Precise Representation of Volume Properties of Water at One Atmosphere

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The density of ordinary water from 0° to 150° C. is well represented by a rational function with seven parameters. Similar functions, with fewer parameters, are given for D_2O, H_2O^{18}, D_2O^{18}, and T_2O. The density, specific volume, thermal expansivity, and compressibility of ordinary water are given at intervals of 2° from −20° to −10° C. and at intervals of 1° from −10° to +110° C. The density of D_2O is given at 5° intervals from 0° to 101° C.

THE DENSITY of liquid water from 80° to 150° C. was redetermined by Kell and Whalley (*10*) in connection with measurements of the compressibility of water from 0° to 150° C. These densities, plus others (*14*) not yet incorporated in tables, make possible a table of greater range (*22*), or reliability (*20*), than those now available, provided a suitable interpolating function can be found.

A function, chosen for goodness of fit to the most reliable densities of ordinary water, has been used to give a table. The same type of function also has been found satisfactory for water of other isotopic composition.

ORDINARY WATER

Data Used. Tilton and Taylor (*22*) analyzed Chappuis's (*2*) experimental densities for 0° to 42° C. Improvement in that temperature range must wait for further precise experimental data. To avoid reanalyzing the great number of observations of Chappuis, entries from the table of Tilton and Taylor, which provide a good summary, were taken at 5° intervals. From 45° to 75° C. the densities of Owen, White, and Smith (*14*) have been used. Kell and Whalley (*10*) suggested that the standard error of that work is several parts per million, which is large compared with a reproducibility of 0.2 p.p.m. The error of the data obtained by Kell and Whalley above 80° C. is larger yet, but the work is more reliable than any available previously. The data of Owen, White, and Smith, and those of Kell and Whalley, were obtained at 10° intervals. The standard errors of Table I were estimated to obtain weights for the calculation. These estimated errors can claim no more than to seem reasonable, but the general trend with temperature is correct, and small changes in the weighting have little effect on the computations.

The weakest point in Table I is at 80° C. where the values of Owen, White, and Smith join those of Kell and Whalley with a jump of 5 p.p.m. This can be resolved only by further experimental work. The values of Steckel and Szapiro (*19*) stop at 78° C.—a few degrees too low.

The isothermal compressibility at 1 atm. has been calculated from the relation given by Kell and Whalley (*10*)

$$10^6\kappa/\text{bar}^{-1} = 50.9804 - 0.374957\,t + 7.21324 \times 10^{-3}t^2 - 64.1785 \times 10^{-6}\,t^3 + 0.343024 \times 10^{-6}\,t^4 - 0.684212 \times 10^{-9}\,t^5 \quad (1)$$

which represented their data from 0° to 150° C. to 0.04 $\times 10^{-6}$ bar^{-1}.

Choice of Mathematical Function. The densities extend over a sufficient range of temperature that care is needed in the choice of function to represent them. For 0° to 40° C., Thiesen, Scheel, and Diesselhorst (*21*) represented the density ρ by the rational function

$$\rho = 1 - \frac{(t-A)^2\,(t+C)}{B(t+D)} \quad (2)$$

where t is the Celsius temperature. The squared term ensures that ρ = 1 gram per ml. at maximum density. Tilton and Taylor (*22*) found this equation to represent the data of Chappuis (*2*) better than a power series with the same number of parameters. For 17° to 100° C., Thiesen (*20*) used an extended formula of the same type.

Four types of function have been investigated. The first was the polynomial of degree n

$$\rho = P_n(t) = a_0 + a_1t + a_2t^2 + \ldots + a_nt^n \quad (3)$$

with $n + 1$ adjustable parameters. The second was the rational function

$$\rho = R_{nm}(t) = P_n(t)/(1 + b_1t + b_2t^2 + \ldots + b_mt^m) \quad (4)$$

where R_{nm}, with $n + m + 1$ parameters, is a fraction whose numerator is a polynomial of degree n and whose denominator is of degree m. Equation 2 used by Thiesen is a rational function with the constraint that ρ = 1 gram per ml. at maximum density. With rational functions a search must be made for zeros in the denominator, but for certain combinations of the coefficients, R_{nm} can remain well-behaved for all positive values of t.

