels, to pressures of about 3000 bars. The second-stage intensifier is capable of further compressing the argon into the vessels to pressures of 13,000 bars, well beyond those covered in this investigation. Once the desired pressure was reached, the vessels were isolated from the second-stage intensifier by a valve that was especially designed to provide leak-free service with high-pressure gases over long periods of time.

Pressures in the interconnected vessels were measured with the aid of a manganin cell (Hardwood Secondary Pressure Standard No. 1038) connected to a Carey-Foster bridge (Hardwood No. 1027). They also

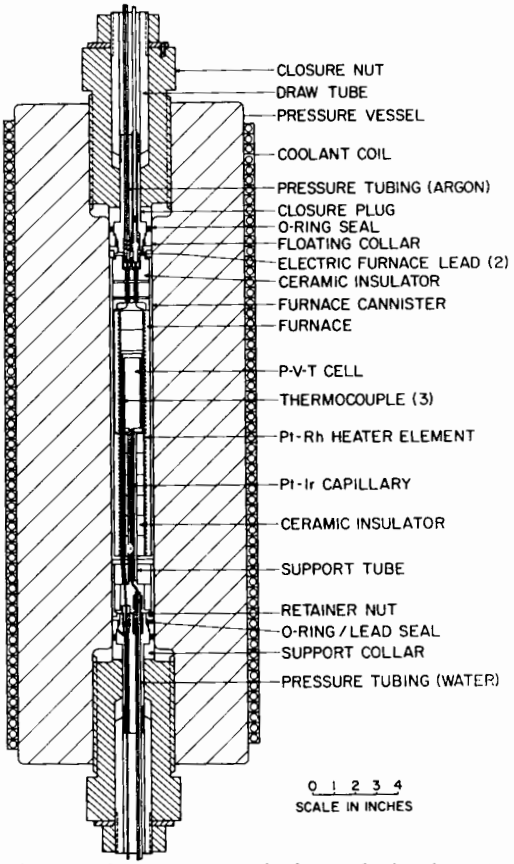

Fig. 1. Internally heated, argon-pressurized vessel showing placement of P-V-T cell in dual-zone furnace. The pressure vessel that contains the bellows and differential transformer is essentially similar in design.

were continuously monitored by another manganin cell connected to a Foxboro Dynalog resistance recorder.

Volumometer system.—The volumometer system consists of the P-V-T cell and interconnected bellows assembly as shown in figure 2. Together, they form a closed system of fixed water content. The cell (PVTC in fig. 2) is a cylinder, approximately 2.9 cm in outside diameter, 2.0 cm inside diameter, and 7.8 cm in overall length, fabricated from Inconel 600 alloy (73.3Ni–15.9Cr–7.65Fe–2.45Nb). The internal volume of the cell at 22°C, 1 bar, is 15.751 cm^3 as determined by numerous refillings and weighings. The wall of the cell contains three thermocouple wells drilled longitudinally to within 0.4 cm of the upper end.

The cell is connected to the rest of the volumometer system by about 27 cm of 0.010 cm-bore capillary tubing made of platinum (90 percent)-iridium (10 percent) alloy. One end of this capillary tube is soldered, with a gold-platinum alloy, into a hole drilled through the bottom of the

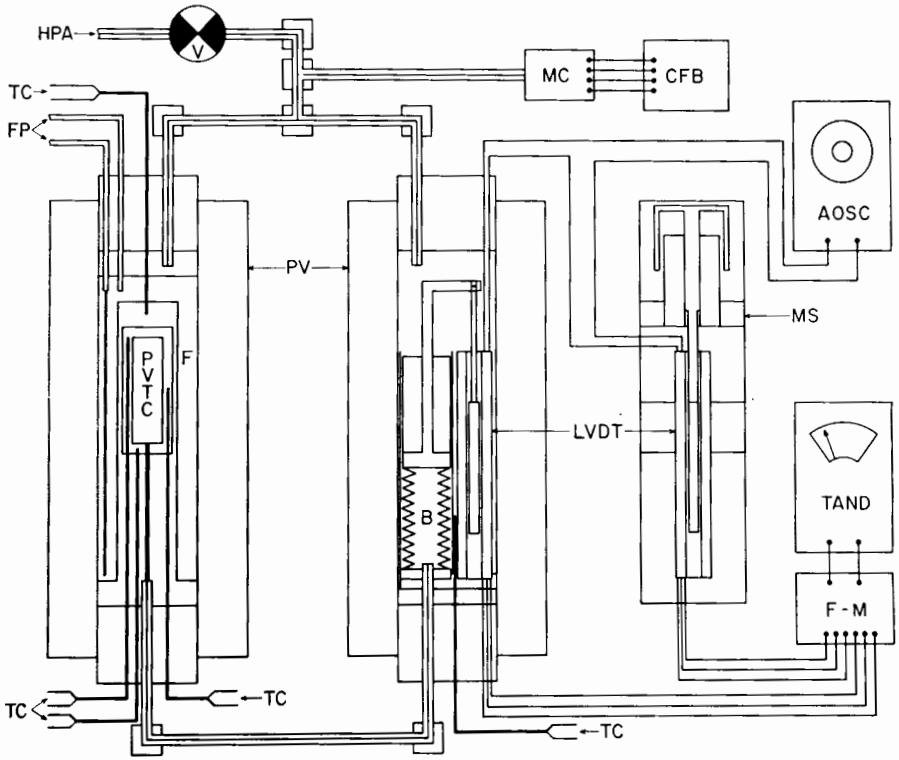

Fig. 2. Schematic diagram of the P-V-T apparatus. AOSC = Audio oscillator, B = bellows, CFB = Carey-Foster bridge, F = furnace, F-M = filter and mixer, FP = furnace-power leads, HPA = high-pressure argon, LVDT = linear variable differential transformer, MC = manganin cell, MS = micrometer stand, PV = pressure vessel, PVTC = P-V-T cell, TAND = tuned amplifier and null detector, TC = thermocouple, and V = valve.

cell; the other end is connected to stainless-steel high-pressure tubing (0.064 cm bore) by a conventional cone-type fitting. The stainless steel tubing passes out through the lower closure plug of the vessel on the left in figure 2, across and into the other pressure vessel through its lower closure plug, where it is connected by a cone-in-cone fitting to the termination of a bellows (B, fig. 2).

The bellows, fabricated from Type 347 stainless steel, is of the nesting-ripple design and all-welded construction. It is 2.54 cm in outside diameter, 1.26 cm in mean inside diameter, and has a stroke length of 5.2 cm. The maximum working discharge, therefore, is about 14.2 cm^3, but only the central 11.4 cm^3 of it actually was used. The nesting-ripple design of bellows convolution was selected because it provides a very long stroke per unit of over-all length, despite the fact that pressure may cause greater non-linearity in volume discharge versus stroke than is found in some other forms of bellows.

Displacement transducer system.—Changes in volume of the bellows assembly were sensed by changes in the output voltage of a linear variable differential transformer (LVDT, fig. 2; Schaevitz Model 1000 HR-Special) which is mounted vertically alongside the bellows and whose core is linked by stainless-steel rods to the free end of the bellows, as indicated in figure 2. The lower end of the transformer housing rests in a bracket that is securely attached to the fixed lower bellows termination so that the midpoint of the core is approximately opposite the free end of the bellows. This transformer—one of a matched pair—has a linear range of plus or minus 2.54 cm and a sensitivity of 0.13 volts cm^{-1} per volt input at an excitation frequency of 2000 Hz.

The other transformer of the matched pair is mounted in a micrometer stand (MS, fig. 2) outside the pressure apparatus, and its primary winding is connected to the power source (AOSC, fig. 2) in series with the primary of the transformer in the pressure vessel. The differential outputs from the two secondary windings of each transformer, which are interconnected in series (opposing), are fed into a tuned amplifier and null detector (TAND, fig. 2; General Radio Type 1232A) where an electronic null balance is achieved simply by displacing the transformer core that is attached to the micrometer spindle. In this way, displacements in the bellows as small as 1×10^{-4} cm—equivalent to a volume change of about 3×10^{-4} cm^3—can be readily detected.

EXPERIMENTAL PROCEDURES

Calibrations

Bellows discharge.—The volume of water discharged from the bellows assembly per unit displacement of the micrometer spindle in the null-balance system was determined by weighing the water discharged over 0.10 to 0.30 cm intervals, throughout the 3.94 cm travel of the bellows. In order to reduce errors caused by evaporation, the water was withdrawn through a valve and stainless-steel capillary tube and into a flask fitted with a diaphragm cap of soft rubber. The capillary, about 10 cm long, was beveled at one end to facilitate piercing of the rubber diaphragm.

Seven runs, with an average of 30 data points each, were made in the pressure range 150 to 1000 bars to establish the calibration curve of bellows discharge (ΔV) versus micrometer displacement (ΔX). In each of these calibration runs, the apparatus was placed in normal operating position, the temperature was held at 22.0 $\pm$ 0.5°C, and the pressure was closely monitored. Preliminary experiments had shown that it was necessary to calibrate the discharge of the bellows under hydrostatic pressure, because when the bellows was depressed under a uniaxial force, the change in volume per unit displacement ($\Delta V/\Delta X$) was neither the same nor as reproducible as when compressed under hydrostatic pressure.

The weight of water discharged was expressed as the average volume discharged per unit displacement of the micrometer for each interval of X, using the specific volume data of Kell and Whalley (1965). The re-

sultant values of $\Delta V/\Delta X$ were then plotted against micrometer setting (X), and a smooth curve was drawn for best fit to these data points. The scatter of experimental points about this $\Delta V/\Delta X$ curve was greatest at values of X less than 0.51 cm and greater than 4.45 cm; therefore, micrometer settings beyond these points were not used. The maximum deviation of any experimental point from this curve, within the interval 0.51 to 4.45 cm, is 0.016 $cm^3\ cm^{-1}$, and one standard deviation of all the points is 0.006 $cm^3\ cm^{-1}$. Inasmuch as the average $\Delta V/\Delta X$ in this interval is about 3.0 $cm^3\ cm^{-1}$, the precision of measurement is plus or minus about 0.2 percent, most of which is attributable to the imprecision with which samples of water could be withdrawn from the system and weighed.

The $\Delta V/\Delta X$ calibration curve obtained graphically was put in analytical form by a least-squares approximation to a polynomial in X. Owing to the complex shape of the curve, however, the fit, even for a polynomial of the 12th degree, was not as good as the fit of the hand-drawn curve to the raw data. Therefore, the $\Delta V/\Delta X$ curve was broken into three segments, and a polynomial equation fitted to each. The standard error of the mean for each segment is as follows: (A) from 0.457 to 1.750 cm, $\pm$ 0.002 $cm^3\ cm^{-1}$; (B) from 1.730 to 3.560 cm, $\pm$ 0.002 $cm^3\ cm^{-1}$; and (C) from 3.54 to 4.450 cm, $\pm$ 0.004 $cm^3\ cm^{-1}$. Thus, the fit of these equations to the $\Delta V/\Delta X$ curve is well within the scatter of the experimental data.

Thermocouples.—The three chromel-alumel thermocouples used to measure temperatures in the P-V-T cell were calibrated over the range 25° to 550° against a platinum resistance thermometer, at 800.4°C against the melting point of NaCl, and at 1063°C against the melting point of gold. All the calibrations, except at the melting point of gold, were carried out with the same potentiometer and with the thermocouples connected to the same extension wires as in the actual temperature measurements. The potentiometer had a range of only 1000°C; hence, the melting point of gold was determined using another potentiometer, and the two potentiometers were then compared at the melting point of NaCl.

