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### The density of seawater solutions at one atmosphere as a function of temperature and salinity

by Frank J. Millero,1 Agustin Gonzalez and Gary K. Ward

#### ABSTRACT

The relative density  $(d - d_o)$  of diluted and evaporated standard seawater solutions have been determined at one atmosphere with a magnetic float densimeter and a suspension balance from 0.5 to 40% salinity and 0 to 40°C. The resulting densities (d) have been fitted to an equation of the form (std. dev. 3.3 ppm)

 $d = d_o + A S(\%_o) + B S(\%_o)^{3/2} + C S(\%_o)^2$ 

where  $d_o$  is the density of water (Kell, 1975),  $S(\infty)$  is the salinity in parts per thousand and A, B, C are temperature dependent parameters. The smoothed densities have been compared to the results of other workers. Near 35% salinity our results agree on the average with Knudsen, et al., (1902) to  $\pm$  8.7 ppm; with Thompson and Wirth (1931) to  $\pm$  13 ppm; with Cox, et al., (1970) to  $\pm$  5.7 ppm; with Kremling (1972b) to  $\pm$  4.8 ppm and with Fofonoff and Bryden (1975) to  $\pm$  4.7 ppm. For Baltic Sea waters, our densities are lower than the results of other workers, and for Red and Mediterranean Sea waters our densities are higher. These deviations are related to the differences that occur (at a fixed chlorinity) between natural sea waters and estuaries and seawater diluted with pure water or slowly evaporated. By determining the total solids using composition data, the densities of all natural waters are shown to have nearly  $(\pm 10 \text{ ppm})$  the same density at the same concentration of total solids or true salinity. The expansibilities determined from the temperature dependence of our densities agree on the average to  $\pm 0.4 \times 10^{-6}$  deg<sup>-1</sup> with the work of Knudsen, et al., to  $\pm 1.8 \times 10^{-6}$  deg<sup>-1</sup> with the work of Cox, et al., and to  $\pm 1.1 \times 10^{-6}$  deg<sup>-1</sup> with the work of Fofonoff and Bryden from 0 to 25°C and salinities of 30 to 40%. These results are in agreement with the earlier findings of Millero and Lepple (1973) and indicate that although the densities calculated from the Hydrographic Tables (Knudsen, 1901) may be in error by as much as  $10 \times 10^{-6}$  g cm<sup>-3</sup>, the temperature dependencies of the densities are internally consistent to within  $\pm 2 \times 10^{-6} \text{ deg}^{-1}$ .

#### 1. Introduction

The density of seawater as a function of temperature, pressure and salinity is needed in a number of oceanographic calculations. The presently used densities of seawater at one atmosphere (Knudsen, 1901) are based on the measurements of Knudsen, et al., (1902). Knudsen, et al., made density measurements (precise to

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 $\pm$  3 ppm or 3  $\times$  10<sup>-6</sup>) on twenty-four samples of seawater from 0 to 30° and 5 to 40% salinity. Most of the samples were from the Baltic and North Atlantic and are now recognized as not being representative of the world oceans. Over the past 70 years, a number of workers have questioned the reliability of these measurements. In 1931, Thompson and Wirth measured the density of thirty-six samples of seawater from various oceans at 0°C. They found that their measured values were on the average 20 ppm higher than those given by Knudsen (1901). They also found that the differences were reduced to  $\pm 6$  ppm if the comparisons were made on different chlorinity scales. Bein, et al., (1935) made extensive investigations into Knudsen's relationships between density and chlorinity. Their results agreed with the hydrographic tables to within ± 20 ppm. More recently, Cox, et al., (1970) measured the densities of fifty samples of seawater with salinities from 9 to 41% from 0 to 25°C (9 to 39% salinity) to a quoted precision of 8 ppm (86 measurements). Only five samples (nine measurements) were ocean waters (Pacific and Atlantic); the remainder of the samples were from the Red, Baltic and Mediterranean Seas or mixtures of Baltic and Red Sea (one Baltic-Atlantic and one Baltic-Pacific mixture were also used). They found that the densities from Knudsen's tables for 35% salinity are on the average too low from 0 to 25°C by 6 ppm (which is within their quoted standard error). Kremling (1972b) determined the densities on nine samples of seawater from 15 to 39% salinity at six temperatures from 0 to 25°C to a precision of 3 ppm. The samples were apparently the same as those prepared by Cox, et al., by mixing Red Sea water with Baltic water. The mean difference between Kremling's results and those of Cox, et al., was 8 ppm. Kremling's results also indicate that Knudsen's tables are on the average 13 ppm too low. Kremling found after making measurements on 200 Baltic samples, that Knudsen's tables (at ~ 5‰ salinity) are on the average too low by 25 ppm, which is lower in magnitude than obtained by Cox, et al., (59 ppm). Millero and Lepple (1973) measured the densities of standard seawater and found results that agree to within 10 ppm with Knudsen's tables. They also found that the effect of temperature on the densities of standard seawater and calculated from Knudsen's tables agreed to within ± 1 ppm from 0 to 30°C. All of these recent studies indicate that Knudsen's tables are reliable to  $\pm 1$  ppm in expansibility or thermal expansion and  $\pm 10$  ppm in density, which is better than what was thought by earlier workers (Thompson and Wirth, 1931; Bein, et al., 1935; Carritt and Carpenter, 1958).

In an attempt to determine a reliable equation of state of seawater, we have been studying the PVT properties of seawater (Lepple and Millero, 1971; Millero and Lepple, 1973; Wang and Millero, 1973; Emmet and Millero, 1973; Fine, Wang and Millero, 1974; Millero and Kubinski, 1975; Chen and Millero, 1975; Millero, *et al.*, 1975 in preparation). In the present paper we will present our one atmosphere density measurements on standard seawater solutions as a function of temperature (0 to  $40^{\circ}$ C) and salinity (0 to  $40^{\circ}$ c). We feel that before it is possible to

make an extensive study of the density of oceanic waters, it is necessary to first characterize the PVT properties of standard seawater of known composition. In future work, we plan to examine in detail the relationship between standard seawater densities and samples from the world oceans and seas.

#### 2. Experimental

The relative densities of most of the seawater solutions were determined with a magnetic float densimeter (Millero, 1967a,b). The methods of calibration and operation of the densimeter are described in detail elsewhere (Millero, 1967a,b). The pyrex glass float, which contains a permanent magnet, floats in the solution contained by a 250 cm<sup>3</sup> cell. The cell is securely mounted to a brass support that contains a solenoid. The entire apparatus is at the bottom of a constant temperature bath. Platinum weights are added to the float, which has a density slightly less than water, to adjust its buoyancy. The current through the solenoid is used to pull the float to the bottom of the solution container. This current is gradually reduced until the float just lifts off the bottom of the solution cell. This "lift off" or equilibrium current is reproducible to  $\pm 5 \mu$  amp (which is equivalent to  $\pm 0.3$  ppm in density). The density (d) is related to the current (i) by the equation

$$d\left(V_{f} + w/d_{pt}\right) = W + w + f i \tag{1}$$

where  $V_f$  is the volume of the float, w is the mass of platinum added to the float,  $d_{pt}$  is the density of platinum (MacInnis, et al., 1951), W is the mass of the float, and f is the magnetic interaction constant. The system is calibrated by measuring the equilibrium current in ion exchanged water (saturated with air) as a function of platinum weights added to the float

$$w (1 - d_o/d_{pt}) = -f i + (d_o V_f - W)$$
(2)

The relative densities or specific gravity of water  $(d_o = \rho/\rho_{max})$  used in the calibration were taken from the work of Kell (1967). The f and  $V_f$  determined in the calibration using at least five platinum weights yielded densities for pure water that agree to within 1 ppm with the value used in the calibration (which represents the precision of the densimeter at a given temperature). The accuracy of the relative densities determind by the magnetic float densimeter is  $\pm 2$  ppm (Millero, 1967a).

The densimeter is used to measure the density difference  $(\Delta d)$  between a solution and pure water from the equation

$$\Delta d = d - d_o = f \Delta i / [V_f + w/d_{pt}]$$
(3)

where  $\Delta i = i - i_o$  is the difference between the equilibrium current in the solution and pure water. It should be pointed out that the values of  $\Delta d$  determined in this manner are independent of the units used for the density of water (that is, g ml<sup>-1</sup> or g cm<sup>-3</sup>) and temperature scale used when calibrating the system. By adding

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 $d_o$  (in units of g cm<sup>-3</sup>), the values of  $\Delta d$  can be converted to absolute values (g cm<sup>-3</sup>). Since the absolute density of water is presently known to only  $\pm 4$  ppm at its maximum density (Kell, 1975), most workers have reported their values for seawater relative to a value of water equal to 1.000000 g ml<sup>-1</sup> at 4°C. In converting relative densities or specific gravities to absolute units, Kell (1967) has used the factor 0.999972 g cm<sup>-3</sup> at 4°C. More recently Menaché and Girard (1970) have suggested that the maximum (1973) density of standard mean ocean water (SMOW) be assigned a value of 0.999975 g cm<sup>-3</sup> at 4°C. The absolute maximum densities of waters of known isotopic composition can be related to the value for *SMOW* by

$$\rho_{max} = \rho_{SMOW} + 2.1 \times 10^{-7} \,\delta_{18} + 1.5 \times 10^{-8} \,\delta_D \tag{4}$$

where  $\delta_D = 10^3 [D/H \text{ (sample) } / D/H \text{ (SMOW)} - 1]$  and  $\delta_{18} = 10^3 [^{18}\text{O}/^{16}\text{O} \text{ (sample) } / ^{18}\text{O}/^{16}\text{O} \text{ (SMOW)} - 1]$  (Craig, 1961). As discussed elsewhere, (Millero and Emmet, 1975) the ion exchanged water used to calibrate our densimeters has a density that is  $1 \times 10^{-6}$  g cm<sup>3</sup> lower than SMOW. Measurements on the absolute density of SMOW are presently being made by the International Bureau of Weights and Measures in France and the National Bureau of Standards in the United States.