Table I. Densities for Ordinary Water at 1 Atm.

Estimated standard errors used as a basis for weighting points. Smoothed values obtained when function $\rho = R_{51}$ was fitted.

t, ° C.	ρ, G./Ml.	Std. Error, P.P.M.	ρ, Smoothed
0	0.999 8676	0.5	0.999 8676
5	0.999 9919	0.5	0.999 9920
10	0.999 7281	0.5	0.999 7280
15	0.999 1286	0.5	0.999 1285
20	0.998 2336	1	0.998 2338
25	0.997 0751	1	0.997 0753
30	0.995 6783	1	0.995 6783
35	0.994 0634	1	0.994 0632
40	0.992 2473	1	0.992 2469
45	0.990 2437	2	0.990 2438
55	0.985 7218	2	0.985 7235
65	0.980 5776	3	0.980 5789
75	0.974 8698	4	0.974 8710
80	0.971 822	5	0.971 819
85	0.968 646	6	0.968 640
90	0.965 345	8	0.965 340
100	0.958 386	10	0.958 384
110	0.950 965	12	0.950 968
120	0.943 100	14	0.943 105
130	0.934 789	16	0.934 797
140	0.926 038	18	0.926 042
150	0.916 839	20	0.916 830

Since ρ is inherently positive, it can be transformed into $\ln \rho$. The third relation was

$$\ln \rho = P_n(t) \qquad (5)$$

At least for $n = 2$ this is superior to Equation 3. The fourth relation was

$$\ln \rho = R_{nm}(t) \qquad (6)$$

This function is relatively inflexible as many combinations of m and n (where n is small) give functions of an unsuitable form.

The weighted data were fitted by least squares. Function $\rho = R_{51}$ gave a standard error of 0.21 p.p.m., and $\ln \rho = R_{51}$, also with seven parameters, gave 0.25 p.p.m.; the difference between these errors is not significant and may be computational. No other rational function with seven parameters gave a standard error as low. The functions $\rho = P_7$ and $\ln \rho = P_7$ gave standard errors of 1.1 p.p.m. Only with nine parameters do $\rho = P_8$ and $\ln \rho = P_8$ have standard errors of 0.24 p.p.m. Function $\rho = R_{51}$ was chosen over $\ln \rho = R_{51}$ as simpler for desk calculations. The coefficients are given in Table III.

Volume Properties of Ordinary Water. Table II gives the density and specific volume from the function $\rho = R_{51}$, the thermal expansion obtained by differentiation, and the compressibility from Equation 1. The errors of the density are given in Table I; the error in the specific volume is never less than 4 p.p.m. The thermal expansions probably are accurate to 0.1×10^{-6} deg.$^{-1}$ near room temperature and to 2×10^{-6} deg.$^{-1}$ at 110° C.; the values are given to two decimal places to facilitate interpolation or numerical differentiation. In the range 0° to 42° C., the densities of Table II agree with those of Tilton and Taylor (*22*) to six places, except for five entries with differences of 1×10^{-6} gram per ml. Between 40° and 100° C., the differences between Table II and the table of Thiesen (*20*) nowhere exceed 2×10^{-5} gram per ml.

The 12th General Conference on Weights and Measurements (1964) redefined the liter to be the cubic decimeter. In the present paper the "old" (1901) milliliter is used, as that has been used in most work on the density of water. The old milliliter is given by

$$1 \text{ ml.} = 1.000028 \text{ cc.}$$

and the densities in Table II should be multiplied by 0.999972 to convert them to units of grams per cubic centimeter. The standard error of these conversion factors is 4 p.p.m., and the errors of the densities in grams per milliliter as estimated in Table I must have this additional error compounded when volumes are measured in cubic centimeters. With the redefinition of the liter, there is no longer the constraint that $\rho = 1$ gram per ml., exactly, at maximum density. The density of ordinary water at its maximum is now obtained from the fitted curve just as is the case for waters of other isotopic compositions.

