Precision Measurements of Densities and Thermal Dilation of Water Between 5° and 80°C

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The densities of air-free water have been measured with an accuracy of about 3 ppm between 5° and 80°C. Since the relative measurements were more precise than the absolute measurements, the densities were adjusted to bring them into agreement with the defined density at 4°C. This was done by calculating the weight of the water in the dilatometers from the densities of Chappuis as expressed by the Tilton and Taylor equation up to 40°C. Comparisons are made with other literature values, particularly above 40°C, including a close examination of the water density data of Owen et al. Finally, a modified form of the Tilton and Taylor equation was derived to fit the water density data from 0–80°C with a mean absolute deviation of 0.7 $\times$ 10^{-6} g/ml. Since we believe these values represent the best data available at this time, a table of water density values calculated from this equation at 0.1° intervals over the entire range of 0–80°C is also presented.

This laboratory has been investigating the thermodynamic properties of aqueous rare earth salt solutions for some years, and as part of this study, precise thermal expansion data were needed. The dilatometric method of measurement chosen to obtain the thermal expansion data required an accurate measurement of thermal expansions of the dilatometers themselves. To this end, water was initially chosen as the calibrating liquid as it was readily available in high purity, and accurate, consistent density data over the required temperature range of 5–80°C seemed to be available.

The water density data of Chappuis (*3*) covering the temperature range of 0–42°C as represented by the Tilton and Taylor equation (*12*) are generally accepted as a standard in this country as well as by the International Bureau of Weights and Measures. Furthermore, these data have been extended to 80°C by Jones et al. (*6*) and Steckel and Szapiro (*11*), and to 85°C by Owen et al. (*9*). Unfortunately these sets of data differ by as much as 27 $\times$ 10^{-6} g/ml at 80°C which is approximately 10 times what we believe to be our allowable error for calibration purposes. Owen et al. attributed this difference to the use by Jones et al. of only a linear equation as opposed to a quadratic equation to represent the volumes of their dilatometers as a function of temperature. This criticism appeared reasonable, and thus the density data of Owen et al. which extended the Chappuis data to 85°C was assumed to be correct.

Owen et al. had found that the expression,

$$\Delta V/\Delta t = a + bt_{\mathrm{av}} \qquad (1)$$

in which t_{av} is the mean temperature of the interval Δt, represented the volume expansions of their dilatometers over the temperature range of 5–85°C. As the borosilicate glass dilatometers used were similar in size and shape to the ones used in this research, it was expected Equation 1 would be obeyed in this research as well. However, when the densities of water determined by Chappuis and by Owen et al. were used as the standards for our data, the $\Delta V/\Delta t$ vs. t_{av} plots obtained were not quite linear. This fact plus the disagreement between the data of Owen et al. and Jones et al. suggested that the densities of water above 40°C should be redetermined, using mercury as a standard.

EXPERIMENTAL

Apparatus and Procedure. The experimental apparatus and procedures were similar to those used by Owen et al. and are fully described elsewhere (*4*). Modifications of the Owen et al. apparatus and procedures included a modified withdrawal pipet making it easier to prevent loss of mercury from the pipet during a withdrawal. The withdrawal arms on the dilatometers were also modified to make it more convenient to prevent condensation of the thermostat water vapor from taking place inside the withdrawal arms at higher temperatures. The degassing and filling apparatus and procedures were similar to those employed by Jones et al. The temperature was controlled to ±0.001°C and was measured with a precision of ±0.001°C over the entire range of 5–80°C using a Leeds and Northrup platinum resistance thermometer calibrated by NBS (1953, 1959) in terms of the International Practical Temperature Scale (1948) and a calibrated Mueller Bridge.

Changes in volume of the contents of the dilatometers were measured with an accuracy of about $\pm 1 \times 10^{-4}$ ml, and since the dilatometers contained about 100 ml of water during the water density measurements, this method should be capable of measuring changes in density with an accuracy of about $\pm 2 \times 10^{-6}$ g/ml. The error in absolute density due to the difficulty of weighing the dilatometers to that precision would be about fivefold greater than this, but since the water density data below 40°C were based on the defined density at 4°C from the Chappuis data, this problem was circumvented.

Two independent series of measurements, G and H, separated by a period of years were made using two different sets of 10 dilatometers. Although, the stopcocks on the dilatometers were individually mated to their shells by grinding, water sometimes leaked out through a stopcock at higher temperatures. Dilatometer number VII, series G, was particularly susceptible to this problem, and consequently its use was discontinued. Leakage from a dilatometer was apparent from the withdrawal data and in most cases air bubbles were observed in the dilatometer following the leakage. All data collected from the dilatometers after leakage had occurred were ignored.

A second problem with this experimental procedure was also observed. Occasionally a small droplet of mercury was left behind in the dilatometer side arm following withdrawal. It was possible to observe these occurrences with the aid of

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a pencil flashlight, and in almost all cases the droplet could be removed for weighing. Thus once this problem was recognized, it did not constitute a serious experimental obstacle.

The thermal expansions of the dilatometers were determined using mercury as the calibrating liquid together with the densities of mercury as determined by Beattie et al. (*1*).

Purification of Materials. The mercury used was obtained from the Special Materials Group of the Ames Laboratory of the Atomic Energy Commission, and the purification procedure they used is reported elsewhere (*4*). Mercury purified by this procedure has been used successfully in polarographs for several years. As a precaution against surface contaminants, the mercury was passed through a pinhole in filter paper before using, and the top layer of mercury in the funnel was then discarded.

The water was obtained from a tin-lined Barnstead Model E-1 conductivity still in which ion exchange purified water was distilled from an alkaline permanganate solution. The distillate was then stored in a tin-lined storage tank which was protected from the atmosphere by a carbon dioxide and dust filter. The specific conductance of the water used was 7×10^{-7} ohm^{-1} cm^{-1} prior to degassing.