The relative densities of a number of seawater solutions at 0 and 25°C have been determined by using a suspension buoyancy densimeter (Ward and Millero, 1974). The suspension densimeter consists of a 300 cm<sup>3</sup> pyrex float that is suspended by a nylon line from a Mettler balance. The volume of the float was determined by weighing in air and water. The relative densities of the seawater solutions were determined from

$$\Delta d = (W - W_o) / V_f \tag{5}$$

where W and  $W_o$  are the weight of the float in the solution and pure water and  $V_f$  is the volume of the float. The suspension densimeter has a precision of  $\pm 1$  ppm and an accuracy of  $\pm 2$  ppm (Ward and Millero, 1974).

Both densimeters are contained in constant temperature baths controlled to better than  $\pm 0.001$  °C (which is equivalent to  $\pm 0.3$  ppm in density) with Tronac or Hallikainen thermoregulators. The temperature of the baths (IPTS – 1968 Temperature Scale) was set with a platinum resistance thermometer (calibrated by the National Bureau of Standards) and a G-2 Mueller Bridge. The temperature of the bath was monitored with a Hewlett-Packard quartz crystal thermometer during an experimental run.

The pure water used in the calibrations and to dilute the seawater samples was ion exchanged (18 meg  $\Omega$ ) water. The isotopic composition of MIAMI water relative to SMOW was found to be  $\delta_D = -9.0$  and  $\delta_{18} = -2.1$  (Millero and Emmet, 1975).

The seawater solutions below 19.375% chlorinity were made by weight diluting standard seawater (P63 (1973) 19.375% chlorinity) with ion exchanged water. The



Figure 1. The differences in the conductivity salinity between standard seawater diluted or slowly evaporated and natural waters (Cox, *et al.*, 1967). The curve is from equation (17).

concentrated seawater solutions were obtained by slowly evaporating (by weight) standard seawater at 30°C. Since it is difficult to control the evaporation in the suspension balance densimeter, the solutions were analyzed after the density was measured by using a Beckman salinometer. The salinometer was calibrated by measuring the conductivity ratio of weight diluted or evaporated samples of standard seawater. The ratios  $(R_t)$  were corrected to 15°C using the relationship developed by Cox, *et al.*, (1967)

$$R_{15} = R_t + 10^{-5} R_t (R_t - 1) (t - 15^{\circ} \text{C}) [96.7 - 72.0 R_t + 37.3 R_t^2 - (0.63 + 0.21 R_t^2) (t - 15^{\circ} \text{C})]$$
(6)

The chlorinities were converted to salinities using the relationship (UNESCO, 1967)

$$S(\%_0) = 1.80655 Cl(\%_0) \tag{7}$$

The weight salinities were related to the conductivity ratios at 15°C by (using a least squares method)

$$S(\%_{c}) = 27.25861 R_{15} + 19.06186 R_{15}^{2} - 27.23835 R_{15}^{3} + 27.09961 R_{15}^{4} - 14.19791 R_{15}^{5} + 3.01619 R_{15}^{6}$$
(8)

(std. dev.  $\pm 0.003\%$ ). The weight salinities determined from this equation are in good agreement ( $\pm 0.003\%$ ) with the work of Brown and Allentoft (1966), but they differ significantly from those determined by the relationship of Cox, *et al.*, (see Figure 1)

$$S(\%_{c}) = -0.08996 + 28.29720 R_{15} + 12.80832 R_{15}^{2} - 10.67869 R_{15}^{3} + 5.98624 R_{15}^{4} - 1.32311 R_{15}^{5}$$
(9)

Over the oceanographic range (30 to 40% salinity) the differences are as large as

				$(d-d_{o})10^{3}$	$(d-d_{o})10^{3 b}$	
	Sample	e	<b>C</b> 1(‰)	Measured	Adjusted	Δ, ppm°
P65	2/12	(1973)	19.381	28.277	28.2665	0.7
Pes	3/6	(1973)	19.375	28.265	28.2635	-2.3
Pes	3/6	(1973)	19.381ª	28.275	28.2645	-1.3
P58	12-13/6	(1971)	19.375	28.266	28.2645	-1.3
P 56	12-13/6	(1971)	19.375	28.269	28.2675	1.7
P52	18-19/10	(1969)	19.3705	28.263	28.2683	2.5
P <sub>47</sub>	15-16/4	(1967)	19.374	28.266	28.266	0.2
				mea	n 28.265 <sub>8</sub>	1.4

Table 1. Comparison of the relative densities of various standard seawater samples.

a) Evaporated to this chlorinity (originally 19.375% Cl); the measurement made on suspension balance.

b) Adjusted by using our density data as a function of  $Cl(\%_{e})$  at 0°C  $[d/Cl(\%_{e}) = 1.5 \text{ ppm}/0.001 Cl(\%_{e})]$ .

c) Differences of the adjusted densities from the mean value (28.265<sub>8</sub>) in parts per million.

0.008%. The cause of these differences is related to the diluted waters used to obtain the conductivity relationship. The low salinity samples used by Cox, *et al.*, were taken from the Baltic; while the high salinity samples were from the Red Sea. The relative composition of the two end members are different (Lyman and Fleming, 1940; Wilson, 1975) causing the conductance to be different from weight diluted or evaporated standard seawater. It should be pointed out that a salinity difference of 0.01% is equivalent to a density difference of 8 ppm.

Since it has been shown (Bradshaw, 1973; Brewer and Bradshaw, 1975) that the pH and alkalinity can affect the density of seawater, we have determined the pH and total alkalinity on a number of samples of standard seawater using potentiometric (Edmond, 1970) and thermometric (Millero, Schrager and Lee, 1974) titrations. The total alkalinity was found to be  $2.332 \pm 0.003 \text{ meq kg}^{-1}$  and the total dissolved  $CO_2$  was  $2.226 \pm 0.009 \text{ m}$  mol kg<sup>-1</sup>. The pH of the standard seawater was about 7.9 when removed from the bottle and increased to 8.1 after equilibration with the atmosphere. No change in the density (within the precision of our measurements) was found for this pH change. All of the calibrations and measurements were made with the solutions in equilibrium with the atmosphere. Thus, the decrease in density due to dissolved air (which can decrease the density by as much as  $3 \times 10^{-6}$ , Millero and Emmet, 1975) essentially cancels, i.e.,  $d - d_0$  is unaffected by dissolved air.

#### 3. Results

In an attempt to determine if various samples of standard seawater have similar densities, we have measured the densities of a number of standard seawater samples at  $0^{\circ}$ C. The results given in Table 1 indicate that the standard seawater samples of

Table 2. The relative densities of seawater solutions determined with the magnetic float densimeter.

0°C			5°C	10°C	
Cl(%)	$1000(d - d_{o})$	Cl(‰)	$1000(d-d_{o})$	Cl(%)	$1000(d-d_{\circ})$
22.144	32.315	22.144	31.685	22.144	31.173
19.375	28.269	19.375	27.709	19.375	27.252
16.636	24.276	16.636	23.793	16.636	23.391
12.448	18.174	15.462	22.119	11.456	16.108
7.905	11.560	11.232	16.077	9.839	13.834
5.077	7.441	8.068	11.564	4.781	6.736
4.043	5.926	5.002	7.185	3.636	5.135
2.918	4.283	3.833	5.509	2.033	2.871
1.898	2.796	2.546	3.667	0.884	1.253
1.063	1.569	1.963	2.828	0.575	0.816
0.767	1.136	1.248	1.802	0.264	0.375
		0.639	0.926		
		0.338	0.490		

15°C

20°C

25°C

C1(%)	$1000(d - d_0)$	Cl(%)	$1000(d - d_{o})$	Cl(%)	$1000(d - d_{o})$
22.144	30.744	22.144	30.390	22.144	30.094
19.375	26.868	19.377	26.562	19.375	26.297
16.636	23.063	19.375	26.559	16.636	22.565
13.918	19.298	16.636	22.790	12.237	16.585
11.171	15.491	15.179	20.790	7.729	10.478
6.544	9.081	11.608	15.896	4.497	6.098
4.907	6.813	5.418	7.434	2.875	3.908
3.525	4.898	2.599	3.576	1.674	2.277
1.132	1.582	1.221	1.685	0.789	1.078
0.248	0.348	0.589	0.817		

30°C

35°C

40°C

Cl(%)	$1000(d - d_o)$	Cl(‰)	$1000(d - d_{\circ})$	Cl(%)	$1000(d - d_o)$
22.160	29.873	22.160	29.653	22.160	29.482
19.377	26.081	19.376	25.898	19.377	25.756
15.182	20.417	14.360	19.176	15.493	20.580
11.564	15.540	11.398	15.220	12.081	16.044
9.114	12.256	8.224	10.984	8.281	11.000
5.398	7.260	6.038	8.068	5.472	7.269
2.551	3.438	4.733	6.327	3.275	4.356
0 589	0 799	3.520	4.709	1.610	2.147
0.505	0.1777	2.579	3.457	0.800	1.071
		2.037	2.733		
		1.763	2.367		
		0.874	1.177		

Table 3. Comparisons of the densities of seawater measured with the magnetic float densimeter and a hydrostatic balance.

