Density, Thermal Expansivity, and Compressibility of Liquid Water from 0° to 150°C: Correlations and Tables for Atmospheric Pressure and Saturation Reviewed and Expressed on 1968 Temperature Scale

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A review is given of the temperature dependence of the density of liquid water from 40° to 150°C. The inclusion of new literature data indicates that most previous correlations have been 10 ppm low at 70–80°C. An expression is derived, Equation 16, expressed on the IPTS-68 and valid from 0° to 150°C, that is in improved agreement with most data sets. Recent literature values of the velocity of sound permit the calculation of more reliable isothermal compressibilities. The errors of these compressibilities, from velocity of sound, density, thermal expansivity, and specific heat, are examined, and the error in the calculated compressibilities is estimated as 0.3 × 10^{-9} bar^{-1} at 4°C and as 7 × 10^{-9} bar^{-1} at 100°C. This paper supersedes two papers previously given by the same author.

The revision of correlating and interpolating equations, and of estimated best values and their errors, must be repeated whenever standards are modified or a significant addition is made to the pool of experimental data. At atmospheric pressure (=1.01325 bar), the volume or density, the thermal expansivity, and the compressibility are among the properties of liquid water that are known with sufficient precision for the introduction of the 1968 International Practical Temperature Scale (*12*) to make it necessary to reexpress them in terms of the new scale. For example, at 60°C on the IPTS-68, the density of liquid water is 5 ppm (parts per million) less than at 60°C on the IPTS-48. In addition, new density data reaching 80°C have been presented by Gildseth et al. (*21*), and extensive new data on the velocity of sound by Del Grosso and Mader (*18*). It seems desirable to reevaluate the experimental data, to express them on the IPTS-68, and to reconsider the computational problems arising in fitting the data by least squares.

There has been no unanimity among correlators about the experimental density data to be taken as most reliable. Bigg (*7*) reanalyzed the data for the range from 0° to 40°C of both Chappuis (*9*) and Thiesen et al. (*42*), and intercomparisons of the tables for this range have been made by Menaché and Girard (*36*); the agreement between tables is to about ±4 ppm. At higher temperatures the uncertainty increases. Indeed, although the new data of Gildseth et al. (*21*) help resolve a previous inconsistency near 80°C, a consequence of the increased attention given in the last few years to thermometry and isotopic composition must be the recognition that the older experimental data are less reliable than was previously thought.

Published tables that use the IPTS-68 are that of Wagenbreth and Blanke (*45*) from 0° to 40°C, and that of Aleksandrov and Trakhtengerts (*1*), which extends to 100°C. The latter authors give higher weight to the data of Owen et al. (*38*) than is done in the present paper. Aleksandrov and Trakhtengerts have also given a table of the isothermal compressibility as determined from velocity of sound measurements (*2*). The present paper supersedes earlier papers on isothermal compressibility (*30*) and, so far as H_2O is concerned, on density and thermal expansion (*29*).

The isotopic composition of the water was not measured in any of the experimental studies so far cited. We will interpret the published "densities," for which the units of g ml^{-1} are given, as giving the relative density $\zeta = \rho/\rho_{\max}$ without assuming that $\rho_{\max}$ has always the same value. Although ζ changes faster with change of isotopic composition at 0°C and less at 100°C, its variation for water as ordinarily purified in different laboratories is small enough that different data sets have negligible inconsistencies arising from isotopic variations. Similarly, the use of ζ eliminates differences arising from different mean barometric pressures in different laboratories.

On the other hand, ρ itself varies approximately linearly with isotopic composition by an amount that cannot be neglected. In the decades before 1950, the maximum absolute density of water was often taken as

$$\rho_{\max} = 999.973 \text{ kg m}^{-3} \qquad (1)$$

while in 1950 this was revised (*39*) to

$$\rho_{\max} = 999.972 \text{ kg m}^{-3} \qquad (2)$$

with an uncertainty that it is perhaps 4 in the last place. The experimental work on which these numbers are based employed doubly distilled water and was done at the International Bureau of Weights and Measures before the discovery of isotopes. Girard and Menaché (*22*) have examined the isotopic composition of water at the International Bureau as purified by this method, measuring the content of both deuterium and ^{18}O, and conclude that the absolute density of standard mean ocean water, as defined by Craig (*16*), probably has the value

$$\rho_{\max} = 999.975 \text{ kg m}^{-3} \qquad (3)$$

While Equation 1 has been used where appropriate, e.g., with data such as that of Jones et al. (*28*), the tables of the present paper are based on the 999.972 of Equation 2. To avoid confusion, another value, such as that of Equation 3, should be adopted only by general agreement.

Changes of temperature scale. The first temperature scale adopted by international agreement was the *Échelle Normale*, defined between 0° and 100°C, based on the hydrogen scale, and with interpolation employing mercury-in-glass (*verre dur*) thermometers. It was on this scale that the measurements of Chappuis (*9*) and Thiesen et al. (*41, 42*) were made. The platinum resistance thermometer was used as the interpolating instrument for the International Temperature Scale of 1927 (*13*), and this scale agreed with the thermodynamic temperature scale as then realized. Hall (*25*) showed that, although individual mercury-in-glass thermometers conforming to the Échelle Normale might differ from each other by as much as 0.02°C, the mean of 15 thermometers did not differ from the ITS-27 by more than 0.002°C in the range 0–50°C.

The temperature scale was revised again in 1948 to give the International Temperature Scale of 1948 (*14*). Temperatures in the range from 0° to 630°C did not change, but the freezing point of water was replaced as a fixed point by the triple point; the text was revised in 1960, again without changing temperatures in this range, and this 1960 version is called the International Practical Temperature Scale of 1948 (IPTS-48) (*15*). Knowledge of the absolute scale had meanwhile improved, and the IPTS-48 was known to differ from the thermodynamic scale. With the IPTS-68, introduced in January 1969 (*12*), the platinum resistance thermometer remains the interpolating instrument in this range, but a new interpolating formula is used to reproduce the thermodynamic scale as realized at the time of its adoption.

The IPTS-68 left the boiling point of water unchanged at 100°C (=373.15K), but recent work at the U.S. National Bureau of Standards (*23, 24*) suggests that the boiling point of water is about 0.03K lower than that value. In the present paper we employ the IPTS-68 with no modification.