The resistance of the platinum resistance thermometer, certified by the manufacturer to be accurate within $\pm$ 0.08°C up to 250°C, was measured on a Mueller bridge with an accuracy of $\pm$ 0.02 percent which, for the thermometer used, is equivalent to about $\pm$ 0.2°C at 500°C.

The calibrations at the melting point of reagent-grade NaCl were carried out with the NaCl in a sealed platinum tube fitted with a fine platinum-iridium alloy capillary through which the air could be withdrawn. This larger platinum tube also was fitted with two smaller platinum tubes, the sealed inner ends of which converged near the center of the NaCl bath. These smaller platinum tubes constituted wells for the thermocouple under calibration and a reference thermocouple which was connected to a recording potentiometer. The heating (or cooling) rate of the furnace was adjusted so that upon reaching the melting (or crystallization) temperature of NaCl, the temperature indicated by

both thermocouples remained constant for 5 to 15 minutes. Temperatures obtained upon melting agreed with those obtained upon crystallization generally within 0.5°C; hence, the accuracy of thermocouple calibration near 800°C was estimated to be ± 0.5°C. The actual temperatures recorded probably are not that accurate, owing to operator bias, but they almost certainly are within ± 1.0°C of the actual temperature.

The calibrations at the melting point of gold were accomplished by determining the indicated temperatures at which a small piece of chemically pure gold wire melted (mp = 1063.0°C), as indicated on the high-resistance scale of an ohmmeter. The gold wire spanned a 0.25 cm gap between two heavier platinum-rhodium wires which were supported by double-bore alumina spaghetti. The thermocouple under calibration was lashed to the alumina spaghetti so that the hot junction was not more than 0.15 cm from the span of gold wire. The reproducibility of melting-point determinations by this method was within ± 0.5°C.

Pressure cell.—The manganin cell and associated Carey-Foster bridge used in these investigations to measure pressure were calibrated just prior to use against a dead-weight gauge by Harwood Engineering Company, Walpole, Massachusetts. This calibration was carried out with the cell connected to the same Carey Foster bridge used in the P-V-T measurements.

Although the precision of calibration against the deadweight gauge generally was within plus or minus 1 bar, the zero-point stability of the bridge over the several-weeks period required to make the P-V-T measurements was not this high. The over-all uncertainty in pressure measurement attributable to this long-term drift in the 0 point and other causes is difficult to assess accurately, but it probably does not generally exceed plus or minus 5 bars.

Determination of Specific Volume

The physical variables measured in these experiments were temperature, pressure, and change in volume of the water in the bellows assembly (ΔV). Values for ΔV were calculated from the micrometer displacements (ΔX), and the equations for $\Delta V/\Delta X$ derived as described previously. The specific volume of water at a given pressure and temperature ($V_{P,T}$) was then obtained by substitution of the appropriate value for $\Delta V_{P,T}$ into the following equation which, in essence, is the volume of the cell divided by the mass of water in it at a given pressure and temperature.

$$V_{P,T} = \frac{V_{1,22}{}^{c}\,(1+\alpha_P{}^{c}T+\beta^{c}P)\,V_{1,22}\,[1+(\Delta V^{o}/V^{o})]}{V_{1,22}{}^{c}+(\Delta V^{o}/V^{o})(V_{1,22}{}^{c}+V_{1,22}{}^{b})-\Delta V_{P,T}-P(\beta^{b}V_{1,22}{}^{b}+\gamma)}. \quad (1)$$

In this equation, $V_{1,22}{}^{c}$ and $V_{1,22}{}^{b}$ are the volumes of the cell and bellows assembly, respectively, at 1 bar and 22°C. The terms β^{c} and β^{b} are the volume coefficients of compressibility of the cell and bellows assembly, respectively, at 22°C, and $\alpha_P{}^{c}$ is the volume coefficient of thermal expansion of the cell (slightly pressure dependent). $V_{1,22}$ is the specific

volume of water at 1 bar, 22°C, and γ is an empirical constant here attributed to the elastic dilation of the bellows assembly under pressure. The term $(\Delta V^\circ/V^\circ)$ is the isothermal compression of water at 22°C and was obtained from four separate sets of measured values for $\Delta V_{P,22}$ as follows:

$$(\Delta V^\circ/V^\circ) = \frac{V_{P,22} - V_{1,22}}{V_{1,22}} = \frac{\Delta V_{P,22} + P(\gamma + \beta^b V_{1,22} + \beta^c V_{1,22}{}^c)}{V_{1,22}{}^c + V_{1,22}{}^b}. \quad (2)$$

The solution of equations (1) and (2) obviously requires prior evaluation of the factors γ, β^b, and β^c; in addition, $\alpha_P{}^c$ must be evaluated before equation (1) can be solved. The constant γ was determined from two sets of $\Delta V_{P,22}$ measurements with different values of $V_{1,22}{}^b$, but without a cell attached, through the following relationship:

$$\gamma = \frac{V_{1,22}{}^b}{P}\left(\frac{\Delta V_{P,22}{}^d}{V_{1,22}{}^d} - \frac{\Delta V_{P,22}}{V_{1,22}{}^b}\right). \quad (3)$$

In this equation, $V_{1,22}{}^d$ and $\Delta V_{P,22}{}^d$ are the differences in $V_{1,22}{}^b$ and $\Delta V_{P,22}$, respectively, between the two sets of measurements, and $V_{1,22}{}^b$ and $\Delta V_{P,22}$ are the initial volume and change in volume with pressure for each of the individual sets. Application of equation (3) to both sets of data, over the entire pressure range of this investigation, yielded a γ with a constant value of 1.5×10^{-5} cm^3 bar^{-1}.

The fact that γ is independent of the bellows volume suggests three possible sources: (1) the elastic dilation of the external capillary tubing and fittings that were under non-hydrostatic stress; (2) changes in the electrical characteristics of the differential transformer that was under pressure, and (3) changes in configuration of the individual bellows convolutions with pressure. Calculations revealed that elastic dilation of the external tubing and fittings could account for no more than 15 percent of γ. Similarly, determinations of the effect of pressure on the output of the differential transformer at several fixed positions of the core revealed that, on one side of the null position, there was no contribution to γ, and on the other side the effect was equivalent to only 2.6×10^{-6} cm^3 bar^{-1}. Because of this assymetry, adjustment was made, where necessary, in the initial micrometer readings, before values of ΔV were calculated. Thus, largely for lack of any other obvious source, about 85 percent of γ is tentatively attributed to changes in configuration of the individual bellows convolutions with pressure and the remainder to elastic dilation of the external tubing and fittings.

The compressibility of the cell (β^c) at 22°C was calculated from the following equations (Birch, 1966, p. 98 and 100):

$$\beta_s{}^c = \frac{3(1 - 2\delta)}{E_s} \quad (4)$$

and

$$\beta_t{}^c = \beta^c = \beta_s{}^c + \frac{\alpha^2 T}{\rho C_P} \quad (5)$$

where $\beta_s{}^c$ is the adiabatic compressibility, δ is Poisson's ratio, E_s is the dynamic Young's modulus, $\beta_t{}^c$ is the isothermal compressibility, α is the

volume coefficient of thermal expansion, ρ is the density, and C_P is the heat capacity at constant pressure, all of Inconel 600. The data for δ and E_s were obtained from J. B. Hartland (personal commun., 1968), Huntington Alloy Products Division, The International Nickel Company, and those for α, ρ, and C_P were taken from Lucks and Deem (1958). The value for β^c (6.2×10^{-7} bar $^{-1}$) calculated from equations (4) and (5) was assumed, for present purposes, to remain constant over the entire range of pressures covered.

Once both γ and β^c were evaluated, the apparent volume compressibility of the bellows assembly (β^b) could be readily determined with the aid of the following equation:

$$\beta^b = \frac{1}{P}\left[\frac{\Delta V_{P,22}}{V_{1,22}{}^c} - \frac{\Delta V_{P,22}{}^d}{V_{1,22}{}^d}\left(1 + \frac{V_{1,22}{}^b}{V_{1,22}{}^c}\right)\right] + \frac{\beta^c}{V_{1,22}{}^d} + \frac{\gamma}{V_{1,22}{}^c}. \quad (6)$$

In this equation, $\Delta V_{P,22}{}^d$ and $V_{1,22}{}^d$ have the same significance as in equation (3), whereas $V_{1,22}{}^b$ $V_{1,22}{}^c$, and $\Delta V_{P,22}$ are the volumes and changes in volumes, respectively, in the two sets of ΔV measurements made with the cell attached. The mean value for β^b (5.0×10^{-7} bar^{-1}) calculated from equation (6), over the pressure range 2000 to 8000 bars, is in good agreement with that calculated up to 1000 bars using the specific volume ($V_{P,22}$) data of Kell and Whalley (1965) and the equation:

$$\beta^b = \frac{1}{P}\left(\frac{V_{P,22} - V_{1,22}}{V_{1,22}} - \frac{\Delta V_{P,22}{}^d}{V_{1,22}{}^d}\right). \quad (7)$$

It is noteworthy that this is not a particularly accurate method for determining β^b because it involves small differences between large numbers that themselves are only a little more precise than their differences. However, it yields a value close to that expected (4.7×10^{-7} bar^{-1}) on the basis of the compressibility of Type 304 stainless steel (7.0×10^{-7} bar^{-1}) determined by Kell and Whalley (1965), and the fact that the apparent β^b should be only about two-thirds the true volume compressibility of the bellows material.

The only term in equation (1) that remains to be evaluated before specific volumes ($V_{P,T}$) can be calculated from the $\Delta V_{P,T}$ data is the volume coefficient of thermal expansion ($\alpha_P{}^c$) of the cell as a function of pressure. To do this, values of $K_T{}^c = 1/\beta_T{}^c$ were first calculated at 100°C intervals to 1000°C, using equation (5) and the data on Inconel 600 from the sources cited above. These values of $K_T{}^c$ were next graphed versus T to obtain a value for the slope $(\partial K_T{}^c/\partial T)_P$ which was then used in the following equation (G. R. Barsch, personal commun., 1968):

$$\left(\frac{\partial \alpha_P{}^c}{\partial P}\right)_T = \frac{1}{(K_T{}^c)^2}\left(\frac{\partial K_T{}^c}{\partial T}\right)_P. \quad (8)$$

The change in $\alpha_P{}^c$ with P calculated from this equation, in which $K_T{}^c$ is the isothermal bulk modulus of Inconel 600, was found to increase slightly numerically with T but to average close to -1×10^{-10} °C^{-1} bar $^{-1}$. Inasmuch as the volume thermal expansion of Inconel at 1 bar is in the order of 3×10^{-5} °C^{-1}, it is obvious that an error of 1×10^{-11}

$^{c}C^{-1}$ bar^{-1} introduced by assuming that $(\partial\alpha_P{}^c/\partial P)_T$ is independent of pressure would not significantly alter the calculated specific volumes of water, even at 900°C and 8500 bars. Therefore, the volume thermal expansion term ($\alpha_P{}^c$) in equation (1) was calculated using the 1 atm ($\alpha_1{}^c$) data of Lucks and Deem (1958) and the following simplified equation:

$$\alpha_P{}^c = \alpha_1{}^c - aP, \tag{9}$$

where $a = 1.0 \times 10^{-10}$ $^{\circ}C^{-1}$ bar^{-1}.