#### DENSITY (0°C)

		1000(4	$d-d_{\circ})$	
		Suspension	Magnetic <sup>*</sup>	
S(‰)	<b>R</b> 15	Balance	Float	$\Delta d(\text{ppm})$
40.426	1.13674	32.669	32.669	0
37.662	1.06749	30.423	30.427	4
35.012	1.00030	28.275	28.276	1
30.240	0.87727	24.410	24.408	2
26.002	0.76569	20.986	20.984	2
25.278	0.74641	20.396	20.401	5
20.021	0.60426	16.171	16.172	1
14.424	0.44826	11.678	11.678	0
6.931	0.22844	5.642	5.645	3
3.327	0.11529	2.726	2.726	0
1.386	0.05105	1.149	1.147	2
				1.8 (mean)
		DENSITY (25°C	2)	
40.028	1.12682	30.131	30.127	4
36.934	1.04911	27.772	27.773	1
35.135	1.00345	26.404	26.405	1
29.793	0.86560	22.351	22.352	1
25.676	0.75701	19.245	19.244	1
			All the second sec	

1.293	0.04786	0.989	0.986	3	
3.006	0.10485	2.275	2.273	2	
6.603	0.21841	4.970	4.969	1	
4.414	0.44797	10.805	10.806	1	
9.654	0.59418	14.722	14.724	2	
4.759	0.73255	18.555	18.554	1	
5.070					

1.7 (mean)

a) Determined from the densities at 0 and  $25^{\circ}C$  given in Table 2 fitted to (equation 10) by a least squares method.

various years agree on the average to within  $\pm 1.4$  ppm with a maximum deviation of 2.5 ppm. It thus appears that the standard seawater samples have a composition that is consistent within the experimental precision of our measurements.

The first set of density measurements made on seawater solutions were made from 0 to 40°C (at 5°C intervals) and 0.5 to 40% salinity with the magnetic float system. These relative densities are given in Table 2. The reproducibility of these densities was within  $\pm 2$  ppm over the entire temperature and salinity range.

As a check of these densities, we have made a number of measurements of sea-

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Figure 3. Values of  $(d - d_o)/Cl(\%_o)$  plotted vs  $Cl(\%_o)$  for seawater solutions at various temperatures. The curves are based on a least squares fit of the data to equation (11).

water solutions at 0 and 25°C at various salinities with a suspension balance. These relative densities are given in Table 3. Since evaporation occurs in the suspension balance, the weight diluted or evaporated salinities had to be determined by conductivity methods using equation (8). A comparison of the densities determined with the magnetic float and the suspension balance are also given in Table 3. The densities agree on the average to  $\pm 1.8$  ppm with a maximum deviation of 5 ppm. These comparisons indicate that the two density systems are consistent to  $\pm 2$  ppm and the weight conductivity relationship (equation 8) is reliable to  $\pm 0.003\%$  from 1.3 to 40% salinity.

As discussed elsewhere (Wirth, 1940; Millero and Lepple, 1973; Lepple and Millero, 1971; Millero, 1973a, 1973b, 1974a, 1974b, 1975) the density of seawater solutions as a function of volume concentration ( $Cl_v = Cl(\%) \times d$ ) should be of the following form at high concentrations

$$d = d_o + A_V C l_V + B_V C l_V^{3/2}$$
(10)

where  $A_V = [M - d_o \Phi_V^o] \times 3.12803 \times 10^{-5}$ ,  $B_V = [S_V^* d_o] \times 5.9362 \times 10^{-6}$ , Mis the mean equivalent weight of sea salt,  $\Phi_V^o$  is the infinite dilute apparent equivalent volume of sea salt and  $S_V^*$  is an empirical constant related to ion-ion interactions. At low concentrations, a higher order term,  $C_V Cl_V^2$ , must be added to equation (10). If the  $B_V$  parameter is forced to be the Debye-Hückel limiting law term, the  $C_V$  term (=  $-b_V d_o \times 1.12654 \times 10^{-6}$ ) is related to ionic interactions due to deviations from the limiting law (Millero, 1974a); if  $B_V$  and  $C_V$  are treated as empirical constants they are both related to ion-ion interactions. As a first attempt of examining the concentration dependence of our density measurements, we have

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fitted (using a weighted least squares method) values of  $(d - d_o) / Cl_v$  at each temperature to linear and second degree functions of  $Cl_v^{1/2}$ . The fits were weighted since the errors in the quantity  $(d - d_o) / Cl_v$  are a function of  $Cl_v$  or  $Cl(\%_o)$  the chlorinity (assuming the precision of  $d - d_o$  is independent of concentration). The data was weighted by the factor  $W = 35.5 - |S\%_o - 35.0|$  which weights the dilute salinities (0.5‰) by one and the higher salinities by a factor which is nearly equal to the salinity (i.e., 35‰ was weighted by 35). Since the densities above 35‰ salinity had an uncertainty due to weight evaporation, the weighting factor used was similar to the 30‰ value.

A plot of  $(d - d_o) / Cl_v$  vs  $Cl_v^{1/2}$  is shown in Figure 2. The densities at each temperature fit the linear equation to an overall standard deviation of 3.8 ppm. By adding a second degree term, the standard deviation was decreasing slightly to 3.3 ppm; however, it could not be justified by examining the residuals using the "F-test" (Freund, 1962). Since chlorinities and salinities are normally measured by weight rather than volume, we have also examined the concentration dependence of  $(d - d_o) / Cl(\%_o)$  or  $(d - d_o) / S(\%_o)$  vs  $Cl(\%_o)^{1/2}$  or  $S(\%_o)^{1/2}$ . A plot of  $(d - d_o) / Cl(\%_o)^{1/2}$  is shown in Figure 3. Unlike the plots shown in Figure 2, the function  $(d - d_o) / Cl(\%_o)$  was found to be a second degree function of  $Cl(\%_o)^{1/2}$ . Thus, the final form selected for our 1 atm equation of state was

$$d - d_o = \rho - \rho_o = A S(\%_o) + B S(\%_o)^{3/2} + C S(\%_o)^2$$
(11)

where the parameters A, B and C were determined for all of our measurements using a weighted least squares method and are given by

$$A = 8.25938 \times 10^{-4} - 4.4491 \times 10^{-6}t + 1.0485 \times 10^{-7}t^{2} - 1.2580 \times 10^{-9}t^{3} + 3.315 \times 10^{-12}t^{4}$$

$$B = -6.33777 \times 10^{-6} + 2.8442 \times 10^{-7}t - 1.6871 \times 10^{-8}t^{2} + 2.83265 \times 10^{-10}t^{3}$$

$$C = 5.4706 \times 10^{-7} - 1.9798 \times 10^{-8}t + 1.6641 \times 10^{-9}t^{2} - 3.1204 \times 10^{-11}t^{3}$$

The standard deviation of the fit was 3.3 ppm. Our choice of terms for the temperature dependence of A, B and C was arrived at by examining the residuals of various forms using the "F-test" (Freund, 1962). The F ratios were determined from

$$F = \Delta \Sigma \left( X_{ij} - \overline{X}_i \right)^2 / \left[ \Sigma (X_{ij} - \overline{X}_i)^2 / N \right]$$
(12)

where  $\Sigma(X_{ij} - \overline{X}_i)^2$  is the sum of the squares of the deviations, N is the degrees of freedom and  $\Delta \Sigma (X_{ij} - \overline{X}_i)^2$  is the difference in the sum of the squares between the two polynomials being considered. By comparing the F ratios with F-values at the 99% confidence level (Freund, 1962), we were able to arrive at a statistically valid temperature polynomial for the theoretically based concentration equation.

#### 1976] Millero, Gonzalez & Ward: The density of seawater solutions

To convert our values of  $(d - d_o) = (\rho - \rho_o)$  to specific gravities (d) or absolute densities ( $\rho$ ), values for  $d_o$  or  $\rho_o$  must be used. The relative densities of water  $d_o = \rho_o/\rho_{max}$  which we have used in our previous work are those tabulated by Kell (1967) (based on  $t^{\circ}C$  being on the 1948 Temperature Scale)

$$d_{o} = [0.9998676 + 18.225454 \times 10^{-3}t - 7.922432 \times 10^{-6}t^{2} - 55.45001 \times 10^{-9}t^{3} + 149.7604 \times 10^{-12}t^{4} - 393.306 \times 10^{-15}t^{5}] [1 + 18.159725 \times 10^{-3}t]^{-1}$$
(13)

The densities determined from this equation from 0 to 40°C agree to  $\pm 1 \times 10^{-6}$  with the equation of Tilton and Taylor (1937) used by others (Cox, *et al.*, and Kremling). More recently Kell (1975) has re-examined the density of water from 0 to 150°C and expressed them on the 1968 Temperature Scale. Kell (1967, 1975) used the value of  $\rho_{max} = 0.999972$  g cm<sup>-3</sup> to convert the relative densities to absolute values. Since the value for the maximum density of *SMOW*,  $\rho_{max} = 0.999975$  g cm<sup>-3</sup> has recently been recommended (Kell, 1975) as an interim value, our water (Millero and Emmet, 1975) has an interim value of  $\rho_{max} = 0.999974$  g cm<sup>-3</sup>. Kell's (1975) new equation thus becomes (multiplying by 1.000002)

$$\rho_o (g \text{ cm}^{-3}) = [0.99984152 + 16.945210t \times 10^{-3}t - 7.9870561 \times 10^{-6}t^2 - 46.170553 \times 10^{-9}t^3 + 105.56323 \times 10^{-12}t^4 - 280.54309 \times 10^{-15}t^5] [1 + 16.879850 \times 10^{-3}t]^{-1}$$
(14)

where t is °C on the 1968 scale. The difference between equation (13) times  $\rho_{max} = 0.999974$  and equation (14) is within  $\pm 3 \times 10^{-6}$  g cm<sup>-3</sup> in density and  $\pm 0.2 \times 10^{-6}$ deg<sup>-1</sup> in expansibility.<sup>1</sup>

Since most of the earlier measurements on the relative density or specific gravity of seawater are based on  $d_o$  being 1.000000 at 4°C, we have added values of  $d_o$ determined from equation (13) to obtain the relative densities or specific gravities given in Table 4. We feel that these densities are reliable to  $2\sigma$  or  $\pm 6$  ppm over the entire temperature and salinity range.