The measurements were made on normal water, prepared in the manner described above. No isotopic analysis of this water was made. The same can be said of Chappuis' work. The densities presented refer to normal water prepared in any well-equipped laboratory. Variation in the normal abundance of hydrogen and oxygen isotopes might affect the absolute density perhaps in the sixth or one in the fifth decimal place, but the difference between our water and Chappuis' is probably less than that. Such variation should have no effect, within experimental error, on the thermal expansion of water (*7, 8, 11*). Because our densities were adjusted to be consistent with Chappuis' data, the densities above 40°C reported in this paper are correct for the isotopic composition of the water employed by Chappuis. The isotope effect has been discussed by Kell (*7*) and Kell and Whalley (*8*), and it was concluded that it can be neglected.

Calculations. All calculations were made using an IBM 1130 computer or a Marchant Model 1016 PR electronic calculator in which at least 10 digits were carried throughout the calculations. Most of these calculations were checked with an IBM 7074/1401 and/or an IBM 360/40 computer as well as by spot checks using a hand calculator.

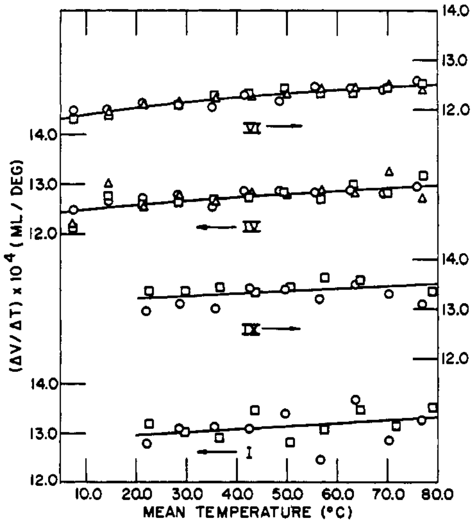

Figure 1. Selected dilatometer calibrations

Series G dilatometers I and IX, ○ = Run I and □ = Run II with mercury
Series H dilatometers IV and VI, ○ = Run I, □ = Run II, and △ = Run III with mercury

RESULTS

Calibration of Dilatometers. In Series G, two calibration runs were made using mercury as the calibrating liquid. Withdrawals were made at approximately 7°C intervals between 20° and 83°C. A weighted least squares calculation was carried out on the calibration data to obtain values of the a and b parameters in Equation 1 for each of the nine dilatometers used. Figure 1 shows some selected dilatometer calibrations.

Equation 1 can be rearranged using the calculus mean value theorem to yield

$$V = V_{25}\,[1 + A(t - 25) + B(t - 25)^2] \qquad (2)$$

in which V_{25} is the volume of the dilatometer at 25°C, $A = (a + 25\,b/V_{25})$ and $B = 0.5\,b/V_{25}$. The values of A and B obtained are listed in Table I for the nine dilatometers, and can be compared with the corresponding dilatometric calibration parameters obtained by other workers (*6, 9*).

In Series H, three calibration runs using mercury were made, and the temperature range was extended to 5°C. A fourth-order least squares analysis of the volume-temperature data for each of the dilatometers was carried out to obtain parameters V_0, A', B', and C' in Equation 3, as listed in Table II.

$$V = V_0 + A't + B't^2 + C't^3 \qquad (3)$$

Table I. Calibration Parameters of Dilatometers, Equations 2, 4

Dilatometer	$A \times 10^6$, deg^{-1}	$B \times 10^9$, deg^{-2}	$C \times 10^{11}$, deg^{-3}
	Series G[a]		
I	9.675	2.08	
II	9.683	2.64	
III	9.743	1.25	
IV	9.660	2.56	
V	9.606	3.48	
VI	9.638	3.08	
VIII	9.623	3.56	
IX	9.690	1.69	
X	9.672	4.36	
	Series H		
I	9.560	3.69	−1.10
II	9.555	4.52	−2.28
III	9.531	3.26	−0.25
IV	9.549	3.19	−1.06
V	9.707	4.07	−0.92
VI	9.602	4.83	−2.44
VII	9.601	4.07	−1.09
VIII	9.644	4.09	−1.71
IX	9.637	3.77	−0.83
X	9.624	3.89	−2.37

[a] The stopcock of dilatometer VII, Series G, leaked and this dilatometer was not usable.

Table II. Series H. Calibration Parameters of Dilatometers, Equation 3

Dilatometer	V_0, ml	$A' \times 10^3$, ml deg^{-1}	$B' \times 10^7$, ml deg^{-2}	$C' \times 10^9$, ml deg^{-3}
I	128.8259_1	1.205_4	5.82_7	-1.4_2
II	132.3628_0	1.229_5	8.23_9	-3.0_1
III	135.2601_3	1.266_7	4.66_6	-0.3_4
IV	132.2262_9	1.239_3	5.26_8	-1.4_0
V	129.1365_9	1.225_4	6.14_2	-1.1_8
VI	125.9023_1	1.173_1	8.38_8	-3.0_7
VII	131.5917_0	1.234_2	6.43_9	-1.4_4
VIII	126.5079_3	1.190_4	6.80_0	-2.1_6
IX	130.0145_2	1.226_7	5.71_1	-1.0_8
X	130.9214_5	1.229_0	7.42_3	-3.1_0

For the purpose of comparing the constants to those obtained from a third-order fit, an equation similar in form to Equation 2 can be obtained

$$V = V_{25}\,[1 + A(t - 25) + B(t - 25)^2 + C(t - 25)^3] \quad (4)$$

where $V_{25} = V_0 + 25\,A' + 625\,B' + 15{,}625\,C'$, $C = C'/V_{25}$, $B = B'/V_{25} + 75\,C$, and $A = A'/V_{25} + 50\,B - 1875\,C$. These constants are listed in Table I.