The isotopic composition of the water used by Chappuis is not known. Christiansen, Crabtree, and Laby (*3*) report that the fractions of a single distillation of tap water may vary in density by 20 p.p.m. However, as the isotopic variation in ordinary water changes the thermal expansion comparatively little, the volume and density columns of Table II, which give the properties of a water of specific volume 1.000028 cc. per gram at 4° C., may be changed in proportion for ordinary waters with other specific volumes at 4° C. If only five decimal places are considered, variations of "ordinary" waters barely are seen and the densities are as given by the table.

The table goes to 110° C. at the high temperature end, although the equations remain valid to 150° C. The values above 100° C., like the corresponding entries in Table I, refer to a liquid at 1 atm., metastable relative to the

Table II. Volume Properties of Ordinary Water

(Specific volume v, density ρ, thermal expansivity $\alpha = d \ln v/dt = -d \ln \rho/dt$, compressibility $\kappa = -d \ln v/dp = d \ln \rho/dp$)

t, ° C.	v, Cc./G.	ρ, G./Ml.	$10^6\alpha$, Deg.$^{-1}$	$10^6\kappa$, bar^{-1}
−20	1.00658	0.99349	−678.48	61.94
−18	1.00532	0.99474	−580.83	60.48
−16	1.00424	0.99581	−495.74	59.11
−14	1.00332	0.99672	−420.85	57.83
−12	1.00254	0.99749	−354.33	56.64
−10	1.001895	0.998137	−294.73	55.52
−9	1.001614	0.998417	−267.18	54.99
−8	1.001359	0.998671	−240.95	54.48
−7	1.001131	0.998899	−215.94	53.98
−6	1.000926	0.999102	−192.06	53.50
−5	1.000746	0.999283	−169.22	53.04
−4	1.000587	0.999441	−147.34	52.60
−3	1.000451	0.999578	−126.36	52.17
−2	1.000334	0.999694	−106.20	51.76
−1	1.000238	0.999790	−86.81	51.36
0	1.000160	0.999868	−68.14	50.98
1	1.000101	0.999927	−50.14	50.61
2	1.000060	0.999968	−32.77	50.26
3	1.000036	0.999992	−15.98	49.92
4	1.000028	1.000000	0.26	49.59
5	1.000036	0.999992	15.98	49.28
6	1.000060	0.999968	31.23	48.98
7	1.000098	0.999930	46.01	48.69
8	1.000151	0.999877	60.37	48.41
9	1.000219	0.999809	74.33	48.15
10	1.000300	0.999728	87.90	47.89
11	1.000395	0.999634	101.12	47.65
12	1.000502	0.999526	113.99	47.42
13	1.000623	0.999406	126.54	47.19
14	1.000755	0.999273	138.78	46.98
15	1.000900	0.999129	150.73	46.78
16	1.001057	0.998972	162.41	46.59
17	1.001225	0.998804	173.82	46.40
18	1.001405	0.998625	184.99	46.23
19	1.001596	0.998435	195.91	46.06
20	1.001797	0.998234	206.61	45.91
21	1.002010	0.998022	217.10	45.76
22	1.002232	0.997801	227.37	45.62
23	1.002465	0.997569	237.45	45.48
24	1.002708	0.997327	247.34	45.36
25	1.002961	0.997075	257.05	45.24
26	1.003224	0.996814	266.59	45.13
27	1.003496	0.996544	275.96	45.02
28	1.003778	0.996264	285.17	44.93
29	1.004069	0.995976	294.23	44.84
30	1.004369	0.995678	303.14	44.75
31	1.004678	0.995372	311.92	44.67
32	1.004995	0.995057	320.55	44.60
33	1.005322	0.994734	329.06	44.54
34	1.005657	0.994403	337.44	44.48
35	1.006000	0.994063	345.71	44.42
36	1.006352	0.993716	353.85	44.37
37	1.006713	0.993360	361.89	44.33
38	1.007081	0.992997	369.81	44.29
39	1.007457	0.992626	377.64	44.25
40	1.007842	0.992247	385.36	44.22
41	1.008234	0.991861	392.99	44.20
42	1.008634	0.991467	400.52	44.18
43	1.009042	0.991067	407.97	44.16
44	1.009458	0.990659	415.33	44.15
45	1.009881	0.990244	422.60	44.15
46	1.010311	0.989822	429.80	44.14
47	1.010749	0.989393	436.91	44.15
48	1.011194	0.988957	443.95	44.15
49	1.011647	0.988515	450.92	44.16
50	1.012107	0.988066	457.81	44.17
51	1.012574	0.987610	464.64	44.19
52	1.013048	0.987148	471.40	44.21
53	1.013529	0.986680	478.10	44.24
54	1.014017	0.986205	484.74	44.26
55	1.014512	0.985723	491.32	44.29
56	1.015014	0.985236	497.84	44.33
57	1.015522	0.984743	504.30	44.37
58	1.016038	0.984243	510.71	44.41
59	1.016560	0.983737	517.07	44.45
60	1.017089	0.983226	523.38	44.50
61	1.017625	0.982708	529.64	44.55
62	1.018167	0.982185	535.85	44.61
63	1.018716	0.981655	542.02	44.66