Temperatures on the IPTS-48 can be easily converted to the IPTS-68, or vice versa, using equations given by Bedford and Kirby (*6*). Between 0° and 630°C we have

$$t_{68} = t_{48} + w(t) + z(t) \tag{4}$$

where t is the Celsius temperature and where $w(t)$, giving the adjustment that must be made to a quadratic interpolation formula to give a scale paralleling the absolute one, is given by

$$w(t) = 0.00045\, t(t/100 - 1) \times (t/419.58 - 1) \times (t/630.74 - 1) \tag{5}$$

and $z(t)$, giving the change owing to the redefinition of the zinc point on the IPTS-68, is given by

$$z(t) = \frac{4.9035 \times 10^{-5}\, t(t/100 - 1)}{1 - 2.94855 \times 10^{-4}\, t} \tag{6}$$

For the range of temperatures considered here, both w and z are small enough that their arguments may be either t_{68} or t_{48} without loss of precision. For temperatures below 0°C, Equation 4 is no longer exact, but it is close enough for all the data considered here.

The change of temperature scales does not, of course, change the density of water, but it does change the density for a given number representing the temperature. For data at atmospheric pressure, the adjustment $\Delta\rho$ to be added to the density given in a table employing the IPTS-48 to give the density on the IPTS-68 at the temperature given by the same number is given by

$$\Delta\rho = \rho_{68} - \rho_{48} = -(\partial\rho/\partial t)_P \Delta t \tag{7}$$

where the minus sign appears because the ρ's relate to different temperatures while the t's relate to different scale readings for the same temperature, and where $\Delta t = t_{68} - t_{48}$ is the difference in the two scales at the same temperature. The magnitude of $\Delta\rho$, a maximum of 5 ppm between 0° and 100°C, is sufficiently small that, even if ρ is wanted to 10^{-4} kg m^{-3}, different sources of data agree on values of $(\partial\rho/\partial t)_P$ to the precision required. The general pattern may be seen from the signs involved, for $(\partial\rho/\partial t)_P$ is positive below 4°C and negative at higher temperatures, while Δt is positive below 0°C, negative between 0° and 100°C, and positive from 100°C to the end of the platinum thermometer range at 630°C. Hence, $\Delta\rho$, shown in Figure 1 (a), is negative below 0°C, positive between 0° and 4°C, negative from 4° to 100°C, and positive above 100°C.

To its precision, Figure 1 (a) can be used to transform any data set on the density of water at atmospheric pressure from either temperature scale to the other; it may also be used for the corresponding changes of density along the saturation curve over this temperature range. For the change of density at saturation owing to the change in scale, the term $(\partial\rho/\partial t)_P$ in Equation 7 must be replaced by $(\partial\rho/\partial t)_{\text{sat}}$ which is given by

$$\left(\frac{\partial\rho}{\partial t}\right)_{\text{sat}} = \left(\frac{\partial\rho}{\partial t}\right)_P + \left(\frac{\partial\rho}{\partial P}\right)_T \left(\frac{\partial P}{\partial t}\right)_{\text{sat}} \tag{8}$$

At 100°C, $(\partial\rho/\partial t)_{\text{sat}}$ differs from $(\partial\rho/\partial t)_P$ by less than 1 part in 400; therefore, the errors produced over the range of Figure 1 are negligible.

Figure 1 also shows the effect of the change of temperature scales on the isothermal compressibility κ_T,

$$\kappa_T = \left(\frac{\partial \ln \rho}{\partial P}\right)_T \tag{9}$$

on the velocity of sound u, and on the specific heat C_p; these last two, with the thermal expansion, permit the calculation of κ_T. The changes in tabulated density and velocity of sound are greater than the precision of the best work. The changes in the specific heat are negligible for all purposes. Those in the isothermal compressibility are less than the errors obtained in direct measurements but are greater than the precision of values obtained from the velocity of sound.

Although the precision of the Echelle Normale was little more than adequate to distinguish the small differences that separate the IPTS-48 and IPTS-68 in this range, there have been two distinct approaches to expressing the data of Thiesen et al. and Chappuis on the IPTS-68. On the one hand, it may be argued that the Echelle Normale (EN) used by those investigators coin-

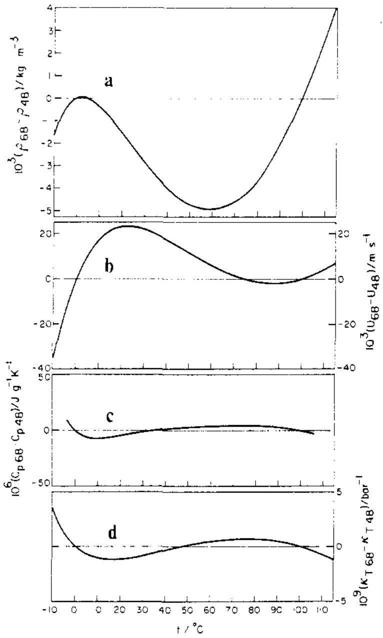

Figure 1. Effect of changes of temperature scale on tabulated properties of water. Each property shows zero change at 0° and 100°C and at temperature of its extreme value.

a: Effect on density ρ, showing zero change at temperature of maximum density, 4°C; b: effect on velocity of sound u, showing zero change at temperature of maximum velocity, 74°C; c: effect on specific heat C_p, showing zero change at temperature of minimum specific heat, 35°C; and d: effect on isothermal compressibility κ_T, showing zero change at temperature of minimum compressibility, 46°C cided with the thermodynamic scale, and so does the IPTS-68; therefore, the temperatures given by those authors can be interpreted as on the IPTS-68. Modern comparisons with the very thermometers used by Chappuis tend to support this, and this approach has been taken by Menaché and Girard (*36*), who assumed

$$\text{EN} = \text{IPTS-68} \neq \text{ITS-27} = \text{IPTS-48}, 0 \leq t \leq 100°\text{C} \quad (10)$$