Table III. Initial Weights of Mercury and Water in Vacuum in Dilatometers, Grams

Dilatometer	Series G	Series H Run I	Series H Run III
		Mercury	
I	270.5552_6	362.9933_3	340.9969_9
II	244.5771_7	332.1719_6	335.6978_7
III	312.9252_9	345.1632_0	342.2725_4
IV	326.8376_2	337.5573_3	389.1171_0
V	365.9969_0	356.1873_4	360.9238_8
VI	290.4013_8	340.8120_3	330.3569_8
VII		335.2628_2	350.2096_4
VIII	316.7316_4	344.6479_4	336.8072_4
IX	323.1569_6	350.6023_5	346.3686_5
X	333.3469_1	337.1835_3	338.8507_4
		Water	
I	114.2264	103.6870_7	104.0207_3
II	114.5605	109.0540_9	108.0019_6
III	110.4636	111.0538_5	110.3317_8
IV	113.8876	108.9786_9	103.8475_4
V	107.2711	104.2423_6	102.8702_2
VI	117.0116	102.3445_9	101.9491_7
VII		108.1638_2	106.2041_8
VIII	109.0483	102.6806_5	102.2607_5
IX	112.6379	105.5368_2	104.8435_7
X	104.0465	107.5645_6	106.4096_3

Densities of Water. Weights of water and mercury in the dilatometers are shown in Tables III and IV. In Series G, one run was made on water following the previously described modifications in experimental procedure. Withdrawals were made every 5°C over the temperature range of 20–80°C. The V_{25} values of the dilatometers were taken to be the mean of the calculated V_{25} values of the 20°, 25°, 30°, 35°, and 40°C withdrawals, basing them upon the water densities calculated according to the Tilton and Taylor equation.

All densities were corrected to what they would have been had the barometric pressure been 1 atm, assuming a value of 45×10^{-6} atm^{-1} for the compressibility of water (*5*). Later calculation checks have shown this correction to be within the error limits of the measurements and thus they were omitted in Series H.

Three runs on water were made in Series H, each covering the range of 5–80°C at 5° intervals. From 5–40°C the Tilton and Taylor densities were used to calculate the mean weight of water in each dilatometer.

Although the relative densities obtained in Run 2, Series H, were in excellent agreement with Runs 1 and 3, the absolute densities were low by approximately 70×10^{-6} g/ml. This deviation was traced to the nylon stopcock retainers, which had absorbed water from the constant temperature bath during Run 1. Before Runs 1 and 3 there was sufficient time for the stopcock retainer to lose the water absorbed during the previous runs. The loss of water with time was measured so that a correction could be made on Run 2. Although this run was not included in the results, the data, when corrected for the absorption of water, were within experimental error, in agreement with the results of Runs 1 and 3.

Table IV. Weight of Mercury in Vacuum Withdrawn, Grams

Dilatometer	Series G	Series H Run I	Series H Run III
		Temp, °C	
		5.039_4	5.064_8
I		21.4516_6	3.9928_0
II		15.4779_6[a]	4.7245_1
III		16.2336_2[a]	3.6029_2
IV		21.7052_4	3.5669_7
V		17.8734_4[a]	4.0774_4
VI		20.7625_4	4.9300_5
VII		16.9742_8	5.2993_8
VIII		20.9373_8	7.3824_2
IX		18.0583_8	4.3994_8
X		19.8456_4[a]	5.8218_5
		9.995_7	10.018_3
I		0.5961_2	0.5928_7
II		0.6012_2	0.5976_7
III		0.6679_2	0.6115_2
IV		0.5886_2	0.6334_7
V		0.6989_6	0.6058_7
VI		0.5719_2	0.5797_7
VII		0.5878_7	6.063_7
VIII		0.5767_7	0.5814_7
IX		0.5951_2	0.5988_2
X		0.5941_7	0.5972_2
		14.993_9	15.023_5
I		1.0681_0	1.0744_0
II		1.0893_9	1.0996_4
III		1.1253_9[a]	1.1231_4
IV		1.0860_9	1.1127_4
V		1.0701_0	1.0791_9
VI		1.0417_0	1.0448_5
VII		1.0898_4[a]	1.0950_4
VIII		1.0443_5	1.0517_5
IX		1.0740_5	1.0817_9
X		1.0757_0	1.0861_9
	20.040_5	20.038_3	19.872_4
I	0.5246_9	1.4986_7	1.4370_3
II	2.9394_2	1.5388_7	1.4718_2
III	1.5532_7	1.5622_2	1.5096_2
IV	2.7573_4[a]	1.5381_7	1.4752_7
V	1.1178_0	1.4985_2	1.4379_8
VI	3.6476_8	1.4615_8	1.4016_3
VII		1.5250_7	1.4664_8
VIII	3.0132_7	1.4712_2	1.4094_8
IX	1.4117_5	1.5111_2	1.4494_3
X	1.2179_5	1.5236_2	1.4589_8
	25.032_4	24.852_3	24.878_5
I	1.9602_0	1.7831_1	1.8491_6
II	1.9356_6	1.8403_6	1.9083_0
III	1.9334_9	1.8849_5	1.9415_0
IV	1.9962_4[a]	1.8396_1	1.8900_5
V	1.9295_5	1.7843_1	1.8507_1
VI	2.0167_5	1.7463_6	1.8115_1
VII		1.8261_6	1.8902_5
VIII	1.9138_9	1.7534_6	1.8173_1
IX	1.9765_4	1.8021_6	1.8671_5
X	1.8524_3	1.8185_1	1.8836_5

(Continued on next page)

The results of Series G and H are presented in Table V in which the second column contains the mean density values obtained from all the dilatometers at that temperature. The third column contains the mean absolute deviation, symbolized by Δ, of the individual dilatometric densities from their mean, and the fourth column, symbolized by δ, contains the