Sources of Uncertainty

The principal sources of uncertainty in the specific volumes measured in this work are not inaccuracies in the corrections for the effects of pressure and temperature on the metal parts of the volumometer system, but in the accuracy of measurement of pressure, ΔV, and especially temperature. The accuracy of temperature measurement already has been discussed; in addition, small uncertainties were introduced by temperature gradients in the cell as high as 5 degrees centigrade and by the effects of pressure on the emf of the thermocouples. The uncertainty caused by gradients was reduced by averaging the temperatures of three thermocouples placed in wells at each end and in the middle of the cell. The effect of pressure on the emf of the thermocouples was estimated from the data of Bundy (1961) to be as much as 2 degrees centigrade at the highest temperature and pressure of these investigations. Combined with the uncertainty in thermocouple calibration, these two sources yield an overall estimated error in the higher temperatures reported here of $\pm$ 0.15 percent at low pressures and $\pm$ 0.20 percent at high pressures. This leads to an uncertainty in the reported specific volumes as high as $\pm$ 0.3 percent at high temperatures and low pressures but not greater than about $\pm$ 0.1 percent at the highest pressure reported here.

The uncertainty in pressure measurement also leads to a potential error in specific volumes that is greatest at low pressures and high temperatures where the slopes of the isotherms are very steep. At high pressures, however, the potential error from this source diminishes to considerably less than 0.1 percent in specific volume.

The total uncertainty in the $\Delta V_{P,T}$ measurements is greatest at large values of $\Delta V_{P,T}$, but in no case does it cause an error in specific volume in excess of 0.1 percent. The remaining sources of error are in the correction factors applied for compressibility, dilation, and thermal expansion of the metals in the volumometer system, as well as for the effect of pressure on the differential transformer. The magnitude of error from these sources has been minimized, however, by experimentally determining those factors that were not accurately known. Altogether, these sources yield an estimated uncertainty of $\pm$ 0.05 percent.

Thus, consideration of all the potential sources of error in the P-V-T measurements and corrections leads to a total uncertainty (systematic errors) of about 0.3 percent in specific volume over most of the pressure-temperature region investigated. It might be slightly greater than this at high temperatures but probably is less at low temperatures.

TABLE 1

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

	PRESSURE IN BARS							
TEMP	1000	1100	1200	1300	1400	1500	1600	1700
20	0.9614	0.9587	0.9559	0.9529	0.9498	0.9468	0.9438	0.9408
40	0.9704	0.9676	0.9646	0.9616	0.9585	0.9554	0.9523	0.9493
60	0.9790	0.9762	0.9731	0.9700	0.9669	0.9638	0.9607	0.9577
80	0.9886	0.9857	0.9826	0.9794	0.9762	0.9731	0.9699	0.9668
100	0.9999	0.9968	0.9936	0.9903	0.9870	0.9837	0.9804	0.9772
120	1.0131	1.0097	1.0063	1.0028	0.9994	0.9959	0.9925	0.9891
140	1.0282	1.0245	1.0208	1.0171	1.0134	1.0097	1.0061	1.0025
160	1.0450	1.0410	1.0370	1.0330	1.0290	1.0250	1.0211	1.0172
180	1.0635	1.0591	1.0547	1.0503	1.0460	1.0417	1.0375	1.0333
200	1.0836	1.0786	1.0737	1.0690	1.0643	1.0596	1.0551	1.0505
220	1.1051	1.0995	1.0942	1.0889	1.0838	1.0788	1.0738	1.0689
240	1.1285	1.1221	1.1160	1.1102	1.1046	1.0991	1.0937	1.0884
260	1.1539	1.1464	1.1395	1.1330	1.1268	1.1207	1.1148	1.1090
280	1.1819	1.1730	1.1650	1.1576	1.1506	1.1438	1.1373	1.1309
300	1.2131	1.2024	1.1929	1.1843	1.1762	1.1686	1.1613	1.1542
320	1.2484	1.2352	1.2238	1.2135	1.2042	1.1954	1.1871	1.1792
340	1.2884	1.2720	1.2581	1.2458	1.2348	1.2246	1.2151	1.2061
360	1.3341	1.3137	1.2966	1.2817	1.2685	1.2565	1.2455	1.2351
380	1.3864	1.3610	1.3398	1.3217	1.3058	1.2916	1.2787	1.2667
400	1.4462	1.4146	1.3885	1.3664	1.3472	1.3303	1.3150	1.3011
420	1.5117	1.4715	1.4432	1.4170	1.3931	1.3729	1.3549	1.3386
440	1.5859	1.5371	1.5021	1.4709	1.4439	1.4197	1.3984	1.3793
460	1.6732	1.6128	1.5688	1.5311	1.4990	1.4712	1.4460	1.4237
480	1.7756	1.7000	1.6444	1.5984	1.5601	1.5273	1.4978	1.4717
500	1.8936	1.7992	1.7295	1.6731	1.6271	1.5884	1.5539	1.5236
520	2.0263	1.9102	1.8239	1.7554	1.7003	1.6545	1.6144	1.5793
540	2.1723	2.0321	1.9273	1.8450	1.7796	1.7259	1.6792	1.6389
560	2.3294	2.1636	2.0389	1.9415	1.8647	1.8021	1.7483	1.7022
580	2.4952	2.3031	2.1575	2.0443	1.9552	1.8830	1.8214	1.7692
600	2.6672	2.4490	2.2822	2.1526	2.0507	1.9683	1.8993	1.8396
620	2.8430	2.5995	2.4117	2.2654	2.1504	2.0575	1.9799	1.9132
640	3.0203	2.7529	2.5447	2.3819	2.2538	2.1502	2.0637	1.9896
660	3.1971	2.9076	2.6799	2.5011	2.3599	2.2456	2.1502	2.0686
680	3.3717	3.0622	2.8162	2.6221	2.4682	2.3433	2.2389	2.1498
700	3.5430	3.2156	2.9527	2.7439	2.5777	2.4424	2.3292	2.2325
720	3.7102	3.3669	3.0884	2.8659	2.6879	2.5425	2.4207	2.3164
740	3.8729	3.5155	3.2227	2.9874	2.7982	2.6431	2.5127	2.4011
760	4.0313	3.6610	3.3553	3.1079	2.9081	2.7436	2.6051	2.4863
780	4.1856	3.8035	3.4857	3.2272	3.0173	2.8439	2.6974	2.5715
800	4.3365	3.9432	3.6142	3.3451	3.1257	2.9436	2.7894	2.6568
820	4.4849	4.0803	3.7407	3.4617	3.2332	3.0428	2.8812	2.7419
840	4.6312	4.2153	3.8656	3.5772	3.3399	3.1416	2.9727	2.8269
860	4.7761	4.3486	3.9892	3.6918	3.4461	3.2400	3.0640	2.9119
880	4.9195	4.4803	4.1116	3.8057	3.5519	3.3381	3.1551	2.9967
900	5.0606	4.6101	4.2330	3.9190	3.6573	3.4361	3.2461	3.0813

EXPERIMENTAL RESULTS

P-V-T data

The unsmoothed data, in the form of specific volume as a function of pressure and temperature, were obtained at intervals of approximately 25°C and 350 bars over the temperature-pressure region from 22° to 900°C and 150 to 8500 bars, except for a small area at low pressures and high temperatures where specific volumes exceed 3.32 cm^3gm^{-1}. Altogether, more than 1000 determinations were made, and nearly 800 of these constitute the basis for table 1. Most of the remainder were almost duplicate determinations in the pressure range 2500 to 5000 bars and were deleted in order to avoid possible adverse effects on the fit of equation (10) to other single determinations.

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

TEMP	PRESSURE IN BARS 1800	1900	2000	2100	2200	2300	2400	2500
20	0.9379	0.9351	0.9323	0.9296	0.9270	0.9245	0.9221	0.9197
40	0.9464	0.9435	0.9407	0.9380	0.9354	0.9329	0.9304	0.9280
60	0.9547	0.9518	0.9490	0.9463	0.9437	0.9411	0.9386	0.9362
80	0.9638	0.9609	0.9580	0.9552	0.9525	0.9499	0.9473	0.9449
100	0.9741	0.9710	0.9680	0.9651	0.9623	0.9596	0.9569	0.9544
120	0.9858	0.9825	0.9794	0.9763	0.9733	0.9704	0.9676	0.9649
140	0.9989	0.9954	0.9921	0.9888	0.9856	0.9825	0.9795	0.9765
160	1.0134	1.0097	1.0060	1.0025	0.9990	0.9956	0.9924	0.9892
180	1.0292	1.0251	1.0212	1.0173	1.0136	1.0099	1.0064	1.0029
200	1.0461	1.0417	1.0374	1.0333	1.0292	1.0252	1.0214	1.0176
220	1.0641	1.0594	1.0547	1.0502	1.0458	1.0415	1.0373	1.0332
240	1.0832	1.0780	1.0730	1.0681	1.0633	1.0586	1.0541	1.0497
260	1.1033	1.0978	1.0923	1.0870	1.0818	1.0767	1.0718	1.0670
280	1.1247	1.1186	1.1127	1.1069	1.1012	1.0957	1.0903	1.0851
300	1.1474	1.1407	1.1342	1.1279	1.1217	1.1157	1.1099	1.1042
320	1.1716	1.1642	1.1570	1.1501	1.1433	1.1368	1.1304	1.1243
340	1.1975	1.1892	1.1813	1.1736	1.1662	1.1591	1.1521	1.1454
360	1.2254	1.2161	1.2072	1.1987	1.1905	1.1826	1.1750	1.1676
380	1.2555	1.2450	1.2350	1.2255	1.2164	1.2076	1.1992	1.1911
400	1.2882	1.2762	1.2649	1.2541	1.2439	1.2342	1.2249	1.2160
420	1.3236	1.3098	1.2969	1.2848	1.2733	1.2625	1.2521	1.2423
440	1.3620	1.3461	1.3314	1.3176	1.3047	1.2925	1.2810	1.2701
460	1.4035	1.3852	1.3684	1.3527	1.3382	1.3245	1.3116	1.2994
480	1.4484	1.4273	1.4080	1.3902	1.3738	1.3584	1.3440	1.3305
500	1.4966	1.4724	1.4503	1.4302	1.4116	1.3943	1.3782	1.3632
520	1.5483	1.5205	1.4954	1.4726	1.4516	1.4323	1.4143	1.3976
540	1.6034	1.5717	1.5433	1.5175	1.4939	1.4722	1.4522	1.4336
560	1.6618	1.6259	1.5938	1.5648	1.5384	1.5142	1.4919	1.4713
580	1.7235	1.6830	1.6469	1.6144	1.5850	1.5581	1.5334	1.5107
600	1.7882	1.7429	1.7026	1.6664	1.6336	1.6039	1.5766	1.5516
620	1.8558	1.8053	1.7605	1.7204	1.6842	1.6514	1.6214	1.5939
640	1.9260	1.8701	1.8206	1.7764	1.7366	1.7006	1.6678	1.6377
660	1.9985	1.9370	1.8826	1.8342	1.7906	1.7513	1.7155	1.6828
680	2.0729	2.0058	1.9464	1.8935	1.8461	1.8034	1.7646	1.7292
700	2.1490	2.0760	2.0116	1.9543	1.9030	1.8567	1.8148	1.7766
720	2.2264	2.1476	2.0781	2.0163	1.9610	1.9112	1.8662	1.8252
740	2.3048	2.2201	2.1455	2.0792	2.0200	1.9667	1.9185	1.8747
760	2.3832	2.2933	2.2137	2.1430	2.0798	2.0230	1.9717	1.9250
780	2.4623	2.3670	2.2824	2.2074	2.1404	2.0801	2.0256	1.9761
800	2.5415	2.4408	2.3515	2.2722	2.2014	2.1377	2.0801	2.0278
820	2.6208	2.5145	2.4206	2.3373	2.2628	2.1958	2.1352	2.0801
840	2.7000	2.5890	2.4898	2.4025	2.3244	2.2542	2.1907	2.1329
860	2.7793	2.6633	2.5587	2.4677	2.3862	2.3128	2.2464	2.1860
880	2.8586	2.7376	2.6274	2.5328	2.4480	2.3716	2.3023	2.2393
900	2.9376	2.8117	2.7009	2.5977	2.5097	2.4303	2.3583	2.2926

Little effort was devoted to the pressure region below 1000 bars because reliable data here already were available, and more accurate results could be obtained at low pressures by other methods. Enough measurements (65) were made in this region, however, to establish agreement, within the specified tolerances, with the International Skeleton Tables (Bain, 1964).