The expansibility of seawater solutions

$$\alpha = -1/d(\partial d/\partial T)_P = -1/\rho(\partial \rho/\partial T)_P = 1/\nu (\partial \nu/\partial T)_P$$
(15)

where  $v = 1/\rho$  is the specific volume, can be determined by differentiating equation (11) and (13) with respect to temperature

1. Recently the International Union of Pure and Applied Chemistry (IUPAC) has suggested that, the interim value for absolute density of SMOW be those given by Bigg (1967)

 $10^{-3}\rho(SMOW)/gm \text{ cm}^{-3} = 999.842594 + 6.793952 \times 10^{-2}t - 10^{-2}t$ 

 $9.095290 \times 10^{-3}t^2 + 1.001685 \times 10^{-4}t^3 -$ 

 $1.120083 \times 10^{-6}t^{4} + 6.536332 \times 10^{-9}t^{5}$ 

The densities of our water  $\rho_o = \rho(SMOW) \times 1.000002$  calculated from this equation agree with those given by equation (14) to  $\pm 2 \times 10^{-6}$  g cm<sup>-3</sup> from 0 to 40°, while the expansibilities agree to within  $\pm 0.4 \times 10^{-6}$ deg<sup>-1</sup>.

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(16)

Table 4. The specific gravity of seawater solutions at one atmosphere.

		Sal	linity		
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)
0°C	0.999868	1.003940	1.007981	1.012012	1.016038
5	0.999992	1.003976	1.007935	1.011886	1.015835
10	0.999728	1.003639	1.007529	1.011413	1.015298
15	0.999129	1.002980	1.006812	1.010641	1.014471
20	0.998234	1.002037	1.005822	1.009604	1.013389
25	0.997075	1.000840	1.004586	1.008329	1.012077
30	0.995678	0.999412	1.003126	1.006838	1.010555
35	0.994063	0.997771	1.001461	1.005149	1.008840
40	0.992247	0.995933	0.999605	1.003275	1.006947
Temp	25(‰)	30(‰)	35(‰)	40(‰)	
0°C	1.020066	1.024097	1.028133	1.032177	
5	1.019787	1.023743	1.027705	1.031674	
10	1.019186	1.023080	1.026982	1.030892	
15	1.018307	1.022150	1.026003	1.029865	
20	1.017181	1.020982	1.024794	1.028617	
25	1.015832	1.019598	1.023375	1.027166	
30	1.014280	1.018015	1.021762	1.025522	
35	1.012539	1.016247	1.019967	1.023698	
40	1.010624	1.014308	1.018000	1.021701	

$$\begin{array}{l} (\partial d/\partial T) \ = \ (\partial d_o/\partial T) \ + \ (\partial A/\partial T) \ S(\%_o) \ + \\ (\partial B/\partial T) \ S(\%_o)^{3/2} \ + \ (\partial C/\partial T) \ S(\%_o)^2 \end{array}$$

where

 $(\partial d_o/\partial T) = (1 + 18.159725 \times 10^{-3})^{-2} [6.8134 \times 10^{-5} - 15.84486 \times 10^{-6}t - 3.102192 \times 10^{-7}t^2 - 1.4148723 \times 10^{-9}t^3 + 6.1922926 \times 10^{-12}t^4 + 2.8569316 \times 10^{-14}t^5 ]$ 

 $\begin{aligned} (\partial A/\partial T) &= -4.4491 \times 10^{-6} + 2.0970 \times 10^{-7}t - \\ &3.7740 \times 10^{-9}t^2 + 1.3260 \times 10^{-11}t^3 \end{aligned}$  $(\partial B/\partial T) &= 2.8442 \times 10^{-7} - 3.3742 \times 10^{-8}t + 8.49795 \times 10^{-10}t^2 \\ (\partial C/\partial T) &= -1.9798 \times 10^{-8} + 3.3282 \times 10^{-9}t - 9.3612 \times -^{11}t^2 \end{aligned}$ 

The expansibilities of seawater calculated from equation (13) and (16) at various salinities and temperatures are given in Table 5. These expansibilities are internally consistent to  $\pm$  0.5 ppm; although, there may be unknown end effects due to the temperature function used. By normalizing these end effects to pure water (as is

				10°(d	leg <sup>-1</sup> )				
				Sal	inity				
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(%)	30(‰)	35(‰)	40(‰)
0°C	-68.1	-48.4	-30.4	-13.3	3.3	19.5	35.6	51.5	67.4
5	16.0	31.9	46.8	60.9	74.6	87.9	100.8	113.5	125.9
10	87.9	100.6	112.8	124.4	135.6	146.4	156.8	166.8	176.4
15	150.7	160.8	170.6	180.0	189.1	197.8	206.1	214.0	221.5
20	206.6	214.4	222.2	229.8	237.0	244.0	250.7	257.0	262.9
25	257.1	263.1	269.0	274.9	280.6	286.2	291.5	296.7	301.7
30	303.1	307.7	312.1	316.4	320.8	325.1	329.5	333.9	338.4
35	345.7	349.1	352.0	354.9	358.0	361.4	365.1	369.2	373.6
40	385.4	387.8	389.4	391.0	393.9	395.4	398.6	402.6	407.4

Table 5. The expansibility of seawater at one atmosphere.

done by using equation 15), these end effects are minimized and  $(\alpha - \alpha_o)$  should not be seriously affected.

#### 4. Density comparisons

In this section we will compare the densities determined from our studies with those obtained by other workers. Because previous measurements have been confined to temperatures below 30°C, the comparisons will only be made from 0 to 25°C. Since errors may have resulted from the fitting of the densities obtained by others, we will first examine the differences between the direct measurements of others and our smoothed data. These comparisons are confined to the 0 and 25°C data of Knudsen, et al., the 0°C data of Thompson and Wirth, the 0 to 25°C data of Cox, et al., and the 0 to 25°C data of Kremling. The deviations,  $(\Delta d)$ , between the densities obtained from our work and that obtained directly by others at various temperatures and salinities are given in Table 6 and are shown graphically in Figure 4. Since Knudsen (1901), Cox, et al., (1970) and more recently Fofonoff and Bryden (1975) have fitted density measurements to equations, we have also made a comparison of their smoothed density data with our results. These comparisons are shown in Table 7. The comparisons given in Tables 6 and 7 and Figure 4 all show three common features: 1. Our densities for seawater at salinities near 35(%)are in reasonable agreement with the results of other studies, 2. Our densities at low salinity are significantly lower than the results of other studies and 3. Our densities at high salinities are significantly higher than the results of other studies. There appears to be a linear shift of the densities at various salinities. This linear shift appears to be nearly independent of temperature. Since these differences at high and low salinities are due to the various compositions of the waters (Lyman and Fleming, 1940; Kremling, 1969, 1970, 1972a, 1972b; Wilson, 1975), we will discuss the density deviations in three sections: Ocean waters, Baltic Sea waters and Red and Mediterranean Sea waters.



Figure 4. Comparison of the densities determined in this study and those obtained by others. The symbols used in this figure are: (★) Baltic Sea, (♦) North Sea, (▲) Atlantic Ocean, (○) Mediterranean Sea, (+) Gulf of Alaska, (□) Pacific Ocean, (▼) Indian Ocean, (☆) Red Sea, (●) Baltic/Red, (◇) Baltic/Atlantic, (◇) Baltic/Pacific.

Table 6. Comparison of our densities with those obtained by various workers.

 $\Delta d imes 10^{
m 0}$ Knudsen, et al. Mediterranean Sea

	0°0	С			24.6°C	
S(‰)	Uncorr.	Eq 24	Eq 25	Uncorr.	Eq 24	Eq 25
36.880	7	4	2	20	18	16
38.672	7	2	-3	13	8	4
40.172	23	15	9	33	25	19
40.161	14	6	0	24	17	11
	13 ± 5.8	7 ± 4.1	± 3.5	$23\pm 6.0$	17 ± 4.5	13 ± 5.0
			Baltic Sea			
	0°0	C			24.6°C	
2.662	-50	4	40	-50	1	33
2.663	-50	5	41	-49	1	34
5.288	-52	- 1	31	-48	- 2	28
				in the first states in	- (	continued.)

Table 6 (continued).

#### Knudsen, et al.

Baltic Sea

	0°	C			24.6°C	
S(‰)	Uncorr.	Eq 24	Eq 25	Uncorr.	Eq 24	Eq 25
5.274	-63	-13	20	-59	-12	18
8.324	-55	-10	19	-53	-11	16
10.545	-48	- 7	20	-48	- 9	15
14.613	-45	-11	11	-44	-12	9
14.614	-44	-10	12	-43	-11	9
18.277	-42	-14	4	-43	-17	0
18.807	-34	- 7	10	-32	- 6	10
18.811	-31	- 4	14	-29	- 3	13
19.643	-35	- 9	7	-32	- 8	7
23.200	-30	-10	2	-25	- 7	5
23.203	-28	- 8	5	-23	- 4	8
25.825	-29	-14	- 4	-21	- 7	3
28.947	-10	1	7	- 7	3	9
28.950	- 7	3	10	- 4	5	11
32.330	-11	- 6	- 3	- 6	- 2	1
33.928	12	14	15	15	17	18
	$-34 \pm 14.8$	$-5 \pm 6.1$	13 ± 9.4	$-32 \pm 16.1$	$-4 \pm 5.9$	$13 \pm 4.0$

North Sea

		0°C			24.6°C	
33.591	4	7	8	10	13	14
33.603	14	17	18	19	22	23
35.078	18	19	18	24	24	24
35.060	4	4	4	10	11	10
35.379	9	8	8	15	15	14
35.392	12	12	12	21	20	20
35.390	12	12	12	19	19	18
32.773	5	9	11	9	13	15
	$10 \pm 4.2$	$11 \pm 4$	11 ± 4	$16 \pm 4.9$	$17 \pm 4.0$	$17 \pm 7.5$

4		0	
At	antic	Iron	h
111	unne	occui	1

	0	°C	24.6°C			
35.703	- 3	- 3	- 4	0	0	- 1
						(continued.)