(*continued on page 68*)

Table II. Volume Properties of Ordinary Water (*Continued*)

(Specific volume v, density ρ, thermal expansivity $\alpha = d \ln v / dt = - d \ln \rho / dt$, compressibility $\kappa = - d \ln v / dp = d \ln \rho / dp$)

t, ° C.	v, Cc./G.	ρ, G./Ml.	$10^6\alpha$, Deg.$^{-1}$	$10^6\kappa$, Bar^{-1}
64	1.019271	0.981120	548.14	44.72
65	1.019833	0.980580	554.22	44.79
66	1.020402	0.980034	560.26	44.85
67	1.020977	0.979482	566.26	44.92
68	1.021558	0.978924	572.22	45.00
69	1.022146	0.978361	578.15	45.07
70	1.022740	0.977793	584.04	45.15
71	1.023340	0.977219	589.89	45.23
72	1.023947	0.976640	595.72	45.32
73	1.024560	0.976056	601.51	45.40
74	1.025180	0.975466	607.27	45.49
75	1.025805	0.974871	613.00	45.59
76	1.026437	0.974271	618.71	45.68
77	1.027076	0.973665	624.39	45.78
78	1.027720	0.973055	630.04	45.88
79	1.028371	0.972439	635.67	45.99
80	1.029027	0.971819	641.27	46.10
81	1.029690	0.971193	646.86	46.21
82	1.030360	0.970562	652.42	46.32
83	1.031035	0.969926	657.96	46.44
84	1.031716	0.969286	663.48	46.56
85	1.032404	0.968640	668.98	46.68
86	1.033098	0.967990	674.47	46.81
87	1.033797	0.967335	679.94	46.94
88	1.034503	0.966674	685.40	47.07
89	1.035216	0.966009	690.84	47.20
90	1.035934	0.965340	696.26	47.34
91	1.036658	0.964665	701.68	47.48
92	1.037389	0.963986	707.08	47.63
93	1.038125	0.963302	712.48	47.77
94	1.038868	0.962613	717.86	47.93
95	1.039617	0.961920	723.24	48.08
96	1.040372	0.961222	728.60	48.24
97	1.041133	0.960519	733.96	48.40
98	1.041900	0.959812	739.32	48.56
99	1.042673	0.959100	744.67	48.73
100	1.043453	0.958384	750.01	48.90
101	1.044239	0.957662	755.36	49.07
102	1.045030	0.956937	760.70	49.25
103	1.045828	0.956207	766.03	49.43
104	1.046633	0.955472	771.37	49.62
105	1.047443	0.954733	776.71	49.80
106	1.048260	0.953989	782.05	50.00
107	1.049083	0.953240	787.39	50.19
108	1.049912	0.952488	792.73	50.39
109	1.050747	0.951730	798.07	50.59
110	1.051589	0.950968	803.42	50.80