Table IV. *(Continued)*

Dilatometer	Series G	Series H	
		Run I	Run III
		Temp, °C	
	30.015_8	29.988_9	30.016_0
I	2.3097_3	2.2484_9	2.2525_9
II	2.3020_4	2.3263_8	2.3220_8
III	2.2856_8	2.3755_3	2.3777_3
IV	2.3599_3	2.3246_3	2.2918_8
V	2.2741_7	2.2542_9	2.2428_9
VI	2.3833_7	2.2036_4	2.2025_4
VII		2.3113_3	2.3003_8
VIII	2.2628_5	2.2126_9	2.2120_4
IX	2.3341_4	2.2742_3	2.2718_8
X	2.1868_5	2.2992_8	2.2935_8
	34.888_0	34.903_0	34.958_7
I	2.6009_5	2.4574_7	2.4772_8
II	2.5834_6	2.5497_7	2.5555_8
III	2.5547_9	2.5990_2	2.6099_3
IV	2.6360_6	2.5482_2	2.5143_5
V	2.5361_7	2.4654_7	2.4715_6
VI	2.6698_9	2.4119_8	2.4236_3
VII		2.5316_7	2.5296_9
VIII	2.5277_8	2.4213_3	2.4332_5
IX	2.6091_5	2.4888_7	2.4986_3
X	2.4375_6	2.5180_7	2.5241_9
	39.970_4	40.034_7	40.079_3
I	3.0371_7	2.8634_5	2.8639_1
II	3.0160_4	2.9754_0	2.9594_9
III	2.9769_8	3.0372_0	3.0246_4
IV	3.0700_2	2.9731_5	2.9036_0
V	2.9432_1	2.8731_0	2.8534_2
VI	3.1171_0	2.8113_1	2.8002_6
VII		2.9542_0	2.9250_5
VIII	2.9433_0	2.8225_6	2.8137_6
IX	3.0365_6	2.9027_0	2.8892_8
X	2.8373_8	2.9387_0	2.9217_5
	44.798_1	44.970_3	44.946_5
I	3.1677_1	3.0220_5	2.9846_4
II	3.1505_7	3.1411_9	3.0887_3
III	3.1040_4	3.2037_4	3.1500_3
IV	3.2002_6	3.1404_9	3.0235_3
V	3.0640_4	3.0320_0	2.9712_5
VI	3.2529_2	2.9687_0	2.9236_9
VII		3.1193_9	3.0483_1
VIII	3.0682_8	2.9792_0	2.9338_2
IX	3.1683_3	3.0632_9	3.0104_6
X	2.9554_4	3.1028_9	3.0455_3
	49.818_6	49.933_9	49.898_9
I	3.5753_1	3.2895_3	3.2871_8
II	3.5565_8	3.4230_3	3.3949_8
III	3.4957_5	3.4943_2	3.4703_2
IV	3.6076_0	3.4228_3	3.3251_8
V	3.4491_7	3.3028_8	3.2693_8
VI	3.6673_2	3.2329_4	3.2162_9
VII		3.4004_8	3.3569_5
VIII	3.4571_6	3.2478_8	3.2292_9
IX	3.5690_7	3.3367_8	3.3172_3
X	3.3266_1	3.3821_3	3.3533_3
	54.959_2	53.868_0	54.859_2
I	3.9228_7	2.7805_6	3.5344_7
II	3.9219_1	2.8970_0	3.6539_6
III	3.8502_3	2.9570_0	3.7330_6
IV	3.9683_8	2.8951_0	3.5671_2
V	3.7962_9	2.7901_6	3.5134_7
	54.959_2	53.868_0	54.859_2
VI	4.0390_1	2.7347_1	3.4588_7
VII		2.8751_0	3.6080_7
VIII	3.8076_5	2.7435_6	3.4716_2
IX	3.9268_3	2.8222_1	3.5633_7
X	3.6592_9	2.8600_0	3.6069_2
	60.043_0	59.943_4	60.373_0
I	4.1651_5	4.5776_7	4.2009_4
II	4.1489_8	4.7680_1	4.3466_3
III	4.0682_8	4.8645_5	4.4391_7
IV	4.1941_6	4.7683_1	4.2415_3
V	4.0034_4	4.5963_7	4.1745_9
VI	4.2708_3	4.4995_2	4.1118_9
VII		4.7355_6	4.2885_8
VIII	4.0194_1	4.5189_2	4.1268_4
IX	4.1501_6	4.6445_1	4.2352_3
X	3.8659_9	4.7108_2	4.2861_3
	64.886_7	63.911_9	64.740_9
I	4.2044_5	3.1677_4	3.5195_2
II	4.1917_6	3.3073_3	3.6447_1
III	4.1049_1	3.3654_8	3.7193_1
IV	4.2355_2	3.3025_8	3.5544_7
V	4.0412_6	3.1748_9	3.4989_2
VI	4.3168_2	3.1137_4	3.4471_2
VII		3.2792_3	3.5950_2
VIII	4.0587_1	3.1294_9	3.4591_7
IX	4.1885_9	3.2177_4	3.5508_7
X	3.8976_2	3.2622_3	3.5931_7
	69.797_7	69.709_2	69.917_9
I	4.4868_9	4.8809_5	4.3867_8
II	4.4798_7	5.0901_9	4.5396_7
III	4.3847_9	5.1972_8	4.6362_6
IV	4.5229_4	5.0874_4	4.4255_7
V	4.3091_5	4.9036_0	4.3591_3
VI	4.6094_8	4.8012_1	4.2945_8
VII		5.0539_9	4.4810_2
VIII	4.3332_0	4.8199_0	4.3132_3
IX	4.4748_6	4.9517_5	4.4265_2
X	4.1635_1	5.0262_4	4.4824_7
	74.828_6	74.616_4	74.985_1
I	4.8361_9	4.3591_8	4.5247_2
II	4.8278_6	4.5479_2	4.6844_6
III	4.7214_0	4.6310_6	4.7851_6
IV	4.8716_5	4.5487_2	4.5605_2
V	4.6439_8	4.3789_3	4.4894_7
VI	4.9638_1	4.2899_3	4.4285_7
VII		4.5168_7	4.6189_1
VIII	4.6671_8	4.3050_3	4.4438_2
IX	4.8180_2	4.4268_7	4.5616_7
X	4.4800_2	4.4917_7	4.6178_6
	79.656_2	79.152_4	79.361_7
I	4.8683_8	4.2087_9	4.0786_4
II	4.8529_4	4.3943_8	4.2232_3
III	4.7440_7	4.4795_2	4.3110_3
IV	4.8939_1	4.3893_8	4.1089_4
V	4.6615_8	4.2249_8	4.0493_4
VI	4.9858_7	4.1389_9	3.9932_5
VII		4.3597_8	4.1639_9
VIII	4.6888_8	4.1565_4	4.0082_0
IX	4.8427_4	4.2724_3	4.1112_4
X	4.5003_2	4.3357_3	4.1647_4