The common practice of graphically smoothing the raw data was not feasible because the data were not obtained on orthogonal coordinates in temperature and pressure or even along isotherms. Therefore, the specific volumes calculated by equation (I) were fitted directly

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

TEMP	PRESSURE IN BARS 2600	2700	2800	2900	3000	3100	3200	3300
20	0.9173	0.9150	0.9128	0.9106	0.9085	0.9064	0.9043	0.9023
40	0.9257	0.9234	0.9212	0.9190	0.9168	0.9147	0.9127	0.9106
60	0.9338	0.9316	0.9293	0.9271	0.9250	0.9229	0.9208	0.9188
80	0.9425	0.9401	0.9379	0.9356	0.9335	0.9313	0.9292	0.9272
100	0.9519	0.9495	0.9471	0.9448	0.9426	0.9404	0.9382	0.9361
120	0.9623	0.9597	0.9572	0.9548	0.9525	0.9502	0.9479	0.9457
140	0.9737	0.9710	0.9683	0.9657	0.9632	0.9608	0.9584	0.9561
160	0.9862	0.9832	0.9803	0.9775	0.9748	0.9722	0.9697	0.9672
180	0.9996	0.9964	0.9933	0.9902	0.9873	0.9845	0.9817	0.9790
200	1.0140	1.0105	1.0071	1.0038	1.0006	0.9975	0.9945	0.9916
220	1.0293	1.0254	1.0217	1.0181	1.0147	1.0113	1.0080	1.0049
240	1.0454	1.0412	1.0372	1.0333	1.0295	1.0258	1.0223	1.0188
260	1.0623	1.0578	1.0534	1.0491	1.0450	1.0410	1.0372	1.0335
280	1.0801	1.0751	1.0704	1.0658	1.0613	1.0570	1.0528	1.0488
300	1.0987	1.0934	1.0882	1.0832	1.0783	1.0737	1.0691	1.0647
320	1.1183	1.1125	1.1069	1.1014	1.0962	1.0911	1.0862	1.0814
340	1.1389	1.1326	1.1264	1.1206	1.1148	1.1093	1.1040	1.0989
360	1.1605	1.1536	1.1470	1.1406	1.1344	1.1284	1.1227	1.1171
380	1.1833	1.1758	1.1686	1.1616	1.1549	1.1484	1.1421	1.1361
400	1.2074	1.1992	1.1913	1.1837	1.1763	1.1693	1.1625	1.1560
420	1.2328	1.2238	1.2151	1.2068	1.1988	1.1912	1.1838	1.1767
440	1.2596	1.2497	1.2402	1.2311	1.2224	1.2140	1.2060	1.1983
460	1.2879	1.2769	1.2665	1.2565	1.2470	1.2379	1.2292	1.2209
480	1.3177	1.3056	1.2941	1.2832	1.2728	1.2629	1.2534	1.2443
500	1.3490	1.3356	1.3230	1.3110	1.2997	1.2888	1.2785	1.2687
520	1.3819	1.3671	1.3532	1.3401	1.3277	1.3159	1.3047	1.2940
540	1.4163	1.4000	1.3847	1.3704	1.3568	1.3439	1.3318	1.3202
560	1.4522	1.4343	1.4175	1.4018	1.3870	1.3730	1.3598	1.3473
580	1.4896	1.4699	1.4516	1.4344	1.4183	1.4031	1.3888	1.3752
600	1.5284	1.5069	1.4869	1.4682	1.4506	1.4341	1.4186	1.4040
620	1.5686	1.5451	1.5233	1.5030	1.4840	1.4661	1.4494	1.4336
640	1.6101	1.5846	1.5609	1.5389	1.5183	1.4991	1.4810	1.4641
660	1.6528	1.6251	1.5995	1.5757	1.5536	1.5329	1.5135	1.4953
680	1.6967	1.6668	1.6392	1.6136	1.5898	1.5675	1.5468	1.5273
700	1.7417	1.7095	1.6799	1.6524	1.6269	1.6031	1.5808	1.5600
720	1.7877	1.7532	1.7215	1.6921	1.6648	1.6394	1.6157	1.5935
740	1.8346	1.7978	1.7639	1.7326	1.7035	1.6765	1.6513	1.6277
760	1.8823	1.8432	1.8072	1.7739	1.7431	1.7144	1.6876	1.6627
780	1.9309	1.8894	1.8512	1.8160	1.7833	1.7530	1.7247	1.6983
800	1.9801	1.9363	1.8960	1.8587	1.8242	1.7922	1.7623	1.7345
820	2.0299	1.9837	1.9413	1.9021	1.8658	1.8320	1.8006	1.7712
840	2.0801	2.0317	1.9871	1.9459	1.9078	1.8723	1.8392	1.8084
860	2.1307	2.0800	2.0333	1.9901	1.9501	1.9129	1.8782	1.8458
880	2.1816	2.1286	2.0797	2.0346	1.9926	1.9537	1.9173	1.8834
900	2.2325	2.1772	2.1262	2.0790	2.0351	1.9943	1.9563	1.9207

by a ninth degree polynomial[1] in PV as a function of T and P. This equation, which has the form:

$$PV = \sum_{j=0}^{9} \sum_{i=0}^{9-j} a_{ij} T^i P^j \qquad (10)$$

fits the data within 0.1 percent (one standard deviation) in specific volume everywhere in the pressure range 1300 to 8100 bars, except a small wedge-shaped area that extends from 1300 to 1900 bars at 900°C and pinches out at 1300 bars and 410°C. Equation (10) also did not fit the measurements well between 1000 and 1300 bars and above 8100 bars

[1] The basic computer program for these calculations was taken from O'Leary, Lippert, and Spitz (1966) and expanded to the ninth degree, as well as adapted for use on the IBM-360/67 system.

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

	PRESSURE IN BARS							
TEMP	3400	3500	3600	3700	3800	3900	4000	4100
20	0.9002	0.8982	0.8963	0.8943	0.8924	0.8904	0.8886	0.8867
40	0.9086	0.9066	0.9046	0.9027	0.9008	0.8988	0.8969	0.8951
60	0.9168	0.9148	0.9128	0.9109	0.9090	0.9070	0.9051	0.9033
80	0.9252	0.9232	0.9212	0.9192	0.9173	0.9154	0.9135	0.9116
100	0.9340	0.9320	0.9300	0.9280	0.9261	0.9241	0.9222	0.9203
120	0.9436	0.9415	0.9394	0.9373	0.9353	0.9333	0.9313	0.9294
140	0.9538	0.9516	0.9494	0.9473	0.9451	0.9431	0.9410	0.9390
160	0.9648	0.9624	0.9601	0.9578	0.9556	0.9534	0.9512	0.9491
180	0.9764	0.9739	0.9714	0.9690	0.9666	0.9643	0.9620	0.9597
200	0.9888	0.9860	0.9834	0.9807	0.9782	0.9757	0.9733	0.9709
220	1.0018	0.9988	0.9959	0.9931	0.9904	0.9877	0.9851	0.9825
240	1.0155	1.0123	1.0091	1.0061	1.0031	1.0003	0.9974	0.9947
260	1.0298	1.0263	1.0230	1.0197	1.0165	1.0134	1.0103	1.0074
280	1.0448	1.0410	1.0374	1.0338	1.0304	1.0270	1.0237	1.0206
300	1.0605	1.0564	1.0524	1.0486	1.0448	1.0412	1.0377	1.0343
320	1.0768	1.0724	1.0681	1.0640	1.0599	1.0560	1.0523	1.0486
340	1.0939	1.0891	1.0845	1.0800	1.0756	1.0714	1.0674	1.0634
360	1.1117	1.1065	1.1015	1.0967	1.0920	1.0875	1.0831	1.0789
380	1.1303	1.1247	1.1193	1.1141	1.1090	1.1042	1.0994	1.0949
400	1.1497	1.1436	1.1378	1.1322	1.1267	1.1215	1.1164	1.1115
420	1.1699	1.1634	1.1571	1.1510	1.1451	1.1395	1.1340	1.1288
440	1.1910	1.1839	1.1771	1.1705	1.1642	1.1582	1.1523	1.1467
460	1.2129	1.2052	1.1979	1.1908	1.1840	1.1775	1.1712	1.1652
480	1.2357	1.2274	1.2195	1.2119	1.2045	1.1975	1.1908	1.1843
500	1.2593	1.2504	1.2418	1.2336	1.2257	1.2182	1.2110	1.2040
520	1.2839	1.2742	1.2649	1.2561	1.2476	1.2395	1.2318	1.2243
540	1.3092	1.2988	1.2888	1.2793	1.2702	1.2615	1.2532	1.2452
560	1.3354	1.3241	1.3134	1.3031	1.2934	1.2841	1.2751	1.2666
580	1.3624	1.3502	1.3387	1.3277	1.3172	1.3072	1.2977	1.2886
600	1.3902	1.3771	1.3647	1.3529	1.3417	1.3310	1.3208	1.3111
620	1.4187	1.4047	1.3914	1.3787	1.3667	1.3553	1.3445	1.3341
640	1.4481	1.4330	1.4187	1.4052	1.3924	1.3802	1.3687	1.3576
660	1.4781	1.4620	1.4468	1.4323	1.4187	1.4057	1.3934	1.3817
680	1.5089	1.4917	1.4754	1.4601	1.4455	1.4318	1.4187	1.4062
700	1.5405	1.5221	1.5048	1.4885	1.4730	1.4584	1.4445	1.4313
720	1.5727	1.5532	1.5348	1.5174	1.5011	1.4856	1.4709	1.4569
740	1.6057	1.5849	1.5654	1.5470	1.5297	1.5133	1.4978	1.4830
760	1.6393	1.6173	1.5967	1.5773	1.5589	1.5416	1.5252	1.5097
780	1.6735	1.6503	1.6285	1.6080	1.5887	1.5704	1.5531	1.5367
800	1.7084	1.6839	1.6609	1.6393	1.6189	1.5997	1.5815	1.5642
820	1.7437	1.7180	1.6938	1.6710	1.6496	1.6293	1.6102	1.5921
840	1.7795	1.7524	1.7270	1.7031	1.6805	1.6593	1.6392	1.6202
860	1.8155	1.7871	1.7604	1.7353	1.7116	1.6893	1.6683	1.6483
880	1.8516	1.8218	1.7938	1.7675	1.7427	1.7193	1.6972	1.6763
900	1.8875	1.8562	1.8269	1.7993	1.7733	1.7489	1.7257	1.7039

because the number of data points was insufficient to constrain this inherently unstable polynomial near its limits. This shortcoming of high-degree polynomials such as equation (10) was remedied near the 1000-bar boundary by adding, to the measured specific volumes, data for 900 and 1000 bars from the Natl. Engineering Lab. Steam Tables 1964 (Bain, 1964), all of which previously had been found to be in good agreement with the measured values.