On the other hand, Bigg (*7*) considered that the temperature scale used by Chappuis and Thiesen differed little from the IPTS-48, and Wagenbreth and Blanke (*45*) converted Bigg's table to the IPTS-68 on this assumption. It is this second approach that has been used here, for most higher-temperature results—exceptions are Steckel and Szapiro (*40*) and Thiesen (*41*)—have used calibrations based at least in part on the data of Chappuis (*9*) for the range 0–40°C, in most cases as weighted and smoothed by Tilton and Taylor (*43*). Accordingly, the higher-temperature measurements can have little value unless we accept, with those who made the measurements and used the IPTS-48 or ITS-27, that is, with Owen et al. (*38*), Jones et al. (*28*), Kell and Whalley (*32*), and Gildseth et al. (*21*), that Chappuis and Tilton and Taylor employed a scale indistinguishable from the one they used. That is, in the present paper we assume

$$\text{EN} = \text{ITS-27} = \text{IPTS-48} \neq \text{IPTS-68}, 0 \leq t \leq 100°\text{C} \quad (11)$$

Density of Water at Atmospheric Pressure

Liquid water can exist at atmospheric pressure from about −40°C to about 325°C (*10*), although density data are available for only a part of this range. No rigorous form for the equation of state is known; therefore, the question is primarily one of choosing a suitable empirical function. An earlier paper on the thermal expansion of water of the various isotopic compositions (*29*) showed that rational functions gave a good and efficient representation of the data, and recommended for ordinary water a rational function with seven adjustable parameters, namely,

$$\rho = R_{51} = \frac{a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5}{1 + bt} \quad (12)$$

The present study still finds this empirical function good.

To minimize inconsistencies produced by isotopic variations in different laboratories, we wish to fit, not ρ, but ζ. Strictly, this should be accomplished by modifying the equation to be identically unity at its maximum, as was done by Steckel and Szapiro (*40*) and Tilton and Taylor (*43*). However, with negligible loss of quality of fit, we can use computer programs already written to fit $\zeta' = R_{51}$, a function that was found to differ by only 1×10^{-7} from unity at maximum density, and ζ was then obtained from

$$\zeta = \zeta'/\zeta'_{\max} \quad (13)$$

[The adjustment indicated by Equation 13 was not made to the coefficients published in 1967, and they gave a maximum density of 999.9722 kg m^{-3}, i.e., 2×10^{-4} kg m^{-3} greater than given by Equation 2; the difference is less than the experimental error, but was noted by Menaché and Girard (*35*). To avoid such errors, the arithmetic in the present paper is believed consistent to 1×10^{-4} kg m^{-3}.]

After the equation to be fitted has been chosen, there remains the arithmetical problem of assuring that problems of numerical analysis in fitting it do not affect the usefulness of the result. The 1967 calculations were made with an IBM 1620 with 12 decimal digit precision. The present calculations were performed using double precision (56 bits or 16 decimal digits) on an IBM 360/67 first using the same programs as before. As the change of computer produced small changes in the calculated standard error and in the coefficients, a test function of the form of Equation 12 was taken, eight-figure data were generated and used as input, and the accuracy with which the coefficients could be determined by least squares was found.

Only for three points above 120°C was the error of the fitted curve greater than 1 in the eighth place, a_0 was recovered correct to 1 in 10^8, the other coefficients being small by about 1 in 10^4 but differing from the correct ones by more than the error estimated from the least-squares analysis. Nevertheless, the differences between the thermal expansion calculated from the recovered function and from the starting one differed by only 1×10^{-6} K^{-1} at 150°C, and by less at lower temperatures. Accordingly, computational problems produce errors at least two orders of magnitude less than the experimental error of density measurements. The least-squares fits given here were obtained by solving the normal equations by Gaussian elimination with pivoting.

As the values chosen in 1967 form the basis of the present revision, the values of t and ζ, and the weights assigned to ζ, taking t as exact, are shown in Table I. Fitting Equation 12 to these data gave

$$\zeta = (0.9998676 + 17.801161 \times 10^{-3} t - 7.942501 \times 10^{-6} t^2 - 52.56328 \times 10^{-9} t^3 + 137.6891 \times 10^{-12} t^4 - 364.4647 \times 10^{-15} t^5)/(1 + 17.735441 \times 10^{-3} t) \quad (14)$$

where t is on the IPTS-68. This equation provides the basis for the reexamination of the experimental data above 40°C that follow.

Reexamination of densities above 40°C. Figure 2 shows $\Delta\zeta$, defined by

$$\Delta\zeta = \zeta_{\text{obs}} - \zeta \text{ (Equation 14)} \quad (15)$$

for the data at atmospheric pressure from 40° to 120°C. Equation 14 gives densities that are lower than most of the data shown, particularly at 70–80°C. The data of Steckel and Szapiro (*40*) do show a rising trend from 40° to 78°C but are too scattered to establish its magnitude. The data and equation of Gildseth et al. (*21*) rise to 10 ppm above Equation 14 at 70° and 80°C. Those authors also reexamined the data of Owen et al. (*38*), recalculating the thermal expansion of the pycnometers using their own equation for the thermal expansion of water. According to this revision, the error in the values published by Owen et al. comes, not from an inconsistency between the thermal expansion of water and mercury, but from the use of calibration values that are slightly in error.

The observations of Kell and Whalley (Figure 10 of ref. *32*) could suggest—a conclusion not drawn by them—that the expansion of water was inconsistent with that of mercury, but the explanation given by Gildseth et al. could also apply there, as the Kell and Whalley densities of water were based on those of Owen et al. in the region of inconsistency. Accordingly, the thermal expansion data of Kell and Whalley should be recalculated using an equation for the thermal expansion of water that is not dependent on the values of Owen et al. Kell and Whalley gave three equations for the thermal expansion of their vessel: based on measurements relative to mercury from 10° to 150°C (their equation 18); relative to water in the range 10–75°C (their equation 17); and combining the two sets of data (their equation 19). It was this last that was the basis of their density values from 80° to 150°C. These data have now been recalculated relative to the