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Table 6 (continued).

#### Thompson and Wirth

	Mediterr	anean Sea		Baltic Sea				
S(%))	Uncorr.	Eq 24	Eq 25	S(‰)	Uncorr.	Eq 24	Eq 25	
36.418	- 2	- 4	- 5	5.474	-78	-28	4	
38.420	- 1	- 6	-10	3.819	-78	-26	8	
38.704	- 4	-10	-14		70	27	< + a	
38.304	4	- 2	- 5		-/8	-27	$6\pm 2$	
38.696	8	2	- 2		1.1			
38.662	0	- 6	-10		Inalar	i Ocean		
38.635	0	- 5	-10	34.984	-10	- 9	- 9	
	+ 2	+ 5	0 - 2 5	34.680	-14	-13	-13	
	- 3	± 3	$-8 \pm 3.5$	35.105	-10	-10	-10	
				35.016	-17	-16	-17	
				34.807	-15	-14	-14	
					-13	-12	$-13 \pm 3$	

	Pacifi	c Ocean		Gulf of Alaska				
33.600	- 8	- 5	- 4	32.776	-16	-12	-10	
33.573	- 7	- 5	- 3	32.787	-19	-15	-13	
33.535	- 4	- 1	0	32.782	-24	-20	-18	
33.535	-17	-14	-13	32.818	-23	-19	-17	
33.858	-28	-26	-25	33.082	-36	-32	-30	
34.151	-14	-12	-11	33.139	-25	-21	-20	
34.205	-21	-19	-19	33.396	-22	-19	-18	
34.267	-25	-23	-23	33.564	-19	-16	-15	
34.314	-13	-11	-11			10	10 - 4	
33.501	-12	- 9	- 7		-23	-19	$-18 \pm 4$	
	-15	-13	$-12 \pm 6$					

#### Atlantic Ocean (soft glass bottles)

35.549	-62	-63	-63	34.892	-48	-47	-47
35.052	-94	-93	-94	34.884	-59	-59	-59
					-66	-66	$-66 \pm 14$

Table 6 (continued).

Cox, et. al.

	Med	literranear	ı Sea		2210		Baltic Sea		
Temp	S(‰)	Uncorr.	Eq 24	Eq 25	Temp	S(‰)	Uncorr.	Eq 24	Eq 25
20°C	39.216	5	- 1	- 6	25	9.623	-56	-16	10
17.5	39.232	6	0	- 5		9.621	-19	-19	6
	39.230	14	7	3	20	9.940	-63	-23	2
15	39.232	5	- 2	- 6		9.626	-57	-17	8
10	39.232	15	8	4		9.618	-64	-23	2
5	39.232	8	2	- 3	17.5	9.942	-62	-22	4
0	39.232	8	2	- 3		9.629	-55	-14	12
		$9 \pm 3.3$	±3.1	±4.3		9.621	-62	-21	4
						9.579	-88	-47	-21
	AI	lantic Oce	ean		15	9.579	-91	-50	-24
25	25.000				10	9.896	-91	-50	-24
25	35.006	0	6	6		9.579	-93	-52	-25
17.5	35.017	9	10	10	5	9.896	-92	-50	-23
17.5	35.027	15	15	15		9.579	-92	-50	-23
15	35.004	- 1	- 1	- 1	0	9.579	-53	-11	17
10	35.004	- 1	- /	- /			-72±5.4	$-31\pm13$	.9 ±13.7
5	35.004	- 0	- 0	- 6					
0	35.004	- 5	_ 1	- 1		D	acific Oca	<b>an</b>	
v	55.004	5				1	icijic Ocei		
		±6.1	±6.2	±6.2	20	29.721	- 2	7	12
		Red Sea				1	Baltic/Red	ł	
25	41.398	49	40	33	25	34,890	1	2	2
	41.365	30	21	14		29.712	- 3	5	11
20	41.379	28	19	12		20.158	-30	- 6	9
	40.315	26	18	12		20.156	-30	- 7	8
17.5	41.390	32	22	15		20.130	-50	-26	-11
17.5	40.336	18	10	4	25	15.536	-48	-18	2
	40.288	- 3	-11	-17	20	34.905	7	7	7
15	40.288	3	- 6	-11		29.710	-11	- 2	3
10	40.288	- 1	- 9	-14		25.440	-26	-11	- 1
5	40.288	- 3	-11	-17		20.147	-21	3	18
0	40.288	9	1	- 5		15.543	-45	-14	6
		+10.4	+152	+140	17.5	34.919	13	13	13
		-18.4	-15.5	-14.0		34.885	5	- 5	5
						29.729	4	13	18
	Ba	ltic/Atlan	tic			29.723	8	17	22
25	25.436	-27	-11	- 2		29.698	- 7	1	7
	20.450	~ /		T Torte		25.445	-23	- 7	2
	R	altic/Pacin	fic			25.439	- 8	7	17
	Di					20.152	-18	6	21
25	29.701	- 8	1	6		20.128	-22	2	17
								(00	ontinued.)

Table 6 (continued).

				Cox	, et. al.				
				Balt	ic/Red				
					Temp	S(‰)	Uncorr.	Eq 24	Eq 25
	15.553	-36	- 5	14		15.541	-43	-11	9
	15.541	-38	- 7	13	5	34.885	10	-10	-10
15	34.885	-16	-15	-15		29.698	-10	- 1	4
	29.698	-18	- 9	- 4		25.439	-23	- 7	3
	25.439	-22	- 6	4		20.128	-44	-20	- 4
	20.128	-44	-20	- 4		15.541	-29	3	24
	15.541	-42	-11	9	0	29.698	-25	-16	-10
10	34.885	10	10	10		25.439	-29	-12	- 2
10	29.698	-18	- 9	- 4		20.154	-32	- 6	9
	25.439	-23	- 7	3		20.130	-51	-26	-10
	20.128	-47	-23	- 7		15.541	-45	-12	9
							$-22\pm14.5$	±9.9	±9.1

#### Kremling

#### Baltic/Red

S(%) = 39.232

S(%) = 35.495

Temp	Uncorr.	Eq 24	Eq 25	Temp	Uncorr.	Eq 24	Eq 25
0.36°C	- 3	- 9	-14	0.36°C	3	2	2
5.11	14	7	3	5.11	25	25	24
10.04	-10	-17	-21	10.04	0	- 1	- 1
15.01	- 2	- 8	-13	15.01	- 4	- 4	- 5
20.01	- 2	- 9	-13	20.01	- 4	- 4	- 5
25.02	- 5	-11	-16	25.02	13	12	11
	±6.0	±10.2	±13.3		±8.2	±8.0	±8.0
	S(%) =	32.319			$S(\%_{c}) =$	31.920	

0.36	- 4	1	4	0.36	-11	- 6	- 3
5.11	- 5	0	3	5.11	- 2	4	7
10.04	-15	-10	- 7	10.04	-11	- 6	- 3
15.01	-20	-16	-13	15.01	- 9	- 3	0
20.01	-17	-13	-10	20.01	-12	- 7	- 4
25.02	1	6	8	25.02	- 7	- 2	1
	±10.3	±7.7	±7.5		-8.7	±4.5	±3.0

(continued.)

1976] Millero, Gonzalez & Ward: The density of seawater solutions

Table 6 (continued).

			Kre	emling			
			Balt	ric/Red			
	S(‰) =	31.191			S(‰) =	29.839	
Гетр	Uncorr.	Eq 24	Eq 25	Temp	Uncorr.	Eq 24	Eq 25
0.36	- 9	- 2	2	0.36	-13	- 4	1
5.11	- 4	3	7	5.11	- 5	4	9
10.04	- 9	- 2	2	10.04	-12	- 3	2
15.01	- 8	- 2	2	15.01	-14	- 5	0
20.01	-15	- 8	- 5	20.01	-20	-12	- 7
25.02	-10	- 3	0	25.02	-17	- 8	- 3
	-9.2	±3.3	±3.0		-13.5	±6.0	±3.7
	S(‰) =	25.013			S(%) =	20.083	
0.36	-38	-21	-10	0.36	-44	-19	- 3
5.11	-30	-13	- 3	5.11	-40	-15	1
0.04	-25	- 8	2	10.04	-40	-16	0
5.01	-25	- 9	1	15.01	-42	-18	- 3
20.01	-37	-21	-11	20.01	-48	-24	- 9
25.02	-30	-14	- 4	25.02	-38	-14	1
	-30.8	±14.3	±5.2		-42	-17.7	±2.8
					S(%) =	15.247	
				0.36	-57	-24	- 2
				5.11	-46	-13	7
				10.04	-53	-21	0
				15.01	-61	-29	- 9
				20.01	-64	-32	-12
				25.02	-63	-31	-12
					-57.3	-25.0	±7.0

a. Ocean Waters. Although many workers have measured the densities of seawater at various salinities, only a few measurements have been made on open ocean waters (near 35% salinity). In the studies of Knudsen, *et al.*, density measurements (at 0 and 25°C) were made on one sample from the Atlantic and nine samples from the North Sea. Our density results agree to within  $3 \times 10^{-6}$  with the measurements made by Knudsen, *et al.*, on the Atlantic sample. At 0°C our results are high by (9.8 ± 4.2) × 10<sup>-6</sup> and at 25°C our results are high by (15.9 ± 4.9) × 10<sup>-6</sup> compared to the direct measurements of the North Sea samples by Knudsen, *et al.*, near 35(‰) salinity. When the comparisons are made with the smoothed densities

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Table 7. Comparison of the densities obtained by various workers.