At pressures above 8100 bars, where no previous reliable data were available, a different procedure necessarily had to be employed to obtain additional specific volumes. First, a preliminary form of equation (10) was fitted to the measured data between 4000 and 8000 bars to obtain specific volumes at intervals of 20°C and 100 bars, as in table 1. Second, a quadratic equation was fitted to each 20° isotherm between 20° and

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

	PRESSURE IN BARS							
TEMP	4200	4300	4400	4500	4600	4700	4800	4900
20	0.8848	0.8830	0.8811	0.8793	0.8776	0.8758	0.8741	0.8724
40	0.8932	0.8913	0.8895	0.8877	0.8859	0.8841	0.8823	0.8806
60	0.9014	0.8995	0.8977	0.8959	0.8941	0.8923	0.8905	0.8888
80	0.9097	0.9079	0.9060	0.9042	0.9024	0.9006	0.8988	0.8970
100	0.9184	0.9165	0.9147	0.9128	0.9110	0.9091	0.9073	0.9056
120	0.9275	0.9255	0.9236	0.9218	0.9199	0.9180	0.9162	0.9144
140	0.9370	0.9350	0.9331	0.9311	0.9292	0.9273	0.9254	0.9235
160	0.9470	0.9450	0.9429	0.9409	0.9389	0.9369	0.9350	0.9330
180	0.9575	0.9554	0.9532	0.9511	0.9490	0.9470	0.9449	0.9429
200	0.9685	0.9662	0.9640	0.9617	0.9595	0.9574	0.9552	0.9531
220	0.9800	0.9776	0.9752	0.9728	0.9705	0.9682	0.9660	0.9637
240	0.9920	0.9894	0.9868	0.9843	0.9819	0.9794	0.9770	0.9747
260	1.0045	1.0017	0.9990	0.9963	0.9936	0.9911	0.9885	0.9860
280	1.0175	1.0145	1.0115	1.0087	1.0059	1.0031	1.0004	0.9978
300	1.0310	1.0278	1.0246	1.0215	1.0185	1.0156	1.0127	1.0099
320	1.0450	1.0416	1.0382	1.0349	1.0317	1.0286	1.0255	1.0225
340	1.0596	1.0559	1.0523	1.0488	1.0453	1.0420	1.0387	1.0355
360	1.0747	1.0708	1.0669	1.0631	1.0595	1.0559	1.0524	1.0490
380	1.0905	1.0862	1.0820	1.0780	1.0741	1.0703	1.0666	1.0630
400	1.1068	1.1022	1.0978	1.0935	1.0893	1.0852	1.0813	1.0774
420	1.1237	1.1188	1.1140	1.1094	1.1050	1.1006	1.0964	1.0923
440	1.1412	1.1360	1.1309	1.1259	1.1212	1.1165	1.1120	1.1077
460	1.1593	1.1537	1.1483	1.1430	1.1379	1.1330	1.1282	1.1235
480	1.1780	1.1720	1.1662	1.1606	1.1551	1.1499	1.1448	1.1398
500	1.1973	1.1909	1.1846	1.1786	1.1729	1.1672	1.1618	1.1566
520	1.2171	1.2103	1.2036	1.1972	1.1910	1.1851	1.1793	1.1737
540	1.2375	1.2302	1.2231	1.2163	1.2097	1.2034	1.1972	1.1913
560	1.2584	1.2506	1.2430	1.2358	1.2288	1.2221	1.2155	1.2093
580	1.2799	1.2715	1.2635	1.2557	1.2483	1.2412	1.2343	1.2276
600	1.3018	1.2929	1.2843	1.2761	1.2683	1.2607	1.2534	1.2463
620	1.3242	1.3147	1.3057	1.2970	1.2886	1.2806	1.2729	1.2654
640	1.3471	1.3371	1.3274	1.3182	1.3094	1.3009	1.2927	1.2848
660	1.3705	1.3598	1.3497	1.3399	1.3306	1.3216	1.3129	1.3046
680	1.3944	1.3831	1.3723	1.3620	1.3521	1.3427	1.3336	1.3248
700	1.4188	1.4068	1.3954	1.3846	1.3741	1.3641	1.3546	1.3453
720	1.4437	1.4311	1.4190	1.4075	1.3965	1.3860	1.3759	1.3662
740	1.4690	1.4557	1.4430	1.4309	1.4194	1.4083	1.3977	1.3875
760	1.4949	1.4809	1.4675	1.4548	1.4426	1.4310	1.4198	1.4091
780	1.5212	1.5064	1.4924	1.4790	1.4662	1.4540	1.4423	1.4311
800	1.5479	1.5324	1.5176	1.5035	1.4901	1.4773	1.4650	1.4533
820	1.5749	1.5586	1.5431	1.5284	1.5143	1.5009	1.4880	1.4757
840	1.6022	1.5851	1.5688	1.5533	1.5386	1.5245	1.5111	1.4982
860	1.6294	1.6115	1.5945	1.5783	1.5629	1.5482	1.5342	1.5207
880	1.6565	1.6378	1.6200	1.6031	1.5870	1.5716	1.5570	1.5430
900	1.6832	1.6636	1.6450	1.6273	1.6106	1.5946	1.5793	1.5648

900°C. Then, these quadratic equations were used to extrapolate the isotherms to 10,000 bars and thereby generate additional specific volumes above 8100 bars. These additional specific volumes, when combined with the measured values and the Natl. Engineering Lab. Steam Table 1964 data up to 410°C, yielded an equation, (10), that fits all the measurements between 1000 and 8500 bars (outside the wedge-shaped area) within 0.1 percent (one standard deviation).

Part of the wedge-shaped area between 1000 and 1600 bars includes specific volumes that exceed 3.32 cm^3gm^{-1}, the largest value measured in this investigation. In order to complete this part of table 1 and to secure the optimum fit to the measured data, additional specific volumes were interpolated in the following manner. First, equation (10) and a preliminary seventh-degree polynomial for the wedge-shaped area were

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

TEMP	PRESSURE IN BARS 5000	5100	5200	5300	5400	5500	5600	5700
20	0.8707	0.8691	0.8675	0.8659	0.8643	0.8628	0.8613	0.8598
40	0.8789	0.8772	0.8756	0.8739	0.8723	0.8708	0.8692	0.8677
60	0.8870	0.8853	0.8836	0.8820	0.8803	0.8787	0.8772	0.8756
80	0.8953	0.8936	0.8919	0.8902	0.8885	0.8869	0.8852	0.8837
100	0.9038	0.9020	0.9003	0.8986	0.8969	0.8952	0.8936	0.8919
120	0.9126	0.9108	0.9090	0.9073	0.9055	0.9038	0.9021	0.9005
140	0.9217	0.9198	0.9180	0.9162	0.9144	0.9127	0.9110	0.9092
160	0.9311	0.9292	0.9274	0.9255	0.9237	0.9219	0.9201	0.9183
180	0.9409	0.9389	0.9370	0.9351	0.9332	0.9313	0.9294	0.9276
200	0.9511	0.9490	0.9470	0.9450	0.9430	0.9410	0.9391	0.9372
220	0.9615	0.9594	0.9573	0.9552	0.9531	0.9511	0.9490	0.9471
240	0.9724	0.9701	0.9679	0.9657	0.9635	0.9614	0.9593	0.9572
260	0.9836	0.9812	0.9788	0.9765	0.9742	0.9720	0.9698	0.9676
280	0.9952	0.9927	0.9902	0.9877	0.9853	0.9829	0.9806	0.9783
300	1.0072	1.0045	1.0019	0.9993	0.9967	0.9942	0.9918	0.9893
320	1.0196	1.0167	1.0139	1.0112	1.0085	1.0058	1.0032	1.0007
340	1.0324	1.0294	1.0264	1.0235	1.0207	1.0179	1.0151	1.0124
360	1.0457	1.0425	1.0393	1.0362	1.0332	1.0302	1.0273	1.0245
380	1.0595	1.0560	1.0527	1.0494	1.0462	1.0430	1.0399	1.0369
400	1.0737	1.0700	1.0664	1.0629	1.0595	1.0562	1.0529	1.0497
420	1.0883	1.0844	1.0806	1.0769	1.0733	1.0698	1.0663	1.0629
440	1.1034	1.0993	1.0953	1.0913	1.0875	1.0837	1.0801	1.0765
460	1.1190	1.1146	1.1103	1.1061	1.1021	1.0981	1.0942	1.0904
480	1.1350	1.1303	1.1258	1.1214	1.1171	1.1129	1.1087	1.1047
500	1.1515	1.1465	1.1417	1.1370	1.1324	1.1280	1.1236	1.1194
520	1.1683	1.1630	1.1579	1.1530	1.1481	1.1434	1.1388	1.1343
540	1.1855	1.1800	1.1746	1.1693	1.1642	1.1592	1.1544	1.1496
560	1.2032	1.1973	1.1915	1.1860	1.1806	1.1753	1.1702	1.1652
580	1.2212	1.2149	1.2089	1.2030	1.1973	1.1918	1.1864	1.1811
600	1.2395	1.2329	1.2265	1.2203	1.2143	1.2085	1.2028	1.1973
620	1.2582	1.2512	1.2445	1.2380	1.2316	1.2255	1.2195	1.2137
640	1.2772	1.2699	1.2628	1.2559	1.2493	1.2428	1.2365	1.2304
660	1.2966	1.2889	1.2814	1.2742	1.2672	1.2604	1.2538	1.2474
680	1.3164	1.3082	1.3004	1.2928	1.2854	1.2783	1.2713	1.2646
700	1.3365	1.3279	1.3196	1.3117	1.3039	1.2964	1.2892	1.2821
720	1.3569	1.3479	1.3392	1.3309	1.3228	1.3149	1.3073	1.2999
740	1.3777	1.3683	1.3592	1.3504	1.3419	1.3337	1.3257	1.3180
760	1.3988	1.3889	1.3794	1.3702	1.3613	1.3527	1.3444	1.3363
780	1.4203	1.4099	1.3999	1.3903	1.3810	1.3720	1.3633	1.3549
800	1.4420	1.4311	1.4207	1.4106	1.4009	1.3915	1.3824	1.3736
820	1.4639	1.4526	1.4417	1.4312	1.4210	1.4112	1.4018	1.3926
840	1.4859	1.4741	1.4627	1.4517	1.4412	1.4310	1.4211	1.4116
860	1.5079	1.4955	1.4837	1.4723	1.4613	1.4507	1.4405	1.4306
880	1.5296	1.5168	1.5045	1.4926	1.4813	1.4703	1.4597	1.4494
900	1.5509	1.5376	1.5248	1.5126	1.5008	1.4894	1.4785	1.4680

used to obtain specific volumes on orthogonal coordinates in the temperature range 250° to 900°C and the pressure range 1000 to 2000 bars. Second, the differences in specific volume at 20° intervals along each 100-bar isobar were computed and graphed versus temperature to obtain smoothed curves of $(\Delta V/\Delta T)_P$. Third, these curves were cross-smoothed and interpolated, where necessary, along isotherms between 1000 (data from the Natl. Engineering Lab. Steam Tables 1964) and 2000 bars. These smoothed values of $(\Delta V/\Delta T)_P$ were then used to compute specific volumes at 20° intervals relative to a reference specific volume on each 100-bar isobar that was calculated by equation (10), outside the wedge-shaped area.