Table I. Relative Densities $\zeta = \rho/\rho_{\max}$ of Ordinary Water at 1 Atm (=1.01325 Bar)[a]

t, °C						
IPTS-48	IPTS-68	ζ, ref. *12*	$10^6\sigma$, ref. *12*	ζ, revised	$10^6\sigma$, revised	ζ, Equation 16
0	0	0.9998676	1/2			0.9998676
5	4.9977	0.9999919	1/2			0.9999919
10	9.9957	0.9997281	1/2			0.9997281
15	14.9940	0.9991286	1/2			0.9991286
20	19.9926	0.9982336	1	Unchanged		0.9982337
25	24.9915	0.9970751	1			0.9970752
30	29.9906	0.9956783	1			0.9956782
35	34.9900	0.9940635	1			0.9940633
40	39.9896	0.9922473	1			0.9922477
45	44.9895	0.9902437	2	0.9902457	2	0.9902455
	50			0.9880643	2	0.9880640
55	54.9899	0.9857218	2	0.9857281	2	0.9857278
	60			0.9832264	2	0.9832265
65	64.9911	0.9805776	3	0.9805871	2	0.9805873
	70			0.9777971	2	0.9777971
75	74.9930	0.9748698	4	0.9748806	2	0.9748805
80	79.9941	0.971822	5	0.9718289	3	0.9718288
85	84.9954	0.968646	6	0.9686507	3	0.9686505
90	89.9968	0.965345	8	0.9653496	4	0.9653494
100	100	0.958386	10	0.9583900	5	0.9583906
110	110.0036	0.950965	12	0.950968	6	0.950971
120	120.0075	0.943100	14	0.943104	7	0.943103
130	130.0116	0.934789	16	0.934796	8	0.934792
140	140.0159	0.926038	18	0.926036	9	0.926038
150	150.0204	0.916839	20	0.916835	10	0.916836

[a] Estimated standard error σ was the basis for weighting in the least-squares calculations. Revised values of ζ were obtained by use of Figure 2.

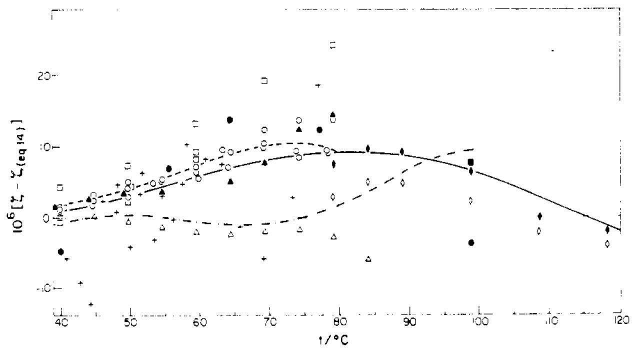

Figure 2. Deviation of relative density of water from Equation 14
○ Gildseth et al. (*21*); ◇ Kell and Whalley (*32*); ◆ data of Kell and Whalley as recalculated in Table II; △ Owen et al. (*38*); ▲ data of Smith as recalculated by Gildseth et al. (*21*); + Steckel and Szapiro (*40*); □ Jones et al. (*28*); ● Thiesen (*41*); ■ Chappuis (*9*); —— Equation 16 of present paper; - - Gildseth et al. (*21*); -·- Aleksandrov and Trakhtengerts (*1*). Because of crowding, a number of unimportant distortions have been made below 50°C

Table II. Relative Density of Water According to Kell and Whalley[a]

t_{48}, °C	$\zeta = \rho/\rho_0$, ref. **32**	ζ, revised	$10^6\,\Delta\zeta$
80	0.971822	0.971827	$-4._6$
85	0.968646	0.968651	$-4._7$
90	0.965345	0.965350	$-4._6$
100	0.958386	0.958390	$-4._2$
110	0.950965	0.950968	$-3._4$
120	0.943100	0.943102	$-2._1$
130	0.934789	0.934789	$-0._4$
140	0.926038	0.926036	$1._6$
150	0.916839	0.916835	$4._1$

[a] Thermal expansion of the vessel used in ref. *32* was partly dependent on the data of Owen et al. (*38*). Revised values are based on the thermal expansion of the vessel relative to mercury.

equation for mercury only; the results are given in Table II and are included in Figure 2.

The data from other sources shown in Figure 2 may be summarized briefly. Jones et al. (*28*) gave densities greater than those of Owen by up to 20 times the error claimed for Owen data, but Figure 2 shows that Jones et al. agree more closely with Gildseth et al. than do Owen et al. The values of Thiesen (*41*) are high relative to Equation 12 at 65° and 78°C, but the point at 100°C is low and appears even lower after the revision to be described. The equation given by Aleksandrov and Trakhtengerts (*1*) follows Owen et al. to 80°C.

On the basis of Figure 2, we conclude that, despite their high internal consistency, the data of Owen et al. contain some systematic error, possibly that pointed out by Gildseth et al., and they have been omitted from further consideration. Figure 2 then shows that Equation 14 gives densities that are too low by about 10 ppm at 70–80°C. Values of $\Delta\zeta$ were taken from Figure 2, from 45° to 75°C about 1 ppm below Gildseth et al., and near the values of Table II to 110°C. The values of ζ so arrived at are included in Table I. From 120° to 150°C, ζ is taken from Table II without smoothing. The greater smoothness of the data as revised suggests that the estimated standard errors of the points should be reduced, and this reduction is included in Table I.

With this revision, the equation for ρ (rather than ζ) is

$$\rho/\mathrm{kg\,m^{-3}} = (999.83952 + 16.945176\,t - 7.9870401 \times 10^{-3}\,t^2 - 46.170461 \times 10^{-6}\,t^3 + 105.56302 \times 10^{-9}\,t^4 - 280.54253 \times 10^{-12}\,t^5)/(1 + 16.879850 \times 10^{-3}\,t) \quad (16)$$

where t is on the IPTS-68. This equation was obtained by fitting ζ', $\rho_{\max}$ was obtained from Equation 2, and $\zeta'_{\max}$ was found to be 0.999999929. Densities and thermal expansivities calculated from Equation 16 are tabulated in Table III.

What estimate can be made of the errors of Equation 16? The "estimated standard errors" of Table I were obtained by estimating the scatter of determinations of the weighted mean about the mean values. To them must be added an estimate of the errors of the means and an estimate of the error of Equation 2. As the values obtained by Thiesen (*41, 42*) are independent of those of Chappuis, we may take the difference between those sets as a measure of the systematic errors, and we find 7 ppm at 40°C, corresponding to temperature differences of 0.02°C, and 11 ppm at 100°C, corresponding to 0.015°C. Thus, we may take the systematic error as approximately equal to a thermometric error of 0.02°C for older work, while an error corresponding to 0.01°C is more appropriate for more recent work. The error of Equation 2 need not be added for most purposes, but where relevant, it is probably about 4 ppm (*11*).