d(Ours) - d	(Others), 10 <sup>e</sup>
-------------	---------------------------

		30‰			35‰	
Temp	a	b	с	а	b	с
0°C	-8(1)	-11(3)	-21(-7)	7	- 1	-6
5	-4(4)	-16(-2)	-13(1)	8	- 9	-3
10	-3(5)	-18(-5)	-12(1)	10	-10	-5
15	-5(3)	-12(1)	-13(1)	10	- 1	-3
20	-8(1)	- 5(9)	-12(2)	9	9	3
25	-8(0)	- 8(5)	-10(3)	8	4	8
	-6.0(2.3)	-11.7(± 4.2)	-13.5(± 2.5)	8.7	± 5.7	± 4.7

		40%	
Temp	а	b	c
0°C	18(10)	9(-4)	17(3)
5	14(6)	-2(-15)	7(-6)
10	17(9)	0(-13)	1(-12)
15	12(13)	13(0)	7(-6)
20	22(15)	26(13)	23(10)
25	20(13)	19(7)	34(21)
	18.7(11)	± 11.5(± 8.7)	14.8(± 9.7)

a) Values of d(Ours) - d(Knudsen); the values in parentheses have been corrected by using equation (24).

b) Values of d(Ours) - d(Cox, et al.); the values in parentheses have been corrected by using equation (25).

c) Values of d(Ours) - d(Fofonoff & Bryden); the values in parentheses have been corrected by using equation (25).

determined from Knudsen's density equations, our results are high by  $(8.7 \pm 1.0) \times 10^{-6}$  near 35(‰) over the entire temperature range. These results indicate that in the smoothing process, the densities of Knudsen, *et al.*, increase by  $4 \times 10^{-6}$ . These comparisons with Knudsen's density equation are in general agreement with other workers (Thompson and Wirth, 1931; Cox, *et al.*, 1970 and Kremling, 1970) in that Knudsen's densities are too low by  $\sim 10 \times 10^{-6}$  near 35(‰) salinity over the entire temperature range. Since the direct measurements made on the Atlantic sample by Knudsen, *et al.*, are in good agreement with our results (as well as other workers), these comparisons indicate that the density measurements made on the North Sea samples are too low by 10 to  $16 \times 10^{-6}$ . Since the deviations are nearly independent of temperature, one might expect the deviation to be due to errors in the chlorinity determinations or composition differences.

Thompson and Wirth made the most extensive measurements on open ocean samples. They made measurements at 0°C on five samples from the Indian Ocean,

four samples from the Atlantic Ocean, eight samples from the Gulf of Alaska and 10 samples from the Pacific Ocean. Since the Atlantic samples were stored in soft glass bottles, the measured densities are too high by about  $66 \times 10^{-6}$  (which is equivalent to increasing the salinity by 0.08% presumingly due to the solubility of silicates). Our density results are lower on the average by  $13.2 \times 10^{-6}$  with their measurements on the Indian Ocean samples, by  $23.0 \times 10^{-6}$  with their measurements on the Gulf of Alaska samples and by  $14.9 \times 10^{-6}$  with their results on the Pacific samples. From these comparisons, it appears that the density measurements made by Thompson and Wirth are too high by  $17.3 \times 10^{-6}$ . It should be pointed out that if these comparisons are made at chlorinities determined by using the 1930 molecular weights, their results are too high by only  $6 \times 10^{-6}$ . At present, it is not possible to state with certainty the cause of these deviations.

Although the two major objectives of the recent work of Cox, et al., was "to establish the relationship between specific gravity and salinity (as determined by electrical conductivity) on samples more representative of ocean waters" and to make the measurements "with a higher precision than was possible in Knudsen's time", their work fails to fulfill these objectives. The samples measured by Cox, et al., were mostly confined to artificial mixtures of Baltic and Red Sea waters [which certainly do not have the same relative composition (Lyman and Fleming, 1940; Kremling, 1970, 1972a,b) as open ocean waters] and the precision of their density measurements ( $\pm$  8 ppm) does not compare very well with the precision of the measurements of Knudsen, et al.,  $(\pm 3 \text{ ppm})$ . As will be shown later by measuring the densities of the mixtures whose concentration was determined by conductivity, their measurements can be compared to seawater diluted with pure water at the same conductivity. All of the measurements made by Cox, et al., on the Atlantic and Pacific samples agree on the average with our measurements to  $\pm 6 \times 10^{-6}$ . It should be pointed out that the Atlantic samples of S(%) = 35.004 and 35.006are standard seawater samples (Culkin - personal communication) and they agree to  $\pm 4 \times 10^{-6}$  with our results. It is interesting to note that although the salinity of the Pacific sample is quite low (29.721%) the density determined by Cox, et al., agrees very well (2 ppm) with our results (unlike their low salinity results obtained on mixtures of Baltic and Red Sea waters or the smoothed data - Table 7). These comparisons indicate that the density of low salinity ocean samples are the same as standard seawater diluted with pure water (not Baltic Sea waters or Baltic/Red Sea water mixtures). On the seven samples of Red Sea-Baltic Sea water mixtures near 35(%) salinity, our results agree on the average with the work of Cox, et al., to  $\pm$  8.8 ppm. These larger deviations are due to composition differences between Baltic/Red seawater mixtures and ocean waters. The differences would probably be greater if the comparisons were made at a constant chlorinity rather than at a constant conductivity salinity. Since Cox, et al., did not give the fraction of Baltic and Red seawaters used to make the mixtures, it is not possible to make any further analysis of their density results. The smoothed densities, Table 7, calculated from the equation of Cox, *et al.*, for 35(%) salinity agree on the average with our measurements to  $\pm 5.7 \times 10^{-6}$  from 0 to  $25^{\circ}$ C. Unlike the smoothed results of Knudsen, the smoothed densities of Cox, *et al.*, disagree in a random manner with our results from 0 to  $25^{\circ}$ C — which as we shall see later causes large errors in the expansibilities.

Kremling made six measurements on Red Sea-Baltic Sea water mixtures that had a salinity near 35(%). Our results agree with his measurements from 0 to  $25^{\circ}$ C to  $\pm 7.2 \times 10^{-6}$ . By eliminating the measurement at  $5^{\circ}$ C (which can be shown to be out of line with other measurements by examining the concentration and temperature dependence of the densities) the average deviation is reduced to  $\pm 4.8 \times 10^{-6}$ .

Recently Fofonoff and Bryden (1975) have statistically analyzed the density measurements of other workers. A comparison of their smoothed results with our work is shown in Table 7. Our results agree on the average to  $\pm 4.7 \times 10^{-6}$  with their results. Since Fofonoff and Bryden's analysis rely heavily on the measurements of Cox, *et al.*, the deviations are similar to their smoothed data.

To summarize these comparisons, our density measurements near 35(%) salinity agree on the average to  $\pm 5 \times 10^{-6}$  with the recent measurements of Cox, *et al.*, and Kremling and the statistical analysis of Fofonoff and Bryden. It is interesting to note that the smoothed densities determined from the fitted data of Kremling (not used by Fofonoff and Bryden) agree with our results to  $\pm 3 \times 10^{-6}$ . The earlier results of Knudsen, *et al.*, and Knudsen's fit of this data appear to be too low by  $8.7 \pm 1.0 \times 10^{-6}$ .

b. Baltic waters. The densities determined from our measurements of seawater diluted with pure water do not agree with the law salinity measurements made by Knudsen, et al., Thompson and Wirth, Cox, et al., and Kremling on Baltic Sea waters (Tables 6 and 7). At a given salinity or chlorinity, the densities determined from our results are too low. Near 5% salinity our results are lower by  $\sim$  70 ×  $10^{-6}$ , near 15% our results are too low by ~ 50 × 10<sup>-6</sup> and near 30% our results are too low by  $\sim 10 \times 10^{-6}$  than the direct measurements of other workers. These differences are due to the fact that at a given chlorinity there are more salts in Baltic water than in seawater diluted with pure water, due to river run off (Lyman and Fleming, 1940). Although the relative composition of Baltic waters (Lyman and Fleming, 1940; Kremling, 1966, 1967, 1968) are different than seawater, it is possible to detertmine the density of the Baltic (as well as other estuaries - Millero, 1975) by assuming the densities are equal to those of seawater at the same total solid concentration. The total solids in Baltic water can be determined by two methods: 1) conductivity and 2) composition calculations. By using the conductivity method the differences between the relationship of Cox, et al., for the salinity and  $R_{15}$  (equation 9) and those determined in this study (equation 8) yield

		$S(\%o)_T$		
S(%)	а	ь	с	d
0	0.090	0.030	0.073	0.120
2	2.065	2.028	2.069	2.113
4	4.040	4.027	4.065	4,106
5	5.028	5.026	5.063	5.103
6	6.030	6.025	6.061	6.099
8	8.035	8.023	8.056	8.093
10	10.039	10.021	10.052	10.086
15	15.031	15.017	15.042	15.069
20	20.018	20.013	20.031	20.052
25	25.008	25.009	25.021	25.035
30	30.003	30.003	30.011	30.017
32	32.002	32.003	32.007	32.011
34	34.001	34.001	34.003	34.004
35	35.000	35.000	35.000	35.000
36	35.997	35.999	35.998	35.997
38	37.994	37.997	37.994	37.990
40	39.992	39.996	39.990	39.983

Table 8. Comparisons of the total salinity of seawater determined by various methods.

a)  $S(\%_{e})_{T} = -0.041 + 1.8926 \times 10^{-2} S(\%_{e}) - 1.4973 \times 10^{-3} S(\%_{e})^{2} + 4.3396 \times 10^{-5} S(\%_{e})^{3} - 4.3196 \times 10^{-7} S(\%_{e})^{4}$ 

b)  $S(\%_{o})_{T} = 0.030 + 0.999142 S(\%_{o})$ 

c)  $S(\%_{0})_{T} = 0.073 + 0.99793 S(\%_{0})$ 

d)  $S(\%_{o})_{T} = 0.120 + 0.99659 S(\%_{o})$ 

$$S(\%_{o})_{T} = -0.041 + 1.8926 \times 10^{-2} S(\%_{o}) - 1.4973 \times 10^{-3} S(\%_{o})^{2} + 4.3396 \times 10^{-5} S(\%_{o})^{3} - 4.3196 \times 10^{-7} S(\%_{o})^{4}$$
(17)

This relationship gives the total solid salinity  $S(\%_{0})_{T}$  given in Table 8. These values are in reasonable agreement with the earlier relationship developed by Knudsen (1901)

$$S(\%_0)_T = 0.030 + 1.8050 Cl(\%_0)$$
 (18)

$$= 0.030 + 0.999142 S(\%)$$
(19)

Thus, the new definition of salinity (UNESCO, 1966) causes the major differences between salinities determined from conductance of weight diluted samples and Baltic seawater (as well as the evaporated seawater and Red and Mediterranean waters). If the Knudsen salinity/chlorinity relationship were used to define the conductivity salinity, the differences between our conductance relationship (equation 8) and that developed by Cox, *et al.*, (equation 9), would be within  $\pm 0.005\%$  from 20 to 40% salinity. It should also be pointed out that over the oceanographic range

of salinity (33 to 37% salinity), the two conductance equations only differ by  $\pm$  0.004% (which is equivalent to ~ 3 ppm in density).