[a] A droplet of mercury was left behind during withdrawal. These values were not used.

Table V. Experimental Densities of Water

Temp, °C	Exptl density, g/ml	$\Delta^a \times 10^6$, g/ml	$\delta^b \times 10^6$, g/ml	Calcd density,[c] g/ml	$f^d \times 10^6$, g/ml
Series G					
20.040	0.9982246	0.8	−0.6	0.9982253	−0.7
25.032	0.9970663	1.2	−0.5	0.9970669	−0.6
30.016	0.9956744	0.8	0.9	0.9956735	0.9
34.888	0.9941022	0.6	0.4	0.9941022	0.0
39.970	0.9922593	0.6	0.8	0.9922596	−0.3
44.798	0.9903298	1.2	2.0	0.9903306	−0.8
49.819	0.9881503	1.6	4.9	0.9881517	−1.4
54.959	0.9857486	1.7	12.5	0.9857488	−0.2
60.043	0.9832108	2.3	22.4	0.9832109	−0.1
64.887	0.9806508	2.7	36.1	0.9806506	0.2
69.798	0.9779213	2.7	56.0	0.9779190	2.3
74.829	0.9749875	2.9	80.2	0.9749844	3.1
79.656	0.9720473	3.5	108.7	0.9720428	4.5
Series H, Run 1					
5.039	0.9999907	0.5	−0.5	0.9999912	−0.5
9.996	0.9997276	0.6	−0.8	0.9997285	−0.9
14.994	0.9991285	0.8	−1.0	0.9991295	−1.0
20.038	0.9982257	0.6	0.0	0.9982257	0.0
24.852	0.9971132	0.5	0.3	0.9971129	0.3
29.989	0.9956821	0.5	0.5	0.9956817	0.5
34.903	0.9940973	0.3	0.5	0.9940970	0.2
40.035	0.9922348	0.6	0.7	0.9922351	−0.3
44.970	0.9902593	0.7	3.4	0.9902587	0.6
49.934	0.9881005	1.0	7.3	0.9880996	0.9
53.868	0.9862725	1.6	10.6	0.9862729	−0.4
59.943	0.9832614	1.8	21.5	0.9832621	−0.7
63.912	0.9811777	2.5	33.8	0.9811767	1.0
69.709	0.9779700	2.5	53.9	0.9779694	0.6
74.616	0.9751101	3.0	75.1	0.9751109	−0.8
79.152	0.9723554	3.0	101.1	0.9723554	0.0
Series H, Run 3					
5.065	0.9999904	0.4	−0.4	0.9999908	−0.4
10.018	0.9997268	0.6	0.3	0.9997265	0.3
15.024	0.9991246	0.4	−0.4	0.9991250	−0.4
19.872	0.9982597	0.7	−0.2	0.9982599	−0.2
24.879	0.9971061	0.5	−0.1	0.9971062	−0.1
30.016	0.9956734	0.4	0.0	0.9956735	−0.1
34.959	0.9940779	0.3	0.2	0.9940779	0.0
40.079	0.9922175	0.7	0.5	0.9922180	−0.5
44.947	0.9902681	1.2	2.2	0.9902686	−0.5
49.899	0.9881154	1.5	6.2	0.9881154	−0.1
54.859	0.9857969	1.5	12.2	0.9857971	−0.2
60.373	0.9830388	1.8	21.2	0.9830408	−2.0
64.741	0.9807277	2.5	33.3	0.9807296	−2.0
69.918	0.9778503	3.2	54.0	0.9778504	−0.2
74.985	0.9748890	3.8	75.9	0.9748909	−1.9
79.362	0.9722252	4.1	101.9	0.9722257	−0.5

[a] The mean absolute deviation. [b] Experimental density − Tilton and Taylor equation. [c] Equation 5. [d] Experimental density − calculated density.

difference between the experimental mean densities and the densities as calculated from the unmodified Tilton and Taylor equation. The Tilton and Taylor equation, of course, is only valid for the temperature range 0–40°C.

DISCUSSION

A modified form of the Tilton and Taylor equation,

$$1 - d = \frac{(t - 3.9863)^2(t + 288.9414)}{508929.2\,(t + 68.12963)} - 0.011445 \exp(-374.3/t) \quad (5)$$

was derived to fit the experimental density of water data of Chappuis and this research over the entire 0–80°C range. Except for the exponential term, Equation 5 is identical to the Tilton and Taylor equation, and below 40°C the exponential term is negligible.