The important value of Equation 16 is that it is continuous and differentiable over a wide temperature range and is in good agreement with the high-temperature data reviewed here without any loss of agreement at low temperatures. Its derivation is thus a necessary preliminary to the calculation of compressibilities given below. To be sure, as references to isotopic and thermometric uncertainties have made clear, at lower temperatures this equation is subject to as great uncertainties as the other equations reviewed by Menaché and Girard (*36*) which are based on the same experimental data.

Specific Heat at Atmospheric Pressure

The commonly accepted values of the specific heat at constant pressure C_p of liquid ordinary water at atmospheric pressure are those given by de Haas (*19*), in which the temperature dependence was taken from Osborne et al. (37), and the value at 15°C, 4.1855 (absolute) J $\mathrm{g^{-1}\,K^{-1}}$, was a mean based on the best determinations. The equation fitted by Osborne et al. was based on weighted values of 20 temperature intervals. De Haas' form is (*31*)

$$C_p(1\ \mathrm{atm})/\mathrm{J\,g^{-1}\,K^{-1}} = 4.1855\,[0.996185 + 0.0002874[(t + 100)/100]^{5.26} + 0.011160 \times 10^{-0.036\,t}] \quad (17)$$

with t on the IPTS-48 and where five constants have been adjusted.

While Figure 1 (c) shows that t_{68} could be used as the argument in Equation 17 without significant change, it is to be noted that Equation 17 requires exponentiation and is relative costly to evaluate. As rational functions of the type shown in Equation 12, with a suitable number of coefficients in the numerator, can represent the density and compressibility, it seemed worthwhile to check whether Equation 17 could be replaced by such a function.

The data of Table 5 of ref. *37* were used, with temperatures changed to the IPTS-68 and with approximately the original weightings. While a rational function $C_p = R_{31}$ could probably be imposed on the data, a function with six parameters $C_p = R_{41}$ has a standard error 10% lower and gives essentially the same fit as Equation 17. The scatter about the fits is about 0.003 J $\mathrm{g^{-1}\,K^{-1}}$ at low temperatures and about 0.001 J $\mathrm{g^{-1}\,K^{-1}}$ at the higher ones. The data are more scattered near 0°C, and neither function seemed satisfactory there, so reliable measurements are needed. There is no reason to replace Equation 17, so it was used, with t_{68} as argument, in the calculations in the following section. The superiority of Equation 17 to a rational function raises the possibility, which will not be pursued here, of tailoring a function that is better than a rational function for representing the density or compressibility.

Velocity of Sound and Compressibility

At frequencies where dispersion is not important, the velocity of sound u is related to the isentropic compressibility κ_S by

$$\kappa_S = (\partial \ln \rho/\partial P)_S = \frac{1}{\rho u^2} \quad (18)$$

and the isothermal compressibility κ_T can then be calculated by

$$\kappa_T = \left(\frac{\partial \ln \rho}{\partial P}\right)_S + T\,\frac{\left(\frac{\partial \rho}{\partial T}\right)_P^2}{\rho^3 C_p} = \frac{1}{\rho u^2} + \frac{T\alpha^2}{\rho C_p} \quad (19)$$

It was shown earlier (*30*) that reliable determinations of the velocity of sound (*4, 8, 34*) were in good agreement with each other, superseded previous measurements of the velocity of sound in liquid water at atmospheric pressure, provided reliable values of the isentropic compressibility of water at temperatures not too far from the maximum density, and gave isothermal compressibilities more accurate than have been obtained with a piezometer by measuring volume changes near atmospheric pressure. Del Grosso (*17*) and Del Grosso and Mader (*18*) have given more observations, for a total of 148 points, that provide a good distribution of data over the range from 0° to 95°C. These two data sets of Del Grosso's have less scatter than previous sets.

The isothermal compressibility was calculated by Equation 19, taking densities and thermal expansitivities from Equation 16 and C_p from Equation 17. The 148 data points of Del Grosso (*17, 18*), given equal weights, give compressibilities that can be represented by the rational function

$$10^6\,\kappa_T/\mathrm{bar^{-1}} = (50.88496 + 0.6163813\,t + 1.459187 \times 10^{-3}\,t^2 + 20.08438 \times 10^{-6}\,t^3 - 58.47727 \times 10^{-9}\,t^4 + 410.4110 \times 10^{-12}\,t^5)/(1 + 19.67348 \times 10^{-3}\,t) \quad (20)$$

with a standard error of 0.2×10^{-9} $\mathrm{bar^{-1}}$. The differences between Equation 20 and the compressibilities calculated from the velocity of sound data of other authors (*4, 8, 34*) are shown in Figure 3. The compressibilities calculated from Barlow and Yazgan are all above Equation 20, and those of McSkimin (*34*) and Carnvale et al. (*8*) are mostly above it. The data of references (*4, 8, 34*) average 3×10^{-9} $\mathrm{bar^{-1}}$ above Equation 20. The temperature dependence of these other data sets does not differ much from Equation 20 which is recommended as giving best values from 0° to 100°C. The short-dashed lines of Figure 3 indicate the error in Equation 20, which is the error of 0.2×10^{-9} $\mathrm{bar^{-1}}$ at 4°C found in fitting Equation 20 increased by the contribution from uncertainty of the thermal expansivity in the second term of Equation 19, taking this uncertainty as 0.05×10^{-6} $\mathrm{K^{-1}}$ at 4°C and increasing to 0.5 × 10^{-6} K^{-1} at 100°C. The added uncertainty from the specific heat is negligible. The correlation given by Aleksandrov and Trakhtengerts (*2*) resembles that given previously by the present author (*30*).

Ref. *30* gave an extended function for the compressibility, valid to 150°C, which had been obtained by fitting the acoustic data, where available, along with the higher-temperature data of Kell and Whalley from 100° to 150°C. Those authors (*33*) have revised their work to eliminate a disagreement with the velocity of sound data, and the revised values were used here. Their values have a standard error about 10 times that of those from the velocity of sound and were given one hundredth the weight. Fitting an equation of the form of Equation 20 over this extended range gave

$$10^6 \kappa_T/\text{bar}^{-1} = (50.884917 + 0.62590623\,t + 1.3848668 \times 10^{-3}\,t^2 + 21.603427 \times 10^{-6}\,t^3 - 72.087667 \times 10^{-9}\,t^4 + 465.45054 \times 10^{-12}\,t^5)/(1 + 19.859983 \times 10^{-3}\,t) \quad (21)$$

representing best values of the compressibility of water from 100° to 150°C.