The combined calculated and measured specific volumes, together with the 900- and 1000-bar data above 410°C from the Natl. Engineering

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

	PRESSURE IN BARS							
TEMP	5800	5900	6000	6100	6200	6300	6400	6500
20	0.8584	0.8570	0.8556	0.8543	0.8530	0.8517	0.8504	0.8491
40	0.8662	0.8648	0.8633	0.8619	0.8605	0.8592	0.8579	0.8566
60	0.8741	0.8726	0.8711	0.8696	0.8682	0.8668	0.8655	0.8641
80	0.8821	0.8805	0.8790	0.8775	0.8761	0.8747	0.8732	0.8719
100	0.8903	0.8887	0.8872	0.8857	0.8842	0.8827	0.8812	0.8798
120	0.8988	0.8972	0.8956	0.8940	0.8925	0.8910	0.8895	0.8880
140	0.9076	0.9059	0.9042	0.9026	0.9010	0.8995	0.8979	0.8964
160	0.9166	0.9148	0.9131	0.9115	0.9098	0.9082	0.9066	0.9050
180	0.9258	0.9240	0.9223	0.9205	0.9188	0.9171	0.9155	0.9138
200	0.9353	0.9335	0.9316	0.9298	0.9281	0.9263	0.9246	0.9229
220	0.9451	0.9432	0.9413	0.9394	0.9375	0.9357	0.9339	0.9321
240	0.9551	0.9531	0.9511	0.9492	0.9472	0.9453	0.9435	0.9416
260	0.9654	0.9633	0.9612	0.9592	0.9572	0.9552	0.9532	0.9513
280	0.9761	0.9738	0.9716	0.9695	0.9674	0.9653	0.9632	0.9612
300	0.9870	0.9846	0.9823	0.9801	0.9778	0.9757	0.9735	0.9714
320	0.9982	0.9957	0.9933	0.9909	0.9886	0.9863	0.9840	0.9818
340	1.0098	1.0072	1.0046	1.0021	0.9996	0.9972	0.9949	0.9925
360	1.0217	1.0189	1.0162	1.0136	1.0110	1.0085	1.0060	1.0035
380	1.0340	1.0311	1.0282	1.0254	1.0227	1.0200	1.0174	1.0148
400	1.0466	1.0435	1.0405	1.0376	1.0347	1.0319	1.0291	1.0263
420	1.0596	1.0564	1.0532	1.0501	1.0470	1.0440	1.0411	1.0382
440	1.0730	1.0696	1.0662	1.0629	1.0597	1.0565	1.0534	1.0504
460	1.0867	1.0831	1.0796	1.0761	1.0727	1.0693	1.0661	1.0629
480	1.1008	1.0970	1.0932	1.0896	1.0860	1.0824	1.0790	1.0756
500	1.1152	1.1112	1.1072	1.1033	1.0995	1.0958	1.0922	1.0886
520	1.1300	1.1257	1.1215	1.1174	1.1134	1.1095	1.1057	1.1019
540	1.1450	1.1405	1.1361	1.1318	1.1276	1.1234	1.1194	1.1154
560	1.1604	1.1556	1.1510	1.1464	1.1420	1.1376	1.1334	1.1292
580	1.1760	1.1710	1.1661	1.1613	1.1566	1.1521	1.1476	1.1432
600	1.1919	1.1866	1.1815	1.1764	1.1715	1.1667	1.1620	1.1574
620	1.2080	1.2025	1.1971	1.1918	1.1867	1.1816	1.1767	1.1719
640	1.2244	1.2186	1.2130	1.2074	1.2020	1.1967	1.1916	1.1865
660	1.2411	1.2350	1.2291	1.2233	1.2176	1.2121	1.2067	1.2014
680	1.2580	1.2517	1.2454	1.2394	1.2334	1.2277	1.2220	1.2165
700	1.2752	1.2686	1.2621	1.2557	1.2495	1.2434	1.2375	1.2317
720	1.2927	1.2857	1.2789	1.2723	1.2658	1.2595	1.2533	1.2472
740	1.3104	1.3031	1.2960	1.2891	1.2823	1.2757	1.2693	1.2629
760	1.3284	1.3208	1.3134	1.3061	1.2991	1.2922	1.2854	1.2789
780	1.3467	1.3387	1.3309	1.3234	1.3160	1.3088	1.3018	1.2950
800	1.3651	1.3568	1.3487	1.3408	1.3332	1.3257	1.3184	1.3113
820	1.3837	1.3750	1.3666	1.3584	1.3505	1.3427	1.3351	1.3277
840	1.4023	1.3934	1.3846	1.3761	1.3679	1.3598	1.3520	1.3443
860	1.4210	1.4117	1.4027	1.3939	1.3853	1.3770	1.3689	1.3609
880	1.4395	1.4299	1.4206	1.4115	1.4027	1.3941	1.3858	1.3776
900	1.4577	1.4479	1.4383	1.4290	1.4199	1.4111	1.4025	1.3942

Lab. Steam Tables 1964, were finally fitted by an eighth degree polynomial of the following form:

$$PV = \sum_{j=0}^{8} \sum_{i=0}^{8-j} a_{ij} T^i P^j \qquad (11)$$

This equation fits all the values used within 0.08 percent (one standard deviation) and the measured specific volumes within 0.16 percent. Equation (11) was then used in conjunction with equation (10) to calculate all the specific volumes tabulated in table 1.

The actual deviations of the measured specific volumes from the smooth P–V–T surface defined by equations (10) and (11) are shown in figure 3. The deviations of all the data points within ± 10°C of the 100°,

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

TEMP	PRESSURE IN BARS 6600	6700	6800	6900	7000	7100	7200	7300
20	0.8479	0.8467	0.8454	0.8442	0.8431	0.8419	0.8407	0.8395
40	0.8553	0.8540	0.8528	0.8515	0.8503	0.8491	0.8479	0.8467
60	0.8628	0.8615	0.8602	0.8590	0.8577	0.8565	0.8553	0.8540
80	0.8705	0.8692	0.8678	0.8665	0.8652	0.8640	0.8627	0.8615
100	0.8784	0.8770	0.8757	0.8743	0.8730	0.8717	0.8704	0.8691
120	0.8865	0.8851	0.8837	0.8823	0.8809	0.8796	0.8783	0.8769
140	0.8949	0.8934	0.8919	0.8905	0.8891	0.8877	0.8863	0.8850
160	0.9034	0.9019	0.9004	0.8989	0.8975	0.8960	0.8946	0.8932
180	0.9122	0.9106	0.9091	0.9075	0.9060	0.9045	0.9030	0.9016
200	0.9212	0.9196	0.9179	0.9163	0.9147	0.9132	0.9116	0.9101
220	0.9304	0.9287	0.9270	0.9253	0.9237	0.9220	0.9204	0.9189
240	0.9398	0.9380	0.9362	0.9345	0.9328	0.9311	0.9294	0.9278
260	0.9494	0.9475	0.9457	0.9439	0.9421	0.9403	0.9386	0.9369
280	0.9592	0.9573	0.9554	0.9535	0.9516	0.9498	0.9479	0.9462
300	0.9693	0.9673	0.9652	0.9633	0.9613	0.9594	0.9575	0.9556
320	0.9796	0.9775	0.9754	0.9733	0.9713	0.9692	0.9673	0.9653
340	0.9902	0.9880	0.9857	0.9836	0.9814	0.9793	0.9772	0.9752
360	1.0011	0.9987	0.9964	0.9941	0.9918	0.9896	0.9874	0.9853
380	1.0122	1.0097	1.0073	1.0049	1.0025	1.0002	0.9979	0.9956
400	1.0237	1.0210	1.0184	1.0159	1.0134	1.0110	1.0085	1.0062
420	1.0354	1.0326	1.0299	1.0272	1.0246	1.0220	1.0194	1.0169
440	1.0474	1.0445	1.0416	1.0388	1.0360	1.0333	1.0306	1.0280
460	1.0597	1.0566	1.0536	1.0506	1.0477	1.0448	1.0420	1.0392
480	1.0723	1.0690	1.0658	1.0627	1.0596	1.0566	1.0536	1.0507
500	1.0851	1.0817	1.0783	1.0750	1.0718	1.0686	1.0654	1.0624
520	1.0982	1.0946	1.0911	1.0876	1.0842	1.0808	1.0775	1.0743
540	1.1116	1.1077	1.1040	1.1004	1.0968	1.0932	1.0898	1.0864
560	1.1251	1.1211	1.1172	1.1134	1.1096	1.1059	1.1022	1.0987
580	1.1389	1.1347	1.1306	1.1266	1.1226	1.1187	1.1149	1.1111
600	1.1529	1.1485	1.1442	1.1400	1.1358	1.1317	1.1277	1.1238
620	1.1672	1.1625	1.1580	1.1536	1.1492	1.1449	1.1407	1.1366
640	1.1816	1.1767	1.1720	1.1673	1.1628	1.1583	1.1539	1.1496
660	1.1962	1.1911	1.1862	1.1813	1.1765	1.1719	1.1673	1.1628
680	1.2110	1.2057	1.2006	1.1955	1.1905	1.1856	1.1808	1.1761
700	1.2261	1.2205	1.2151	1.2098	1.2046	1.1995	1.1945	1.1896
720	1.2413	1.2355	1.2299	1.2243	1.2189	1.2136	1.2084	1.2032
740	1.2568	1.2507	1.2448	1.2391	1.2334	1.2278	1.2224	1.2171
760	1.2724	1.2661	1.2600	1.2540	1.2481	1.2423	1.2366	1.2311
780	1.2883	1.2817	1.2753	1.2690	1.2629	1.2569	1.2510	1.2452
800	1.3043	1.2975	1.2908	1.2843	1.2779	1.2717	1.2655	1.2595
820	1.3205	1.3134	1.3065	1.2997	1.2931	1.2866	1.2802	1.2740
840	1.3368	1.3295	1.3223	1.3153	1.3084	1.3017	1.2951	1.2887
860	1.3532	1.3456	1.3382	1.3310	1.3239	1.3170	1.3102	1.3035
880	1.3696	1.3618	1.3542	1.3468	1.3395	1.3323	1.3253	1.3185
900	1.3860	1.3780	1.3703	1.3626	1.3552	1.3479	1.3407	1.3337

400°, and 700°C isotherms are shown in figure 3A, and it is evident that most of them are within ± 0.1 percent of the surface. That the scatter of data points about the surface near these isotherms is representative is clearly indicated by the histogram of figure 3B, which includes all the measured specific volumes above 1000 bars used to construct table 1. It is especially noteworthy that only 2 out of 726 data points deviate as much as 0.4 percent from the P-V-T surface.