The densities as calculated from Equation 5 at the experimental temperatures are given in Table V. The differences between the experimental densities and those calculated from Equation 5 are given under the heading, *f*, in Table V. Equation 5 fits the experimental data with a mean absolute deviation of 0.7×10^{-6} g/ml.

Table VI contains densities calculated from Equation 5 and some selected literature values. The experimental densities from this research differ from those of Smith as reported in Owen et al. by as much as 13×10^{-6} g/ml at 80°C. Since both sets of measurements strived for an accuracy of ±3 ×

Table VI. Comparison of Experimental and Literature Densities of Water, G/Ml

Temp	d^a	d^b	d^c	d^d
40.000	0.992248	0.992247	0.992248	
45.000	0.990246	0.990244	0.990246	
50.000	0.988070	0.988065	0.988069	0.988073
55.000	0.985729	0.985722	0.985727	
60.000	0.983233	0.983223	0.983233	0.983239
65.000	0.980589	0.980578	0.980585	
70.000	0.977804	0.977791	0.977801	0.977813
75.000	0.974882	0.974870	0.974884	
80.000	0.971829	0.971816	0.971834	0.971843

[a] This research, Equation 5. [b] Owen et al. (Smith's values) (*9*). [c] Smith's recalculated values (this paper). [d] Jones et al. (Taylor's values) (*6*).

10^{-6} g/ml or better, and since both used similar experimental methods, it is difficult to attribute the difference of 13×10^{-6} g/ml entirely to experimental errors.

Initially it was considered possible that the mercury density data of Beattie et al. used for calibration purposes in this research were not consistent with the water density data of Chappuis. Fortunately Chappuis also measured densities of mercury using the same apparatus as was used for part of his water density measurements (*2*). A comparison of the two sets mercury density data indicated that this factor did not explain the discrepancy with Smith's data.

As a second alternative, Smith's data (*9*, *10*), was closely examined. Smith calibrated his dilatometers with water assuming the water densities calculated from the Tilton and Taylor equation to be correct from 0–45°C. He made one run on water at approximately 10° intervals from 5–85°C and used the data at approximately 5°, 15°, 25°, 35°, and 45°C as his calibration points. Thus he had four $\Delta V/\Delta t$ values per dilatometer with which to obtain the a and b parameters of Equation 1. Obviously this placed considerable reliance on each single $\Delta V/\Delta t$ value, and herein lies part of the problem.

First, the data of Chappuis upon which the Tilton and Taylor equation is based did not extend beyond 42°C. Consequently, the density of water used by Smith at 45°C was based upon an extrapolation via the Tilton and Taylor equation which yields low-density values at temperatures greater than 42°C. Second, Chappuis had only nine density of water determinations above 35°C and seven of these values have values greater than those calculated according to the Tilton and Taylor equation (*12*). In general, the densities of these nine values lie slightly above that which would be calculated using the Tilton and Taylor equation.

For the two highest calibration temperatures used by Smith, i.e., 34.938° and 44.935°C, the densities of water calculated using Equation 5 are 0.3 and 2.8×10^{-6} g/ml larger than those calculated using the Tilton and Taylor equation, respectively. These are certainly minor differences, but they set the calibration slope which especially affects the densities at the higher temperatures. When Smith's data were recalculated using

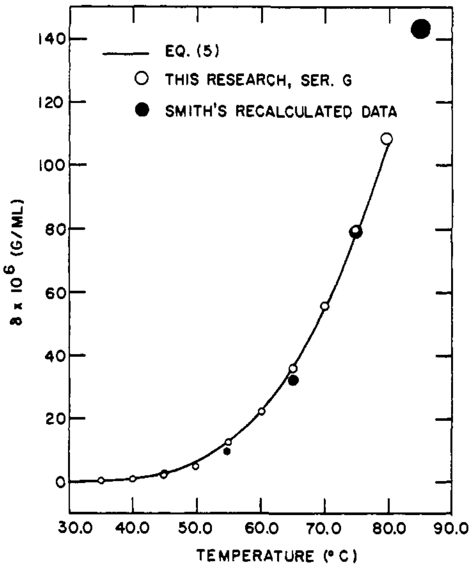

Figure 2. Comparison of Smith's recalculated data with this research

Table VII. Density of Water, G/Ml, Equation 5

Temp, °C		Tenths of degrees 0	1	2	3	4	5	6	7	8	9
0	0.999	8676	8743	8808	8871	8933	8993	9051	9107	9161	9214
1		9265	9314	9362	9407	9451	9493	9534	9572	9610	9645
2		9678	9710	9740	9769	9796	9821	9844	9866	9886	9905
3		9922	9937	9950	9962	9972	9981	9988	9993	9997	9999
4	1.000	0000	*9999	*9996	*9992	*9986	*9979	*9970	*9960	*9948	*9934
5	0.999	9919	9902	9884	9864	9843	9820	9796	9770	9742	9713
6		9683	9651	9618	9583	9546	9508	9469	9428	9386	9342
7		9297	9250	9202	9153	9102	9049	8995	8940	8883	8825
8		8765	8704	8642	8578	8513	8446	8378	8309	8238	8166
9		8092	8017	7941	7863	7784	7704	7622	7539	7454	7368
10		7281	7193	7103	7011	6919	6825	6730	6633	6536	6437
11		6336	6234	6131	6027	5922	5815	5706	5597	5486	5374
12		5261	5146	5030	4913	4795	4675	4555	4432	4309	4184
13		4059	3931	3803	3674	3543	3411	3278	3143	3007	2870
14		2732	2593	2453	2311	2168	2024	1879	1732	1584	1436
15		1285	1134	0982	0828	0674	0518	0361	0202	0043	*9882
16	0.998	9721	9558	9394	9229	9062	8895	8726	8557	8386	8214
17		8041	7867	7691	7515	7337	7159	6979	6798	6616	6433
18		6248	6063	5877	5689	5501	5311	5120	4928	4735	4541
19		4346	4150	3953	3754	3555	3355	3153	2950	2747	2542
20		2336	2130	1922	1713	1503	1292	1080	0867	0653	0437
21		0221	0004	*9786	*9567	*9346	*9125	*8903	*8679	*8455	*8230