Table III gives the density and thermal expansivity calculated from Equation 16, the isothermal compressibility to 100°C from Equation 20, and from 90° to 150°C from Equation 21. A few values are shown down to −30°C, to permit comparison with data such as those of Zheleznyí (*47*); his density of (982.9 ± 0.3) kg m^{-3} at −30°C may be compared with the 983.9 kg m^{-3} calculated from Equation 16. The denominators of Equations 16 and 20

Table III. Volume Properties of Ordinary Water at 1 Atm[a]

t, °C, IPTS-68	ρ, kg m^{-3}, Equation 16	$10^6\,\alpha$, K^{-1}, Equation 16	$10^6\,\kappa_T$/bar^{-1} Equation 20	$10^6\,\kappa_T$/bar^{-1} Equation 21
−30	983.854	−1400.0	80.79	
−25	989.585	−955.9	70.94	
−20	993.547	−660.6	64.25	
−15	996.283	−450.3	59.44	
−10	998.117	−292.4	55.83	
−9	998.395	−265.3	55.22	
−8	998.647	−239.5	54.64	
−7	998.874	−214.8	54.08	
−6	999.077	−191.2	53.56	
−5	999.256	−168.6	53.06	
−4	999.414	−146.9	52.58	
−3	999.550	−126.0	52.12	
−2	999.666	−106.0	51.69	
−1	999.762	−86.7	51.28	
0	999.8395	−68.05	50.8850	
1	999.8985	−50.09	50.5091	
2	999.9399	−32.74	50.1505	
3	999.9642	−15.97	49.8081	
4	999.9720	0.27	49.4812	
5	999.9638	16.00	49.1692	
6	999.9402	31.24	48.8712	
7	999.9015	46.04	48.5868	
8	999.8482	60.41	48.3152	
9	999.7808	74.38	48.0560	
10	999.6996	87.97	47.8086	
11	999.6051	101.20	47.5726	
12	999.4974	114.08	47.3474	
13	999.3771	126.65	47.1327	
14	999.2444	138.90	46.9280	
15	999.0996	150.87	46.7331	
16	998.9430	162.55	46.5475	
17	998.7749	173.98	46.3708	
18	998.5956	185.15	46.2029	
19	998.4052	196.08	46.0433	
20	998.2041	206.78	45.8918	
21	997.9925	217.26	45.7482	
22	997.7705	227.54	45.6122	
23	997.5385	237.62	45.4835	
24	997.2965	247.50	45.3619	
25	997.0449	257.21	45.2472	
26	996.7837	266.73	45.1392	
27	996.5132	276.10	45.0378	
28	996.2335	285.30	44.9427	
29	995.9448	294.34	44.8537	
30	995.6473	303.24	44.7707	
31	995.3410	312.00	44.6935	
32	995.0262	320.63	44.6221	
33	994.7030	329.12	44.5561	
34	994.3715	337.48	44.4956	
35	994.0319	345.73	44.4404	
36	993.6842	353.86	44.3903	
37	993.3287	361.88	44.3452	
38	992.9653	369.79	44.3051	
39	992.5943	377.59	44.2697	
40	992.2158	385.30	44.2391	
41	991.8298	392.91	44.2131	
42	991.4364	400.43	44.1917	
43	991.0358	407.85	44.1747	
44	990.6280	415.19	44.1620	
45	990.2132	422.45	44.1536	
46	989.7914	429.63	44.1494	
47	989.3628	436.73	44.1494	
48	988.9273	443.75	44.1533	
49	988.4851	450.71	44.1613	
50	988.0363	457.59	44.1732	
51	987.5809	464.40	44.189	
52	987.1190	471.15	44.209	
53	986.6508	477.84	44.232	
54	986.1761	484.47	44.259	
55	985.6952	491.04	44.290	
56	985.2081	497.55	44.324	
57	984.7149	504.01	44.362	
58	984.2156	510.41	44.403	
59	983.7102	516.76	44.448	
60	983.1989	523.07	44.496	
61	982.6817	529.32	44.548	
62	982.1586	535.53	44.603	
63	981.6297	541.70	44.662	
64	981.0951	547.82	44.723	
65	980.5548	553.90	44.788	
66	980.0089	559.94	44.857	
67	979.4573	565.95	44.928	
68	978.9003	571.91	45.003	
69	978.3377	577.84	45.081	
70	977.7696	583.74	45.162	
71	977.1962	589.60	45.246	
72	976.6173	595.43	45.333	
73	976.0332	601.23	45.424	
74	975.4437	607.00	45.517	
75	974.8490	612.75	45.614	
76	974.2490	618.46	45.714	
77	973.6439	624.15	45.817	
78	973.0336	629.82	45.922	
79	972.4183	635.46	46.031	
80	971.7978	641.08	46.143	
81	971.1723	646.67	46.258	

become small as the temperature is lowered, so these equations do not extrapolate downward well.

It should be noted that before the publication of ref. *32*, few compressibilities of liquids had been measured to a precision of 0.1 × 10^{-6} bar^{-1}. The 1970 paper by the present author (*30*) showed that velocity of sound measurements were available to increase the precision to 0.002 × 10^{-6} bar^{-1} for water, and the present paper increases this to 0.0003 × 10^{-6} bar^{-1}, a three-hundred-fold increase in precision in less than 10 years.

Errors in compressibility from velocity of sound. In the treatment above, Equation 18 was simply asserted, and the limits of its validity were not sought. However, as Hayward (*26*) has pointed out, this equation cannot be used uncritically. There are difficult problems at the kinematic level bearing on the meaning of velocity of propagation in the presence of absorption, others in establishing that the approximations and linearizations made to the rigorous equations to permit solutions have not masked some behavior of physical significance, and thermodynamic ones of relating the observed behavior, in which entropy is produced, to the isentropic coefficient of Equation 18.