vapor, and are based on measurements in the stable region at higher pressures.

The entries for the region below 0° C., metastable relative to ice, are based on extrapolations of the equation for the density and the equation for the compressibility outside the range where they were fitted. Some other properties of liquid water have been measured at low temperatures—Hallett (*8*) measured the viscosity at −24° C.—and, as densities may be wanted, it seems worth while to see what confidence applies to the equations fitted above 0° C. when they are extrapolated to lower temperatures.

Properties below 0° C. Agreement among measurements of liquid densities in the range below 0° C. is normally to a few parts in 10^5. In the 19th century, measurements were made by Despretz (*4*) to −9° C., Pierre (*15*) to −13° C.—his data were corrected and interpolated by Frankenheim (*5*)—Weidner (*24*) to −10° C., and Rossetti (*16*) to −6° C. There is no agreement among the handbooks about their reliability, nor how the data should be averaged. In the 20th century, there are measurements by Mohler (*13*) to −13° C., and Lagemann, Gilley, and McLeroy (*12*) to −5° C.

The volumes found by Mohler are high relative to the other values, the difference reaching 1 part in 10^4 at −10° C., and have been eliminated from further consideration. The remaining values agree with each other and with Table II; the greatest experimental differences are about 4 in 10^5 at −9° or −10° C. The values given in Table II are within the range of measurements and, as they join smoothly with the values for higher temperatures, merit more confidence than any previous table. The errors in the thermal expansion in this range are difficult to evaluate; they must be taken as 5×10^{-6} deg.$^{-1}$ or more.

Isothermal compressibilities below 0° C. have been calculated from the velocity of sound measurements of Lagemann, Gilley, and McLeroy and compared with the extrapolated values in Table II. Lagemann, Gilley, and McLeroy obtained a value that is 0.2×10^{-6} bar^{-1} lower than the value in Table II at 0° C., and 0.4×10^{-6} bar^{-1} lower at −5° C. This difference is fairly large, but no conclusion can be made as to the source of the error.

OTHER WATERS

The rational function R_{51} represents the density of ordinary water over the range considered. The densities of the other isotopic waters may be represented by functions of the form $\rho = R_{n1}$, with one parameter in the denominator. A value of n can be found for each set of data that will give a good representation. The coefficients and the errors are given in Table III.

D_2O. The density data for D_2O available in 1957 were reviewed by Whalley (*25*), and later data are available. The densities given by Chang and Tung (*1*) included earlier values for the lower temperatures; they measured the thermal expansion relative to quartz up to the boiling point of D_2O, and presented a smooth table. Schrader and Wirtz (*17*) made measurements relative to H_2O at 5° intervals

Table III. Coefficients and Properties of Functions Representing Density of Water

Coefficients are for rational function given by Equation 4. As smoothness of data is usually somewhat better than its absolute accuracy, estimates of both are given.