A more reliable method that can be used to determine the total solids in Baltic waters (as well as other lakes and estuaries — Millero, 1975b,c,d) is to examine the conservative mixing of the river water and seawaters that make up the estuary. By knowing the river water dissolved solid input,  $g_T$ (River), it is possible to determine the total grams of dissolved solids in the estuary,  $g_T$ (Estuary), as a function of chlorinity or salinity

$$g_T(\text{Estuary}) = g_T(\text{River}) + b S(\%)$$
(20)

where the constant b is given by

$$b = [g_T(\text{Seawater}) - g_T(\text{River})]/S(\%)_{SW}$$
(21)

The value of  $g_T$  (Seawater) is the total solids in the seawater used to form the estuary at a salinity of  $S(\%)_{SW}$ . The total solids in seawater are related to the salinity by (Millero, 1975a)

$$g_T = 1.004880 \ S(\%_0)_T \tag{22}$$

which gives  $g_T = 35.171$  g/kg for a salinity of 35.000. Using the  $g_T$ (River) = 0.073 g/kg estimated by Lyman and Fleming (1940), b = [35.163 - 0.073] / 35.000 = 1.00257. Substituting into equation (20), we have

$$g_T$$
(Estuary) = 0.073 + 1.00280 S(‰) (23)

By substituting equation (23) into equation (22) and rearranging, we can determine the relationship between the total solid salinity of the estuary as a function of salinity

$$S(\%_{c})_{T} = g_{T}(\text{Estuary})/1.004800$$
  
= 0.073 + 0.99793 S(%\_{c}) (24)

A similar calculation using a river water input  $g_T = 0.120 \pm 0.010$  g/kg determined from the composition data of Kremling (1969, 1970, 1972a) yields the equation

$$S(\%_0)_T = 0.120 + 0.99659 S(\%_0) \tag{25}$$

The total salinities determined from equations (24) and (25) are given in Table 8. Since the total solids going into the Baltic determined from the recent work of Kremling (1969, 1970, 1972a) are in good agreement with the average world river input (Livingstone, 1963), equation (25) can be equated to the typical average estuary.

A comparison of the densities determined by using  $S(\%_0)_T$  in our equation with those determined by Knudsen and Cox, *et al.*, at 0°C are shown in Table 9. As is quite apparent from these comparisons, the densities of seawater diluted with pure Table 9. Comparisons of the differences in the densities obtained at 0°C by correcting the salinity.

 $d(\text{Ours}) - d(\text{Others}), 10^{\circ}$ 

	No Corrections		Corrections <sup>a</sup>		
			Conductance		
S(%)	Knudsen	Cox, et al.	Knudsen	Cox, et al	
2	-53	-171 <sup>b</sup>	0	-118 <sup>b</sup>	
4	-50	-140 <sup>b</sup>	-18	-108 <sup>b</sup>	
5	-51	-128 <sup>b</sup>	-28	-105 <sup>b</sup>	
6	-50	-117 <sup>b</sup>	-26	- 93 <sup>b</sup>	
8	-50	- 98 <sup>b</sup>	-22	- 70 <sup>b</sup>	
10	-50	- 82 <sup>b</sup>	-18	- 50 <sup>b</sup>	
15	-47	- 54	-22	- 29	
20	-38	- 35	-24	- 21	
25	-25	- 22	-18	- 15	
30	- 8	- 11	- 6	- 9	
32	- 1	- 7	0	- 6	
34	5	- 3	6	- 2	
35	8	0	8	0	
36	10	1	8	1	
38	16	6	11	1	
40	20	11	13	4	

#### Corrections<sup>a</sup> Composition

S(‰) 2 4 5	(equation 24)		(equa	(equation 25)	
	Knudsen	Cox, et al.	Knudsen	Cox, et al.	
2	3	-115 <sup>b</sup>	39	-79 <sup>b</sup>	
4	3	- 87 <sup>b</sup>	36	-54 <sup>b</sup>	
5	1	- 76 <sup>b</sup>	33	-44 <sup>b</sup>	
6	- 1	- 68 <sup>b</sup>	30	-37 <sup>b</sup>	
8	- 5	- 53 <sup>b</sup>	25	-23 <sup>b</sup>	
10	- 8	- 10 <sup>b</sup>	20	-12 <sup>b</sup>	
15	-13	- 20	9	2	
20	-13	- 10	4	7	
25	- 8	- 5	4	7	
30	1	- 2	5	2	
32	5	- 1	8	2	
34	7	- 1	8	0	
35	8	0	8	0	
36	9	0	8	- 1	
38	11	Sheet and a second	8	- 2	
40	12	3	6	- 3	

a) Corrections made using the total salinities given in Table 8.

b) Values are outside of the range of measurements of Cox, et al.

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water are in good agreement with direct measurements of Baltic seawaters at the same dissolved solids. The conductivity correction is not as reliable as the one made from the composition of the river water input. This is not surprising since the conductivity of river salts and sea salts in dilute solutions are considerably different (Millero, 1975d).

One of the findings of the comparisons of the densities of Baltic waters is that the river input of 0.073 (determined by Lyman and Fleming using older composition data) gives a good correlation with the data of Knudsen, while the river input of 0.120 (determining from the recent work of Kremling) gives a good correlation with the data of Cox, *et al.* If we assume that the densities and compositions are reliable, these results indicate that the present river salt input into the Baltic is greater than at the turn of the century. This increase is due to the decrease in river runoff over the last 70 years (Fonselius, 1969).

A comparison of densities obtained by other workers and in our study by making a correction for the differences in total solids (using equations 24 and 25) are given in columns four and five of Table 6. As is quite apparent from these comparisons, equation (24) lowers the deviations of Knudsen, *et al.*, on the Baltic to  $\pm 7.6 \times 10^{-6}$ ; while equation (25) lowers the deviations of Thompson and Wirth to  $6 \times 10^{-6}$  and the deviations of Cox, *et al.*, to  $13.7 \times 10^{-6}$  on the Baltic. The low salinity measurements on Baltic/Red sea mixtures (corrected by using equation 25) of Cox, *et al.*, agree with our results to  $\pm 9 \times 10^{-6}$  and Kremling's results agree to  $\pm 4.6 \times 10^{-6}$  with our measurements. The comparisons of the corrected smooth densities of Knudsen, Cox, *et al.*, and Fofonoff and Bryden and our results are shown in Figure 5. At low salinities, the corrected results of Cox, *et al.*, and Fofonoff and Bryden show large deviations due to the form used to fit the concentration dependency of the densities (i.e., as  $g_T \rightarrow 0$  the densities do not approach pure water).

c. Mediterranean and Red Seas. The densities determined by Knudsen, et al., Thompson and Wirth, Cox, et al., and Kremling on Mediterranean and Red Sea waters are lower than our measurements made on evaporated seawater. The density measurements of Knudsen, et al., and Cox, et al., on Mediterranean samples are lower than our results, respectively, by  $(12.8 \pm 5.8) \times 10^{-6}$  and  $(8.7 \pm 3) \times 10^{-6}$ ; while the measurements of Thompson and Wirth agree with our results to  $\pm 2.7 \times 10^{-6}$ . Since the measurements of Thompson and Wirth on other seawater samples are too high by  $\sim 17 \times 10^{-6}$ , this agreement is probably fortuitous. These comparisons indicate that evaporated seawater contains more salts than Mediterranean and Red Sea waters (at a fixed chlorinity). However, the high salinity density measurements made by Kremling apparently on a Mediterranean Sea sample (as adjudged from its salinity) agree with our results to  $\pm 6 \times 10^{-6}$ . The density equation of Knudsen, Cox, et al., and Fofonoff and Bryden yield densities at 40% that are also lower than our results for evaporated seawater. Although the composition differences between the Mediterranean Sea and ocean waters are not reliably known,



Figure 5. (left) Comparisons of the densities  $(1 \times 10^{+0} \text{g cm}^{-3})$  determined in this study from 0 to 25°C and 5 to 40% salinity and those obtained by other workers at the same total salt concentration.