Comparison with previous work

Extensive measurements have been made of the P-V-T properties of water, but only a small percentage of them overlap the P-T region covered in table 1. Perhaps the most accurate determinations made thus far are those of Kell and Whalley (1965) which extend only to 1000 bars

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

	PRESSURE IN BARS							
TEMP	7400	7500	7600	7700	7800	7900	8000	8100
20	0.8383	0.8371	0.8359	0.8347	0.8335	0.8323	0.8311	0.8299
40	0.8455	0.8444	0.8432	0.8420	0.8408	0.8397	0.8385	0.8373
60	0.8528	0.8516	0.8505	0.8493	0.8481	0.8469	0.8458	0.8446
80	0.8603	0.8591	0.8578	0.8566	0.8555	0.8543	0.8531	0.8519
100	0.8679	0.8666	0.8654	0.8642	0.8629	0.8617	0.8605	0.8593
120	0.8756	0.8744	0.8731	0.8718	0.8706	0.8693	0.8681	0.8669
140	0.8836	0.8823	0.8810	0.8797	0.8784	0.8771	0.8758	0.8746
160	0.8918	0.8904	0.8890	0.8877	0.8863	0.8850	0.8837	0.8824
180	0.9001	0.8987	0.8973	0.8959	0.8945	0.8931	0.8917	0.8904
200	0.9086	0.9071	0.9057	0.9042	0.9028	0.9013	0.8999	0.8985
220	0.9173	0.9158	0.9142	0.9127	0.9112	0.9097	0.9083	0.9068
240	0.9262	0.9245	0.9230	0.9214	0.9198	0.9183	0.9168	0.9153
260	0.9352	0.9335	0.9319	0.9302	0.9286	0.9270	0.9254	0.9239
280	0.9444	0.9426	0.9409	0.9392	0.9375	0.9359	0.9342	0.9326
300	0.9538	0.9520	0.9502	0.9484	0.9466	0.9449	0.9432	0.9415
320	0.9634	0.9615	0.9596	0.9577	0.9559	0.9541	0.9523	0.9505
340	0.9732	0.9712	0.9692	0.9673	0.9653	0.9635	0.9616	0.9597
360	0.9832	0.9811	0.9790	0.9770	0.9750	0.9730	0.9710	0.9691
380	0.9934	0.9912	0.9890	0.9869	0.9848	0.9827	0.9806	0.9786
400	1.0038	1.0015	0.9992	0.9970	0.9948	0.9926	0.9904	0.9883
420	1.0145	1.0121	1.0097	1.0073	1.0050	1.0027	1.0004	0.9982
440	1.0254	1.0228	1.0203	1.0178	1.0154	1.0130	1.0106	1.0082
460	1.0365	1.0338	1.0311	1.0285	1.0260	1.0234	1.0209	1.0184
480	1.0478	1.0450	1.0422	1.0394	1.0367	1.0341	1.0314	1.0288
500	1.0593	1.0564	1.0534	1.0505	1.0477	1.0449	1.0421	1.0394
520	1.0711	1.0679	1.0649	1.0618	1.0588	1.0559	1.0530	1.0501
540	1.0830	1.0797	1.0765	1.0733	1.0701	1.0670	1.0640	1.0610
560	1.0951	1.0917	1.0883	1.0849	1.0816	1.0784	1.0752	1.0720
580	1.1074	1.1038	1.1002	1.0967	1.0933	1.0899	1.0865	1.0832
600	1.1199	1.1161	1.1124	1.1087	1.1051	1.1015	1.0980	1.0945
620	1.1326	1.1286	1.1247	1.1208	1.1170	1.1133	1.1096	1.1060
640	1.1454	1.1412	1.1371	1.1331	1.1292	1.1253	1.1214	1.1176
660	1.1583	1.1540	1.1497	1.1455	1.1414	1.1374	1.1334	1.1294
680	1.1715	1.1669	1.1625	1.1581	1.1538	1.1496	1.1454	1.1413
700	1.1848	1.1800	1.1754	1.1708	1.1664	1.1619	1.1576	1.1533
720	1.1982	1.1933	1.1885	1.1837	1.1790	1.1744	1.1699	1.1655
740	1.2118	1.2067	1.2017	1.1967	1.1919	1.1871	1.1824	1.1778
760	1.2256	1.2203	1.2150	1.2099	1.2048	1.1998	1.1950	1.1902
780	1.2395	1.2340	1.2285	1.2232	1.2179	1.2128	1.2077	1.2027
800	1.2536	1.2479	1.2422	1.2366	1.2312	1.2258	1.2205	1.2154
820	1.2679	1.2619	1.2560	1.2503	1.2446	1.2390	1.2336	1.2282
840	1.2823	1.2761	1.2700	1.2641	1.2582	1.2524	1.2468	1.2412
860	1.2969	1.2905	1.2842	1.2781	1.2720	1.2661	1.2602	1.2545
880	1.3118	1.3052	1.2987	1.2923	1.2861	1.2799	1.2739	1.2680
900	1.3268	1.3200	1.3134	1.3069	1.3005	1.2942	1.2880	1.2819

and 150°C. Because of this limited overlap, and the fact that their low temperature data were used in the calibration of the present apparatus, a comparison would not be very informative.

Similarly, a comparison with the work of Holser and Kennedy (1958, 1959) at 1000 bars would have little value because the Natl. Engineering Lab. Steam Tables 1964 (Bain, 1964), which were used in the present work, are based largely on their data, especially at temperatures above 400°C. At 1400 bars, however, the equations on which table 1 is based are essentially unaffected by the 1000-bar data. Therefore, the 1400-bar values of table 1 are compared in figure 4 with those of Kennedy, Knight, and Holser (1958) and Holser and Kennedy (1958, 1959) in terms of the percentage deviation of their specific volumes from those in table 1. A majority of the deviations, although generally negative and

SPECIFIC VOLUME IN CUBIC CENTIMETERS PER GRAM

TEMP	PRESSURE IN BARS 8200	8300	8400	8500	8600	8700	8800	8900
20	0.8287	0.8275	0.8262	0.8250	0.8238	0.8226	(0.8214)	(0.8202
40	0.8361	0.8350	0.8338	0.8326	0.8315	0.8303	0.8292	0.8281
60	0.8435	0.8423	0.8412	0.8400	0.8389	0.8378	0.8367	0.8356
80	0.8508	0.8496	0.8485	0.8473	0.8462	0.8451	0.8440	0.8429
100	0.8582	0.8570	0.8558	0.8547	0.8535	0.8524	0.8513	0.8502
120	0.8657	0.8645	0.8633	0.8621	0.8609	0.8598	0.8586	0.8575
140	0.8733	0.8721	0.8708	0.8696	0.8684	0.8672	0.8660	0.8648
160	0.8811	0.8798	0.8785	0.8773	0.8760	0.8748	0.8735	0.8723
180	0.8890	0.8877	0.8864	0.8851	0.8838	0.8825	0.8812	0.8799
200	0.8971	0.8958	0.8944	0.8930	0.8917	0.8903	0.8890	0.8877
220	0.9054	0.9039	0.9025	0.9011	0.8997	0.8983	0.8969	0.8955
240	0.9138	0.9123	0.9108	0.9093	0.9079	0.9064	0.9050	0.9035
260	0.9223	0.9207	0.9192	0.9177	0.9162	0.9147	0.9132	0.9117
280	0.9310	0.9294	0.9278	0.9262	0.9246	0.9230	0.9215	0.9199
300	0.9398	0.9381	0.9365	0.9348	0.9332	0.9315	0.9299	0.9283
320	0.9488	0.9470	0.9453	0.9436	0.9419	0.9402	0.9385	0.9368
340	0.9579	0.9561	0.9543	0.9525	0.9507	0.9489	0.9472	0.9454
360	0.9672	0.9653	0.9634	0.9615	0.9596	0.9578	0.9559	0.9541
380	0.9766	0.9746	0.9726	0.9707	0.9687	0.9668	0.9649	0.9629
400	0.9862	0.9841	0.9820	0.9800	0.9779	0.9759	0.9739	0.9719
420	0.9960	0.9938	0.9916	0.9894	0.9873	0.9851	0.9830	0.9809
440	1.0059	1.0036	1.0013	0.9990	0.9968	0.9945	0.9923	0.9901
460	1.0160	1.0135	1.0111	1.0088	1.0064	1.0040	1.0017	0.9994
480	1.0262	1.0237	1.0211	1.0186	1.0162	1.0137	1.0112	1.0088
500	1.0367	1.0340	1.0313	1.0287	1.0261	1.0235	1.0209	1.0183
520	1.0472	1.0444	1.0416	1.0389	1.0361	1.0334	1.0307	1.0280
540	1.0580	1.0550	1.0521	1.0492	1.0463	1.0435	1.0406	1.0378
560	1.0689	1.0658	1.0627	1.0597	1.0567	1.0537	1.0507	1.0478
580	1.0799	1.0767	1.0735	1.0703	1.0671	1.0640	1.0609	1.0578
600	1.0911	1.0877	1.0844	1.0811	1.0778	1.0745	1.0713	1.0681
620	1.1024	1.0989	1.0954	1.0920	1.0885	1.0851	1.0818	1.0784
640	1.1139	1.1102	1.1066	1.1030	1.0994	1.0959	1.0924	1.0889
660	1.1255	1.1217	1.1179	1.1141	1.1104	1.1068	1.1031	1.0995
680	1.1373	1.1333	1.1293	1.1254	1.1216	1.1178	1.1140	1.1103
700	1.1491	1.1450	1.1409	1.1368	1.1328	1.1289	1.1250	1.1211
720	1.1611	1.1568	1.1525	1.1483	1.1442	1.1401	1.1361	1.1320
740	1.1732	1.1687	1.1643	1.1600	1.1557	1.1514	1.1472	1.1431
760	1.1854	1.1808	1.1762	1.1717	1.1673	1.1629	1.1585	1.1542
780	1.1978	1.1930	1.1882	1.1835	1.1789	1.1744	1.1699	1.1654
800	1.2103	1.2053	1.2004	1.1955	1.1907	1.1860	1.1814	1.1768
820	1.2229	1.2177	1.2126	1.2076	1.2027	1.1978	1.1930	1.1882
840	1.2358	1.2304	1.2251	1.2199	1.2148	1.2097	1.2047	1.1998
860	1.2488	1.2433	1.2378	1.2324	1.2271	1.2219	1.2167	1.2116
880	1.2622	1.2564	1.2508	1.2452	1.2398	1.2344	1.2290	1.2238
900	1.2760	1.2701	1.2643	1.2585	1.2529	1.2473	1.2418	1.2364

outside the 0.1 percent fit of equations (10) and (11), are within the stated 0.3 percent accuracy of table 1. It must be borne in mind, however, that 1400 bars is the upper pressure limit of their work, and the negative character of the deviations may have arisen through the necessity for Holser and Kennedy (1958, p. 745) to make a comparatively large and uncertain correction for the elastic dilation of their unsupported containers. In the present work, on the other hand, it was necessary to make only a small correction for the compressibility of the cell material, as the cell was supported externally by a pressure equal to the internal water pressure.

The sharp peak in the relative deviations of Holser and Kennedy (1958, 1959) near 400°C (fig. 4) is best explained in terms of the curves for the isobaric thermal expansion of water ($\Delta V/\Delta T$) shown in figure 5.

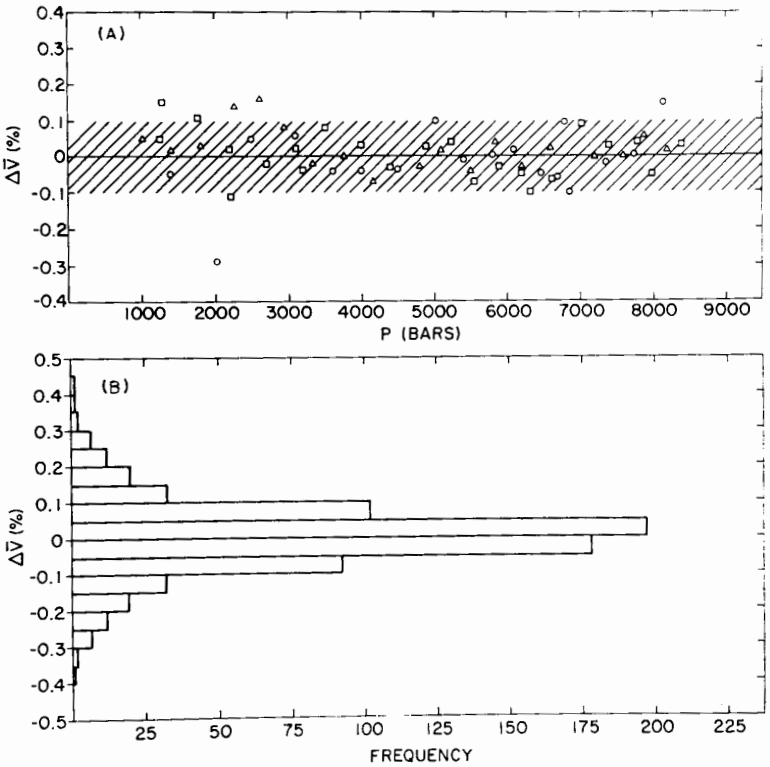

Fig. 3. Deviations of the measured specific volumes from the P-V-T surface defined by equations (10) and (11). (A) Percent deviations from the 100°C (triangles), 400°C (squares), and 700°C (circles) isotherms. (B) Histogram of deviations of all measured specific volumes from the P-V-T surface.