Coefficients, G./Cc.	H_2O	D_2O	H_2O^{18}	D_2O^{18}	T_2O
a_0	0.9998396	1.104690	1.112333	1.215371	1.21293
$10^3 a_1$	18.224944	20.09315	13.92547	18.61961	11.7499
$10^6 a_2$	−7.922210	−9.24227	−8.81358	−10.70052	−11.612
$10^9 a_3$	−55.44846	−55.9509	−22.8730	−35.1257	
$10^{12} a_4$	149.7562	79.9512			
$10^{15} a_5$	−393.2952				
$10^3 b_1$	18.159725	17.96190	12.44953	15.08867	9.4144
Range of function, ° C.	0–150	3.5–100	1–79	3.5–72	5–54
Standard error, p.p.m.	See Table I	3	2	8	20
Estimated accuracy, p.p.m.	See Table I	10	50	100	200
Temp. of maximum density, ° C.	3.984	11.185	4.211	11.438	13.403
Maximum density, g./cc.	0.999972	1.10600	1.11249	1.21688	1.21501

Table IV. Density of D_2O

Calculated by rational function whose coefficients are given in Table III.

t, °C.	ρ, G./Cc.
0	1.10469
3.813	1.10546
5	1.10562
10	1.10599
11.185	1.10600
15	1.10587
20	1.10534
25	1.10445
30	1.10323
35	1.10173
40	1.09996
45	1.09794
50	1.09570
55	1.09325
60	1.09060
65	1.08777
70	1.08475
75	1.08158
80	1.07824
85	1.07475
90	1.07112
95	1.06736
100	1.06346
101.431	1.06232

and their table was smoothed slightly. Their values, like those of Chang and Tung, are tied to a ratio of densities D_2O/H_2O at 20° C. of 1.10726 as given by Tronstad and Brun *(23)*. Isberg and Lundberg *(9)* showed that such values should be increased by nine in the fifth decimal place because of errors in the abundance of the oxygen isotopes. The data of Steckel and Szapiro *(19)* were obtained relative to the thermal expansion of mercury at 62 points up to 77° C. The values of Grossman-Doerth *(7)* from 95° to 160° C. cannot be adjusted reliably to atmospheric pressure. Shatenshtein and others *(18)* presented precise values at four temperatures. The values of Lagemann, Gilley, and McLeroy *(12)* below the freezing point are of lower precision.

The coefficients given in Table III are tied to the density ratio D_2O/H_2O at 25° C. being 1.10772 for the normal abundance of the oxygen isotopes; this gives D_2O a density of 1.10448 gram per ml. or 1.10445 gram per cc. at that temperature. In the calculations, five values at 5° intervals from 80° to 100° C. from the mean of the values of Chang and Tung and Schrader and Wirtz were each given unit weight as was each of the 62 values of Steckel and Szapiro; this gives the two sets of data about the right relative weights. There is a small unavoidable jump where the two sets of data join. With function $\rho = R_{41}$ the standard error is 3 p.p.m., and the jump at 80° C. is 15 p.p.m.

Table IV gives the calculated density of D_2O at 5° intervals. The values probably are accurate to 1×10^{-5} at the lower temperatures and to 5×10^{-5} at 100° C.

H_2O^{18} and D_2O^{18}. Ku and Chang *(11)* tied their densities of H_2O^{18} to the density ratio H_2O^{18}/H_2O being 1.11264 at 30° C. as found by Steckel and Szapiro *(19)*. The two sets of data agree to within experimental error. The data of Steckel and Szapiro have been fitted by the function $\rho = R_{31}$ with a standard error of 2×10^{-6} gram per cc.

The only densities for D_2O^{18}, those of Steckel and Szapiro *(19)*, are of lower precision than the other data of those authors, but are fitted by the function $\rho = R_{31}$ with a standard error of 8×10^{-6} gram per cc.

T_2O. The density of 99.30 mole % T_2O was determined from 5° to 54° C. by Goldblatt *(6)*, and adjusted to pure T_2O. Two series of observations gave densities differing by 28×10^{-5} gram per cc., although his experimental precision was about 2×10^{-5} gram per cc. He was able to represent one series of data by a cubic equation with an average deviation of 3×10^{-5} gram per cc.; with the same number of parameters, $\rho = R_{21}$ represents the same data with a standard error of 2×10^{-5} gram per cc.

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