Table III. Continued

t, °C, IPTS-68	ρ, kg m^{-3}, Equation 16	$10^6\,\alpha$, K^{-1}, Equation 16	$10^6\,\kappa_T/\text{bar}^{-1}$ Equation 20	Equation 21
82	970.5417	652.25	46.376	
83	969.9062	657.81	46.497	
84	969.2657	663.34	46.621	
85	968.6203	668.86	46.748	
86	967.9700	674.37	46.878	
87	967.3148	679.85	47.011	
88	966.6547	685.33	47.148	
89	965.9898	690.78	47.287	
90	965.3201	696.23	47.429	47.428
91	964.6457	701.66	47.574	47.574
92	963.9664	707.08	47.722	47.722
93	963.2825	712.49	47.874	47.873
94	962.5938	717.89	48.028	48.028
95	961.9004	723.28	48.185	48.185
96	961.2023	728.67	48.346	48.346
97	960.4996	734.04	48.509	48.510
98	959.7923	739.41	48.676	48.677
99	959.0803	744.78	48.846	48.847
100	958.3637	750.14	49.019	49.020
101	957.642	755.5		49.20
102	956.917	760.8		49.38
103	956.186	766.2		49.56
104	955.451	771.5		49.74
105	954.712	776.9		49.93
106	953.968	782.2		50.13
107	953.220	787.6		50.32
108	952.467	792.9		50.52
109	951.709	798.3		50.72
110	950.947	803.6		50.93
115	947.070	830.4		52.01
120	943.083	857.4		53.17
125	938.984	884.7		54.43
130	934.775	912.3		55.79
135	930.456	940.3		57.24
140	926.026	968.9		58.80
145	921.484	998.0		60.47
150	916.829	1027.8		62.25

[a] Density ρ, thermal expansivity $\alpha = -(\partial \ln \rho/\partial T)_p$, and isothermal compressibility $\kappa_T = (\partial \ln \rho/\partial p)_T$. For purposes of this table, ordinary water is that with a maximum density of 999.972 kg m^{-3}. Equation 18 for the compressibility should be used for temperatures $0 \leq t \leq 100$°C, and Equation 21 for $100 \leq t \leq 150$°C. The liquid is metastable below 0°C and above 100°C. Values below 0°C were obtained by extrapolation, and no claim is made for their accuracy.

Hayward was satisfied with an agreement to 1%, but here it is desired that Equation 18 be reliable to a few parts per million. It is accepted that this equation would hold in the absence of absorption processes. In the presence of absorption, two changes take place: the velocity of sound—we shall treat $1/u^2$—is shifted from its value u_0 in the absence of absorption; and there is a phase shift between the pressure and density waves so that $\partial\rho/\partial P$ becomes a complex quantity. Here, we do not need an analysis of the wave motion, but only an estimate of the velocity shift, and Equation 18 can then be used.

The acoustic absorption coefficient α is expressed at low frequencies as (*5*)

$$\frac{\alpha}{\omega^2} = \frac{1}{2\rho_0 u_0^3}\left[\frac{4}{3}\frac{\eta_s}{} + \frac{(\gamma - 1)\lambda}{C_p} + \eta_v\right] \qquad (22)$$

where ω is the angular frequency of the sound, η_s the shear viscosity, γ the ratio of specific heats, λ the thermal conductivity, and η_v the volume or bulk viscosity. For water at its maximum density, $\gamma = 1$, so that the thermal conductivity does not make any contribution, and its effect is small even at 100°C. For liquid water the ratio η_v/η_s is about 3 (*27*), with η_s contributing $\sim 22 \times 10^{-18}$ $\text{s}^2\ \text{cm}^{-1}$ of the observed value $\sim 58 \times 10^{-18}$ $\text{s}^2\ \text{cm}^{-1}$ of α/ω^2. The bulk viscosity as used here is an omnibus term, and contributions may come from structural relaxation, from a chemical reaction, should there be one, or from a slowness of exchange of energy among the vibrational degrees of freedom.

Considering only the leading terms in the change of velocity of sound with absorption gives

$$\frac{1}{u_0^2} = \frac{1}{u^2}\left\{1 + 3\,u_0^2\omega^2(\alpha/\omega^2)^2\right\} \qquad (23)$$

Del Grosso's measurements were made at an angular frequency of 30 × 10^6 rad s^{-1}, and from Equation 23 the measured $1/u^2$ differs from the limiting value by only 0.2 in 10^6. Errors will only reach 1 ppm at 65 × 10^6 rad s^{-1} or 10 MHz. This calculation agrees with the experimental observation that to their experimental precision Carnvale et al. (*8*) found that the velocity did not change with frequency from 10 to 70 MHz.

However, as the two viscosities and the thermal conductivity enter differently into the expression of which Equation 23 gives the leading term, it is best to go directly to the more complete expression if values of η_s, η_v, and λ are available. Truesdell (*44*) defined two parameters, the frequency number X

$$X = \frac{\omega(\tfrac{4}{3}\eta_s + \eta_v)}{\rho_0 u_0^2} \qquad (24)$$

and the thermoviscous number Y

$$Y = \frac{\lambda}{(\tfrac{4}{3}\eta_s + \eta_v)C_p} \qquad (25)$$

For low frequencies, he derived

$$\left(\frac{u}{u_0}\right)^2 = 1 + \tfrac{1}{4}X^2[3 + 10(\gamma - 1)Y - (\gamma - 1)(7 - 3\gamma)Y^2] + O(X^4) \qquad (26)$$

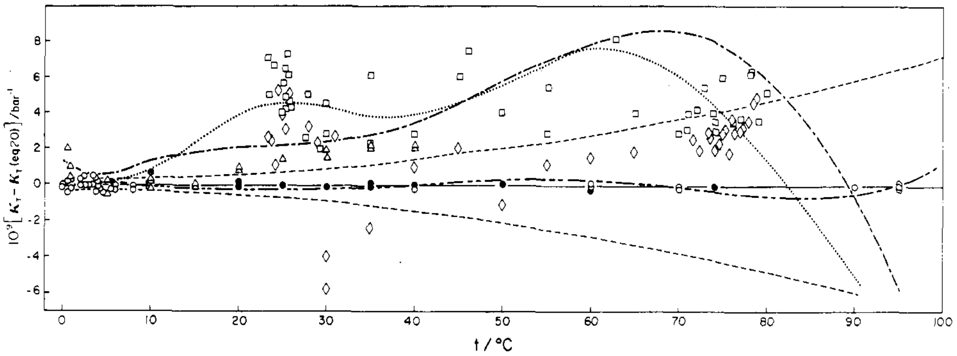

Figure 3. Deviations of isothermal compressibility from Equation 20

○ Del Grosso and Mader (*18*); ● Del Grosso (*17*); △ Carnvale et al. (*8*); □ Barlow and Yazgan (*4*); ◇ McSkimin (*34*); ---- Equation 21; ---- estimate of error of Equation 20; - - - Equation 5 of ref. *30*; . . . . Aleksandrov and Trakhtengerts (*2*). Many points cannot be shown because of overlap, and unimportant distortions have been made to display more points