Figure 6. (right) Comparisons of the expansibilities  $(1 \times 10^{+6} \text{deg}^{-1})$  determined in this study from 0 to 25°C and 5 to 40% salinity and those obtained by other workers at the same total salt concentration.

it is possible to compare the densities at the same total solid concentration by using the methods described earlier for the Baltic. Both the conductance differences and Knudsen's original salinity measurements (see Table 8) indicate that 40% salinity Mediterranean (or Red Sea) waters are equivalent to 39.994  $\pm$  0.002% evaporated seawater. The total salinities determined by evaporating Baltic Sea waters to 40% also indicate that the total solids are lower than evaporated seawater. Thus, the Mediterranean Sea behaves more like an evaporated estuary than evaporated seawater. Although it is not possible, at present, to estimate  $g_T$  for the total river input in the Mediterranean by using equation (25) ( $g_T = 0.120$  g kg<sup>-1</sup>), the densities of

с

0.6

2.1

0.0

-2.5

-3.2

-0.5

 $\pm 1.5$ 

)(%) b Temp b a b с а a с 0°C -0.91.4 -2.41.7 2.7 0.3 -3.20.1 -0.41.2 -0.4-0.41.1 0.5 -0.11.1

-0.3

0.1

0.3

0.0

±0.2

-1.0

-2.3

-1.1

 $\pm 1.8$ 

3.8

0.2

0.9

-1.4

-0.3

 $\pm 1.0$ 

-0.8

-0.6

0.0

0.6

 $\pm 0.6$ 

-1.7

-3.1

-1.4

 $\pm 2.4$ 

4.5

$a(Ours) - a(Others), 10^{\circ}$				
30(‰)	35(‰)	40		

Table 10. Comparisons of the expansibilities obtained by various workers.

0.1

0.0

-0.2

-0.3

±0.7

a)  $\alpha(Ours) - \alpha(Knudsen)$ .

b)  $\alpha(Ours) - \alpha(Cox, et al.)$ .

0.1

0.5

0.4

0.4

±0.5

-0.4

-1.7

-0.9

 $\pm 1.3$ 

3.0

c) a(Ours) - a(Fofonoff and Bryden).

both Knudsen, et al., and Cox, et al., agree with our measurements to  $\pm 4 \times 10^{-6}$ . Although these corrections are needed for Mediterranean Sea waters, they are not needed for high salinity ocean waters that are formed by evaporation. We, thus, feel that our density equation will yield more reliable results for high salinity ocean waters than the equation of Knudsen and Cox, et al., that are based on Mediterranean (or Red) Sea waters. In the future, we plan to examine high salinity ocean waters and Mediterranean Sea waters to prove these contentions.

Cox, et al., were the only workers to make extensive measurements on Red Sea water. Their measurements between 0 to 17.5°C on the sample of salinity equal to 40.288% agree with our results to  $\pm 3.8 \times 10^{-6}$ , while the overall agreement is  $\pm$  18.4  $\times$  10<sup>-6</sup>. The larger overall deviations are due to differences in the high temperature and high salinity measurements. Although the overall differences decrease slightly by correcting the salinities (using the corrections given in Table 8), the deviations are undoubtedly due to composition differences between Red Sea water and ocean waters (Wilson, 1975). The inclusion of the densities for these high salinity samples at high temperatures into the equations of Cox, et al., and Fofonoff and Bryden cause the large deviations at 40% shown in Table 7 at high temperatures. The low temperature deviations between our results at 0°C with Fofonoff and Bryden are probably caused by the linear salinity dependence they used to fit the data (the equation of Cox, et al., as well as his direct measurements agree with our results at 0°C to  $\sim 9 \times 10^{-6}$  for both the Mediterranean and Red Sea waters). As discussed earlier, we feel that evaporated seawater is more representative of the densities one would expect for high salinity open ocean waters (i.e., than either Mediterranean or Red Sea water). In future work we plan to measure the density for Red Sea water and various salt lakes of known composition

5

10

15 20

25

diluted with pure water to examine how the physical chemical properties of high salinity natural waters compare to open ocean waters.

#### 5. Expansibility comparisons

To examine the effect of temperature on the densities of seawater obtained by various workers, it is necessary to fit the data by an empirical function (since we have no prior knowledge of how the density of aqueous solutions depends upon temperature). In Table 10 and Figure 6 we have compared the expansibilities determined from our data with those obtained from the equations of Knudsen, Cox, et al., and Fofonoff and Bryden. It should be pointed out that these comparisons are not greatly affected by differences in the definition of salinity. Our results from 0 to 25°C and 30 to 40% salinity agree on the average to  $\pm 0.4 \times 10^{-6}$ deg<sup>-1</sup> with those determined from the work of Knudsen, to  $\pm 1.8 \times 10^{-6} \text{deg}^{-1}$  with those determined from the work of Cox, et al., and  $\pm 1.1 \times 10^{-6} \text{deg}^{-1}$  with those determined from the work of Fofonoff and Bryden. At lower salinities (see Figure 6), the results of Cox, et al., and Fofonoff and Bryden show larger deviations and the expansibility does not approach pure water when  $S(\%_0)_T$  goes to zero. Since the thermal expansion data used by Knudsen are based on the measurements of Forch, et al., we have made a direct comparison of these measurements and those determined from our work. These comparisons are shown in Table 11. With the exception of a few points (denoted by a superscript asterisk in Table 11) our relative densities agree on the average with those of Forch, et al., to  $\pm$  4  $\times$ 10<sup>-6</sup> from 3 to 35% salinity and 0 to 30°C. These comparisons agree with our earlier findings (Millero and Lepple, 1973) in that the expansibilities determined from Knudsen's equation are reliable to  $\pm 0.5 \times 10^{-6} \text{deg}^{-1}$  and that the density data of Knudsen, et al., are internally consistent to  $\pm 4 \times 10^{-6}$ . We feel that these comparisons prove that our results and those determined from Knudsen's equation yield expansibilities that are reliable to  $\pm 0.5 \times 10^{-6} \text{deg}^{-1}$  and should be used to examine the temperature dependencies for the densities of seawater.

#### 6. Summary and conclusions

The relative densities of diluted and evaporated standard seawater solutions have been determined to a precision of  $\pm 3 \times 10^{-6}$  from 0.5 to 40% salinity. These results confirm the findings of earlier workers that the densities of Knudsen for 35% salinity seawater are too low by  $(8.7 \pm 1.0) \times 10^{-6}$  from 0 to 25°C. Our results near 35% agree with the recent measurements of Cox, *et al.*, and Kremling to  $\pm 5 \times 10^{-6}$  from 0 to 25°C. Our results at low salinities are also in good agreement with recent studies if corrections are made for river input. At higher salinities, our results are higher than those obtained by other workers for the Mediterranean and Red Seas. For the Mediterranean, these differences can be eliminated by con-

mined by	Knudsen, et a	al., at var	ious salinities.					
3.17	3(‰)		8.34	7(‰)		10.589	(‰)	
Temp	∆d, 10 <sup>e</sup>		Temp	Δd, 10 <sup>6</sup>		Temp	∆d, 10°	
0.051°C	0		- 0.296°C	0		– 0.298°C	0	
5.085	6		4.885	2		5.000	5	
9.485	8		9.936	2		9.697	1	
14.895	8		15.004	2		14.907	2	
19.450	6		20.212	8		19.824	-3	
25.319	16*		24.754	8		25.237	8	
30.088	22*		29.899	17*		30.211	16*	
14.64	43(‰)		18.90	6(‰)		23.240	(‰)	
Temp	Δd, 10 <sup>6</sup>		Temp	Δd, 10 <sup>6</sup>		Temp	∆d, 10 <sup>e</sup>	
- 0.164°C	0		- 0.783°C	0	5 5 1 1	– 0.203°C	0	
4.728	9		4.986	8		4.940	9	
9.981	7		9.780	8		9.737	5	
14.868	9		14.793	2		14.946	6	
20.118	7		20.417	3		19.879	5	
24.661	10		24.828	2		25.054	5	
30.607	23*		30.486	16*		30.834	18*	
26.092(‰)			28.895(‰)			32.378(‰)		
Temp	Δd, 10 <sup>6</sup>		Temp	Δd, 10 <sup>8</sup>		Temp	∆d, 10ª	
- 0.262°C	0		- 1.720°C	- 6	Lan-or	- 2.668°C	- 8	
5.310	3		0.074	0	one con	- 0.245	0	
10.124	1		5.016	6		4.917	2	
14.569	0		9.747	6		10.036	3	
20.189	- 8		14.518	7		14.843	4	
25.068	- 6		20.044	8		19.941	0	
30.303	- 3		24.988	10		24.880	6	
			30.683	7		30.435	4	
33.939(‰) 35.0		30(‰)	35.110(%)		35.410(%)			
Temp $\Delta$	d, 10 <sup>8</sup>	Temp	Δd, 10 <sup>6</sup>	Temp	∆d, 10°	Temp	∆d, 10 <sup>6</sup>	
- 2.215°C	- 6	- 2.734°	°C – 8	- 2.488°C	- 9	- 0.387	0	
0.182	0	- 0.024	0	- 0.028	0	5 245	3	
4.777	4	5.104	- 1	5.096	- 1	10.313	3	
9.767	1	9.768	- 5	10.225	- 2	14.523	10	
14.784	11	15.273	1	15.287	- 2	19.770	14*	
19.722	1	19.924	9	19.917	1	24.531	20*	
24.635	0	25.508	- 1	25.645	7	29.840	32*	

29.810

9

30.024

8

sidering it to be an evaporated estuary. The expansibilities determined from our work agree to  $\pm 0.4 \times 10^{-6}$ deg<sup>-1</sup> with those determined from the work of Knudsen, to  $\pm 1.8 \times 10^{-6}$ deg<sup>-1</sup> with those determined from the work of Cox, *et al.*, and to  $\pm 1.1 \times 10^{-6}$ deg<sup>-1</sup> with those determined from the work of Fofonoff and Bryden. Thus, although the density measurements of Knudsen, *et al.*, are too low by  $8.7 \pm 1.0 \times 10^{-6}$  they are internally consistent as a function of temperature to  $\pm 4 \times 10^{-6}$  (or  $\pm 0.5 \times 10^{-6}$  in expansibility).

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