(*Continued on next page*)

Table VII. *(Continued)*

Temp, °C		Tenths of degrees									
		0	1	2	3	4	5	6	7	8	9
22	0.997	8003	7776	7547	7318	7088	6856	6624	6390	6156	5921
23		5684	5447	5208	4969	4729	4487	4245	4002	3758	3512
24		3266	3019	2771	2522	2272	2021	1769	1516	1262	1007
25		0751	0494	0237	*9978	*9718	*9458	*9196	*8934	*8671	*8406
26	0.996	8141	7875	7608	7340	7071	6801	6530	6258	5986	5712
27		5438	5162	4886	4608	4330	4051	3771	3490	3209	2926
28		2642	2358	2072	1786	1499	1211	0922	0632	0341	0049
29	0.995	9757	9464	9169	8874	8578	8281	7983	7684	7385	7084
30		6783	6481	6178	5874	5569	5264	4957	4650	4341	4032
31		3722	3411	3100	2787	2474	2160	1845	1529	1212	0894
32		0576	0257	*9937	*9616	*9294	*8971	*8648	*8323	*7998	*7672
33	0.994	7345	7018	6689	6360	6030	5699	5367	5035	4701	4367
34		4032	3696	3360	3022	2684	2345	2005	1664	1323	0980
35		0637	0293	*9949	*9603	*9257	*8910	*8562	*8213	*7864	*7513
36	0.993	7162	6810	6458	6104	5750	5395	5039	4683	4325	3967
37		3608	3248	2888	2527	2165	1802	1438	1074	0709	0343
38	0.992	9976	9609	9240	8871	8502	8131	7760	7388	7015	6642
39		6267	5892	5517	5140	4763	4385	4006	3626	3246	2865
40		2483	2101	1717	1333	0948	0563	0177	*9790	*9402	*9013
41	0.991	8624	8234	7844	7452	7060	6667	6273	5879	5484	5088
42		4692	4294	3896	3498	3098	2698	2297	1896	1493	1090
43		0687	0282	*9877	*9471	*9065	*8657	*8249	*7841	*7431	*7021
44	0.990	6610	6199	5786	5373	4960	4545	4130	3714	3298	2881
45		2463	2044	1625	1205	0784	0363	*9941	*9518	*9095	*8671
46	0.989	8246	7820	7394	6967	6540	6111	5683	5253	4823	4392
47		3960	3528	3095	2661	2227	1792	1356	0919	0482	0045
48	0.988	9606	9167	8727	8287	7846	7404	6962	6518	6075	5630
49		5185	4739	4293	3846	3398	2950	2501	2051	1600	1149
50		0698	0245	*9792	*9339	*8884	*8429	*7974	*7517	*7060	*6603
51	0.987	6145	5686	5226	4766	4305	3844	3381	2919	2455	1991
52		1527	1061	0595	0129	*9661	*9193	*8725	*8256	*7786	*7316
53	0.986	6844	6373	5900	5427	4954	4480	4005	3529	3053	2576
54		2099	1621	1142	0663	0183	*9703	*9221	*8740	*8257	*7774
55	0.985	7291	6806	6321	5836	5350	4863	4376	3888	3399	2910
56		2420	1930	1439	0947	0455	*9962	*9468	*8974	*8480	*7984
57	0.984	7488	6992	6495	5997	5498	5000	4500	4000	3499	2998
58		2496	1993	1490	0986	0482	*9977	*9471	*8965	*8458	7951
59	0.983	7443	6934	6425	5915	5405	4894	4382	3870	3357	2844
60		2330	1815	1300	0785	0268	*9751	*9234	*8716	*8197	*7678
61	0.982	7158	6638	6117	5595	5073	4550	4027	3503	2979	2454
62		1928	1402	0875	0347	*9819	*9291	*8762	*8232	*7702	*7171
63	0.981	6639	6107	5575	5042	4508	3974	3439	2903	2367	1831
64		1294	0756	0217	*9679	*9139	*8599	*8059	*7517	*6976	*6433
65	0.980	5891	5347	4803	4259	3714	3168	2622	2075	1527	0980
66		0431	*9882	*9332	*8782	*8231	*7680	*7128	*6576	*6023	*5469
67	0.979	4915	4361	3806	3250	2693	2137	1579	1021	0463	*9904
68	0.978	9344	8784	8223	7662	7100	6538	5975	5411	4847	4283
69		3717	3152	2586	2019	1451	0884	0315	*9746	*9177	*8607
70	0.977	8036	7465	6893	6321	5748	5175	4601	4027	3452	2876
71		2300	1724	1147	0569	*9991	*9412	*8833	*8253	*7673	*7092
72	0.976	6510	5928	5346	4763	4179	3595	3011	2425	1840	1253
73		0667	0079	*9492	*8903	*8314	*7725	*7135	*6544	*5953	*5362
74	0.975	4770	4177	3584	2990	2396	1802	1206	0610	0014	*9417
75	0.974	8820	8222	7624	7025	6425	5825	5225	4624	4022	3420
76		2818	2214	1611	1007	0402	*9797	*9191	*8585	*7978	*7371
77	0.973	6763	6154	5546	4936	4326	3716	3105	2493	1882	1269
78		0656	0042	*9428	*8814	*8199	*7583	*6967	6351	*5733	*5116
79	0.972	4498	3879	3260	2640	2020	1399	0778	0156	*9534	*8911
80	0.971	8288	7664	7040	6415	5790	5164	4537	3910	3283	2655

these density values, better agreement was obtained with the density of water values reported in this paper. This particular correction accounts for about one half of the differences. The remainder of the change in densities upon recalculation results because Smith rounded off numbers at each stage in his calculations as opposed to the retention of 10 digits at all steps in the computerized recalculations.