The values of table 1 are fitted very closely by a smooth curve, but those from tables given by Holser and Kennedy are not. That the inflection in the curve produced by their data actually does not exist at 1400 bars is evident by its absence from their 1000-bar data, as also shown in figure 5. Thus, it appears that their tabulated specific volumes contain minor inconsistencies at 1400 bars, between 360° and 500°C; furthermore, these inconsistencies probably resulted from their reliance on ". . . Kirillin's extensive data . . ." (Holser and Kennedy, 1958, p. 749) for the 380° and 400°C isotherms.

It also is noteworthy that, according to the 1000-bar curve in figure 5, minor inconsistencies also exist in the Natl. Engineering Lab. Steam Tables 1964 (Bain, 1964, p. 136) between 300° and 350°C. These inconsistencies give rise to tabulated specific volumes that appear to be high by as much as 0.004 $cm^3\ gm^{-1}$ at 340°C, 1000 bars.

Maier and Franck (1966) reported density measurements on water in the range 200° to 850°C, 1000 to 6000 bars, but the precision claimed by them, in terms of average deviation, is only 1.0 percent. Their tabu-

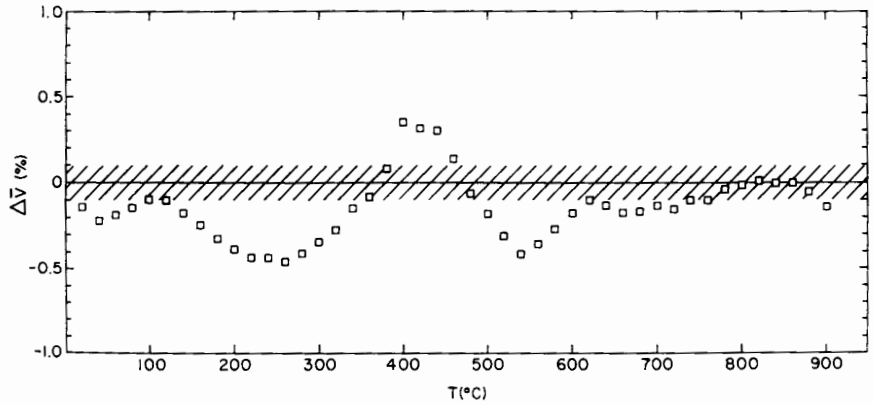

Fig. 4. Percent deviation from table 1 of the specific volumes at 1400 bars tabulated in Kennedy, Knight, and Holser (1958, 20°-100°C), Holser and Kennedy (1958, 120°-400°C), and Holser and Kennedy (1959, 420°-900°C). The fit of equations (10) and (11) to the measured specific volumes is indicated by the width of the shaded band (± 0.1 percent).

lated values were obtained by fitting a sixth degree polynomial in density as a function of P and T to about 200 data points, many of which were almost duplicate determinations. Except for the 500°, 600°, and 700°C isotherms below 2000 bars, their tabulated specific volumes are all smaller than those in table 1 by 0.4 to 1.1 percent up to 4500 bars. At higher pressures, the negative deviations from table 1 increase to a maximum of 3.0 percent at 800°C and 6000 bars.

The generally negative deviation, as well as the scatter, of the tabulated data of Maier and Franck relative to those of table 1 are illustrated, in terms of isobaric (6000 bars) thermal expansion, in figure 6. The discrepancies shown here are most readily ascribed to the corrections applied by Maier and Franck (1966, p. 642) for the elastic, as well as permanent, deformation of the pressure vessel containing the water at high temperatures and pressures. It would appear to be an extremely difficult task to correct accurately for permanent deformation, even if the amount of such deformation were known as a function of pressure and temperature.

A comparison with the recently published tables of Kennedy and Holser (1966) will not be made here because many of the measurements upon which these tables are based apparently were preliminary in nature (W. T. Holser, personal commun., 1967). The previously published data of Holser and Kennedy (1958, 1959) are internally more consistent below 1000 bars, as are the data in table 1 above 1000 bars. Similarly, a comparison will not be made here with the tables of Sharp (1962), as they are based in large part on data from the sources used by Kennedy and Holser (1966).

The early work of Bridgman (1912b) is compared in figure 7 with the present results in terms of deviation of his tabulated data for the

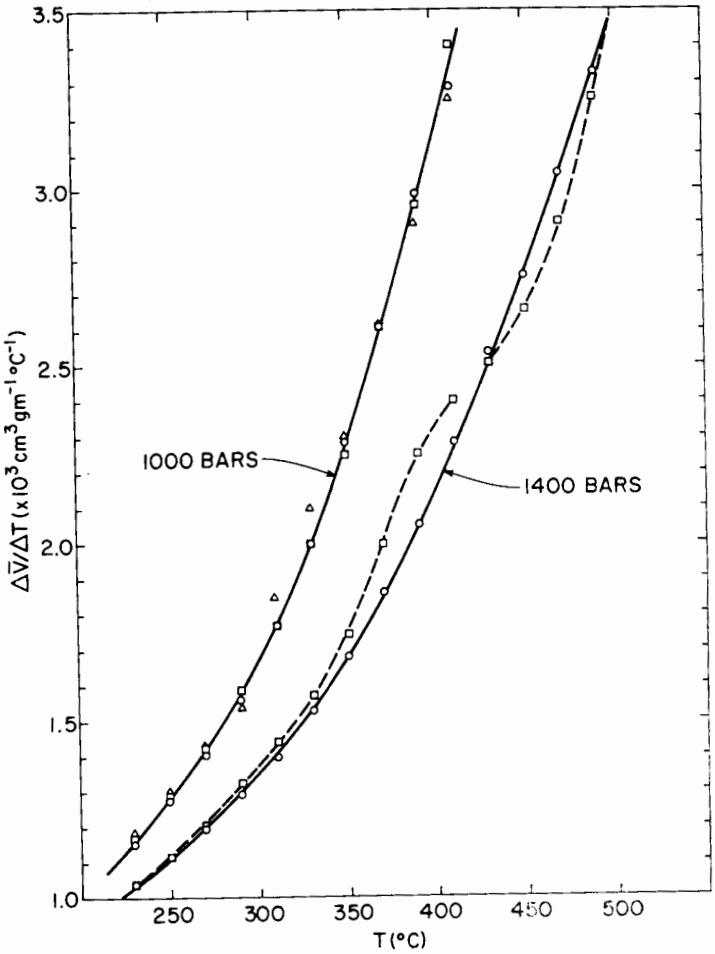

Fig. 5. The thermal expansion of water at 1000 and 1400 bars. The circles represent values from table 1, the squares are from Holser and Kennedy (1958, 1959), and the triangles are from the Natl. Engineering Lab. Steam Tables 1964 (Bain, 1964).

40°C isotherm from those of table 1. In making this comparison, Bridgman's pressures were adjusted to the presently accepted value for the freezing point of mercury at 0°C of 7715.6 kg cm^{-2} (Newhall, Abbott, and Dunn, 1962), instead of 7640 kg cm^{-2} (Bridgman, 1912a). The deviations, as in previous comparisons, are negative, and it is again suggested that they are due primarily to the correction applied by Bridgman for the elastic dilation of his pressure vessels. This hypothesis is supported by a comparison, also in figure 7, with his later determinations (Bridgman, 1935), in which he used a bellows to contain the water inside the pressure vessel. It is apparent from the 40°C isotherms shown in figure 7 that elimination of the elastic dilation factor brings Bridgman's

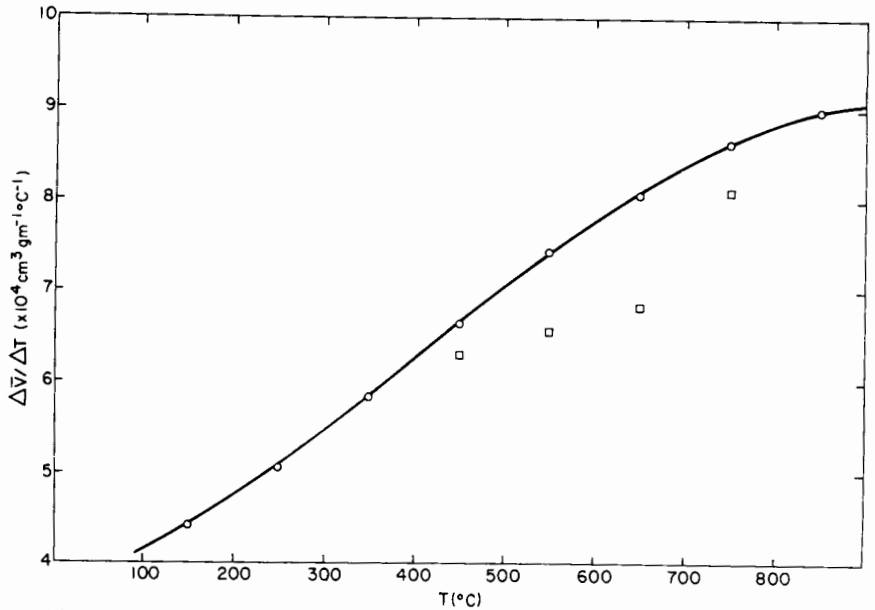

Fig. 6. The thermal expansion of water at 6000 bars. The circles represent values from table 1, and the squares are from Maier and Franck (1966).

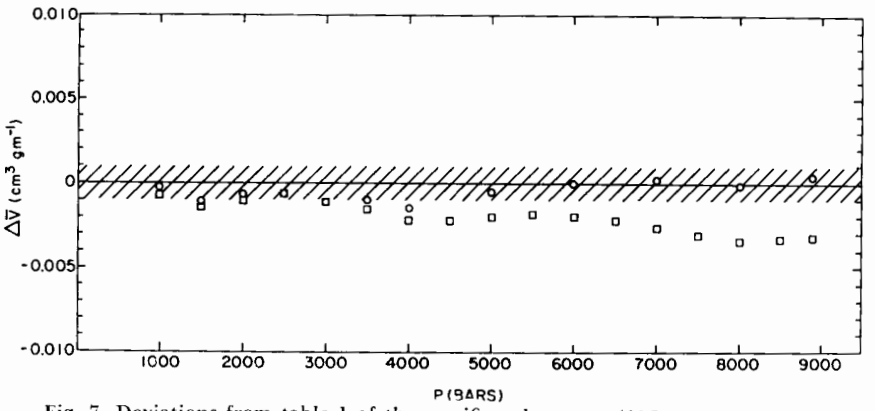

Fig. 7. Deviations from table 1 of the specific volumes at 40°C tabulated in Bridgman (1912b, squares) and Bridgman (1935, circles). The fit of equation (10) to the measured specific volumes is indicated by the width of the shaded band (± 0.001 cm^3gm^{-1}).

data into good agreement with those of table 1. The agreement with the measured specific volumes is even better, as they also deviate from the data in table 1 by as much as -0.001 cm^3 gm^{-1} in the same pressure interval where the deviations of Bridgman's values are greatest.

The very good agreement of the specific volumes measured here with the low-pressure, high-temperature data in the Natl. Engineering

Lab. Steam Tables 1964 (Bain, 1964) and with the low-temperature, high-pressure data of Bridgman (1935) suggests that the earlier estimate of uncertainty in the specific volumes of table 1 is conservative. Although evaluation of the potential sources or error yields an estimated uncertainty of $\pm$ 0.3 percent, the agreement with previous work near the extremes in both temperature and pressure suggests an overall uncertainty closer to $\pm$ 0.2 percent in specific volume.

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