For liquid water at 100°C, $\gamma = 1.119$, $\eta_s = 2.82 \times 10^{-3}$ *P*, $\eta_v = \sim 8.5 \times 10^{-3}$ *P*, and $\lambda = 6.8 \times 10^{-3}$ watt cm^{-1} s^{-1}, so that $Y = 0.13$. Hence, the term in the braces of Equation 26 is 3.14, compared with the numerical coefficient 3 in Equation 23. On the other hand, both viscosities fall with increasing temperature, so that X/ω is smaller at 100°C, and Equation 23 is then adequate to a precision of 1 ppm.

Maximum Density as Function of Pressure

Equation 16 gives the temperature of maximum density, that is the temperature at which

$$\left(\frac{\partial \rho}{\partial T}\right)_P = 0 \qquad (27)$$

as 3.983°C. The change of the temperature of maximum density with pressure is given by

$$\left(\frac{\partial T}{\partial P}\right)_{\text{max den}} = \frac{-\left(\frac{\partial}{\partial T}\left(\frac{\partial \rho}{\partial P}\right)_T\right)_P}{\left(\frac{\partial^2 \rho}{\partial T^2}\right)_P} \qquad (28)$$

and in ref. *30* this was evaluated as $(\partial T/\partial P)_{\text{max den}} = (-0.0200 \pm 0.0003)$ K bar^{-1}. From Equations 16 and 20, we obtain $(\partial T/\partial P)_{\text{max den}} = -0.01999$ K bar^{-1}, and because of the increased reliability of Equation 20 over that given in ref. *30*, it is probably safe to reduce the tolerance to give (-0.0200 ± 0.0002) K bar^{-1}.

Saturated Liquid Density

Saturated densities ρ_{sat} have been calculated from 0° to 150°C by

$$\rho_{\text{sat}} = \rho_a\left[1 + (p_{\text{sat}} - p_a)\kappa_T\right] \qquad (29)$$

where ρ_a is the density at atmospheric pressure obtained from Equation 16, p_{sat} is the saturation pressure, $p_a = 1$ atm [=1.01325 bar], and κ_T is the isothermal compressibility from Equation 21. This calculation produces errors in ρ_{sat} that are negligibly greater than those in ρ_a, viz., probably nowhere greater than 10 ppm. For comparison, Gibson and Bruges (*20*) gave one figure fewer than is possible over this temperature range. For this calculation, values of the saturation pressure are needed, and the equation fitted by Ambrose and Lawrenson (*3*), which expresses the vapor pressure in terms of Chebyshev polynomials, has been used here. From 0° to 100°C, these values given do not differ from those of Wexler and Greenspan (*46*) by more than one in the last place given.

Table IV. Liquid Ordinary Water at Saturation[a]

t, °C, IPTS-68	p_{sat}, bar	ρ_{sat}, kg m^{-3}
0	0.006107	999.7883
0.010	0.006111	999.7890
4.005	0.008133	999.9223
5	0.008720	999.9144
10	0.012276	999.6518
15	0.017051	999.0531
20	0.023384	998.1588
25	0.031686	997.0006
30	0.042451	995.6040
35	0.056264	993.9896
40	0.073812	992.1745
45	0.095898	990.1731
50	0.12345	987.9975
55	0.15752	985.6579
60	0.19933	983.1633
65	0.25024	980.5213
70	0.31177	977.7386
75	0.38564	974.8211
80	0.47375	971.7736
85	0.57817	968.6006
90	0.70120	965.3059
95	0.84532	961.8926
100	1.01325	958.3637
105	1.2079	954.721
110	1.4325	950.967
115	1.6903	947.104
120	1.9849	943.131
125	2.3203	939.051
130	2.7003	934.863
135	3.1294	930.569
140	3.6121	926.167
145	4.1531	921.659
150	4.7574	917.042

[a] Saturation pressure is from the equation of Ambrose and Lawrenson (3), and the saturation density was calculated by Equation 29.

Because κ_T of Equation 29 is $\sim 50 \times 10^{-6}$ bar^{-1}, for the precision of 1 in 10^7 in ρ_{sat} which we give below 100°C, p_{sat} is needed to 0.002 bar, but is known more precisely. Hence, the error in ρ_{sat} produced by the error in p_{sat} is negligible. Another negligible error is that introduced by the use of the compressibility at 1 atm in Equation 29; Kell and Whalley (*32*) have shown that the change of compressibility with pressure is about 0.01×10^{-6} bar^{-2}, negligible in Equation 29 below 150°C.

As Ambrose and Lawrenson did not give values of the saturation pressure for intervals on the Celsius scale, such values are included with the saturated densities in Table IV. Values are shown at the triple point and the maximum of ρ_{sat}. This latter is defined, not by Equation 27, but by

$$(\partial \rho / \partial T)_{\mathrm{sat}} = 0 \qquad (30)$$

and the two partial derivatives are related by Equation 8. The isopiestic maximum density line crosses the saturation line at 4.003°C. The maximum along the saturation line given by Equation 30 is at 4.005°C.

Added in proof. Commission I.4 of the International Union of Pure and Applied Chemistry is recommending 999.975 kg m^{-3}, viz., Equation 3, as an interim value of the maximum density of standard mean ocean water, to be used until new absolute determinations on a sample of known isotopic composition become available. This means that workers are now expected to note that their laboratory water differs in isotopic composition and density from the standard of the tables. The tables of the present paper, without such adjustments, remain a good estimate for laboratory waters of continental origin.

In a paper to appear in the Proceedings of the 8th International Conference on the Properties of Steam, held in Giens (Var), France, 23–27 September 1974, A. A. Aleksandrov and M. S. Trakhtengerts presented a new correlation for the temperature dependence of liquid water that is close to the present one. Normalizing their equation to the value of ρ_{max} used here, the differences in density never reach 0.002 kg m^{-3} between 0° and 100°C. Those authors agree with the present paper in now giving much less weight to the data of Owen et al. (*38*).

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