Smith's recalculated data above 30°C are compared in Figure 2 with the δ values obtained in this research. The error circles in this plot reflect the standard deviation of the mean. Smith made a second approximation in his original calculations, using all of his data for the purpose of obtaining calibration parameters for his dilatometers, and consequently the error in these densities will be less. A second calculation will have some effect on the first approximation data shown in Figure 2, but since such a calculation also smooths the data, it was felt to be less satisfactory regarding reliable error determinations. One of the reasons for the appreciable uncertainty in the two highest temperatures of Smith is that prior to the 75°C withdrawal, two of his dilatometers leaked, leaving only four dilatometric measurements at 75° and 85°C. The recalculated Smith values are listed in the fourth column of Table VI. Similar criticism of the Owen et al. densities has been voiced by Kell and Whalley (*8*).

For the convenience of those workers requiring accurate densities of water between 0° and 80°C, a table of water densities calculated from Equation 5 is presented in Table VII. Although the densities in this table are quoted to the seventh decimal place, it should be realized that at least above 40°C they are uncertain in the sixth decimal place with the uncertainty increasing with temperature.

LITERATURE CITED

(1) Beattie, J. A., Blaisdell, B. E., Kaye, J., Gerry, H. T., Johnson, C. A., *Pro. Am. Acad. Arts Sci.*, **74**, 371 (1941).
(2) Chappuis, P., *Trav. Memoires Bur. Intern. Meas.*, **13**, C10 (1907).
(3) Chappuis, P., *ibid.*, D40 (1907).
(4) Gildseth, W. M., PhD Thesis, Iowa State University, 1964.
(5) Harned, H. S., Owen, B. B., "The Physical Chemistry of Electrolytic Solutions," 3rd ed., Reinhold, New York, N.Y., 1958.
(6) Jones, G., Taylor, E. F., Vogel, R. C., *J. Amer. Chem. Soc.*, **70**, 966 (1948).
(7) Kell, G. S., *J. Chem. Eng. Data*, **12**, 66 (1967).
(8) Kell, G. S., Whalley, E., *Phil. Trans. Roy. Soc.*, **258a**, 565 (1965).
(9) Owen, B. B., White, J. R., Smith, J. S., *J. Amer. Chem. Soc.*, **78**, 3561 (1956).
(10) Smith, J. S., PhD Thesis, Yale University, New Haven, Conn., 1944.
(11) Steckel, F., Szapiro, S., *Trans. Faraday Soc.*, **59**, 331 (1963).
(12) Tilton, L. W., Taylor, J. K., *J. Res. Nat. Bur. Stand.*, **18**, 205 (1937).

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Heat of Formation of Nitroxy Fluoride(G)

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The heat of the reaction $F_2(g) + NaNO_3(s) = O_2NOF(g) + NaF(s)$ has been measured calorimetrically, and from the resulting data, the standard heat of formation of $O_2NOF(g)$, $\Delta H_{f298}°$, has been established as +2.5 ± 0.5 kcal/mol.

Although the physical and chemical properties of nitroxy fluoride have been extensively studied, thermochemical data on the heat of formation of this potentially explosive O—F bonded species have not been published until recently. While work at United Technology Center on this subject was in process, Talakin et al. (*7*) reported a heat of formation of −4.2 ± 0.9 kcal/mol for gaseous O_2NOF at 21°C. However, bond energy estimates yielded a less exothermic value for the derived heat of formation of nitroxy fluoride than the value reported by the Russian workers, and one of the preliminary experimental approaches used in this work, which was similar to the one they used, produced inconsistent results. In an attempt to obtain a more accurate heat of formation value for nitroxy fluoride, which would be useful in describing the O—F bond energy in related compounds, a calorimetric program was selected to minimize side effects inherent in similar reactive systems.

EXPERIMENTAL APPROACH

Several possible reaction systems potentially applicable to the determination of the $\Delta H_{f298}°$ for $O_2NOF(g)$ by calorimetric methods have been reported. Each of the following systems was investigated to determine the most effective procedure. Preliminary emphasis was placed on the reproducibility of well-defined products from a simple reaction system which could be well characterized analytically.

The original preparation of nitroxy fluoride (*1*, *5*) involved the direct fluorination of nitric acid according to the following equation:

$$HNO_3(l,aq) + F_2(g) \rightarrow O_2NOF(g) + HF(g) \qquad (1)$$

In principle, Reaction 1 is ideally suited for calorimetric study; however, experimental difficulties associated with the degree of solubility of the reaction products in the nitric acid, and the application of the correct heat effect values for this process were found to limit the usefulness of this reaction for calorimetric study.

Skiens and Cady (*6*) have reported that the spark-induced decomposition of nitroxy fluoride yielded only nitrosyl fluoride and oxygen according to the following stoichiometry:

$$O_2NOF(g) \rightarrow NOF(g) + O_2(g) \qquad (2)$$

Because of the simple products, Reaction 2 appeared promising from a calorimetric standpoint. However, in tests employing nichrome fuse wire to initiate gas phase decomposition in a modified combustion bomb system, the reaction was more complex than previously reported, with variable formation of nitrogen dioxide, nitric oxide, and nitryl fluoride in conjunction with nitrosyl fluoride and oxygen.

Nitroxy fluoride has been reported (*1*) to decompose with aqueous potassium hydroxide:

$$O_2NOF(g) + 2OH^-(aq) \rightarrow {}^1/_2O_2(g) + F^-(aq) + NO_3^-(aq) + H_2O(l) \qquad (3)$$

The applicability of Reaction 3 was investigated by hydrolyzing

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