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Specific gravity and density of seawater at atmospheric pressure

by N. P. Fofonoff and H. Bryden[1]

ABSTRACT

Four independent sets of specific gravity measurements are intercompared relative to a least squares polynomial in temperature and salinity over the range -2 to $30°C$ and 8 to $40°/_{00}$. Within this range, individual measurements have a standard deviation of 7.1 ppm about the regression polynomial. Over most of the range, the polynomial formula has a standard deviation of 1 to 3 ppm. The data sets are marginal in defining specific gravity below $0°C$ and above $25°C$ and inadequate below $10°/_{00}$ salinity.

1. Introduction

The increase in accuracy and resolution of modern instruments for measuring pressure, temperature and conductivity/salinity imply more exacting standards for accuracy in computation of density, specific volume and other derived variables from the primary observations. The precision laboratory determinations of density or specific gravity and specific volume need to be examined objectively and critically to determine whether or not their accuracy is consistent with the accuracy of measurements attainable in the field. In addition, it is desirable to use a common internationally accepted set of empirical formulas to process and interpret oceanographic data to avoid artificial inconsistencies that may arise from different procedures for analysis. The set of empirical formulas of Knudsen (1901) and Ekman (1908) have served the oceanographic community for many decades. However, recent changes in the definitions of salinity and temperature and new measurements of specific gravity and specific volume have made revision of these classical formulas necessary. With these considerations in mind, a limited study has been undertaken to evaluate the laboratory measurements that are presently available to define the density of seawater at atmospheric pressure as a function of temperature and salinity. The dependence of density on pressure can be calculated with high precision from sound velocity measurements (Wang and Millero, 1973). As the new sound velocity measurements are currently underway (Millero, personal communication), evaluation of data at elevated pressures is postponed.

1. Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, 02543, U.S.A.

Because the determination of a precise functional dependence of density of seawater on temperature and salinity requires an objective evaluation of the precision of laboratory determinations, a decision was made to use least square polynomial forms for the empirical formulas to be fitted to the measurements. Statistical tests are well defined for the least square method so that objective decisions can be made on the quality of available data. The procedures can be generalized to permit flexibility in application of the method. Provided that the number of terms is not restricted, the accuracy of the fit is not compromised. This is supported by McDonald (1969) who, in his extensive review of equations of state, concluded that simple polynomial equations were significantly better fits to many of the data sets than any of the nonlinear equations considered. Optimization of a physically based empirical formula is, therefore, seen as a goal beyond the framework of this statistical evaluation. Similarly, questions of the representativeness of the samples of ocean waters and compositional differences of samples from different sources cannot be answered directly by simple statistics. It can be argued that consistency among independent data sets is a necessary, though not sufficient, condition for acceptability of the data for an equation of state. The evaluation is made in terms of specific gravity rather than specific volume because most laboratory measurements at atmospheric pressure are of specific gravity and because its variation with salinity is nearly linear. Thus, a simpler formula can be used.

The procedure for obtaining polynomial least square regressions is outlined in an appendix together with the statistical tests used to determine the significance of terms included in the regression. The procedure is standard (Brownlee, 1965) and is similar to that used by Bryden (1973) in his construction of empirical formulas for the adiabatic temperature gradient and potential temperature.

Polynomial terms are added to the regression formula and tested to see if the square residuals are reduced significantly. The procedure is continued until no higher order term is significant. The selection of terms in the regression is coupled also with examination of residuals of individual data points. Residuals exceeding 2.5 standard deviations (99% confidence level) were rejected as inaccurate or inconsistent with the accepted data set.

2. Data sources

Four sets of specific gravity measurements on seawater at atmospheric pressure that cover the oceanic range of temperature and salinity were chosen for study. These consist of specific gravity and thermal expansion data of Knudsen and Forch (Knudsen *et al.* 1902a, b) published at the beginning of the century and the recent work of Cox *et al.* (1970) and Kremling (1972). Other studies of limited scope, such as Thompson and Wirth (1931), were included for comparison only. The data sets contain a total of 272 measurements over the range −2 to 30°C in temperature and 0 to 40°/$_{oo}$ in salinity. Knudsen, Sørensen and Forch (1902a, b) carried out a series of chlorinity, salinity, specific gravity and thermal expansion measurements

on seawater samples from the Baltic, North and Mediterranean Seas and North Atlantic Ocean. These measurements are the basis for the Knudsen equation of state for seawater at atmospheric pressure. Specific gravity measurements at 0°C and 24.6°C were made by Knudsen using pycnometers on 23 samples (1902a, Table a, p. 83). The chlorinities for these samples are given in his Tables V, VI, VII. Residuals for sample 20 in his Table are very large at both 0°C and 24.6°C indicating an error in chlorinity. Both values were rejected. The cubic regression formula relating σ_0 to chlorinity (Knudsen, 1901, 1902b) is based on 22 samples (SD = 6.8 ppm). Knudsen considered and rejected an additional 15 samples because of uncertainty in the accuracy of the chlorinity determinations. Slight differences present between Tables published in 1902a and 1902b are not significant at the level of precision considered here. Forch (Knudsen, 1902a, b) reported 95 measurements of relative thermal expansion for 13 samples over the temperature range of −2 to 30°C and salinity 3.2 to 35.41%. Of these, 88 were accepted and 7 at low salinity (3.2%) were excluded. An additional set of measurements at 39.35% (Knudsen, 1902a) was rejected because of apparent inaccuracy in the volume measurement near 0°C. These early precision determinations yielded 139 acceptable values and 24 of questionable precision. Of the acceptable data, 11 low salinity values were excluded. The initial accepted data set consisted of 128 values of sigma-0 and sigma-t.

Thompson and Wirth (1931) measured sigma-0 and chlorinity for 36 samples from the Mediterranean and Baltic Seas; Pacific, Indian and Atlantic Oceans. Their values are consistently higher than the other data sources and were excluded from the data set except for comparison. Cox et al., (1970) measured specific gravity using a ballasted sinker on surface samples from the Baltic, North, Red and Mediterranean Seas; Atlantic, Pacific, Antarctic Oceans and the English Channel. A total of 86 measurements over the temperature range 0 to 25°C and salinities 9–41% are reported in his Table 1. Kremling (1972) reported 54 measurements over the range .36 to 25°C, 15.2 to 39.2% using a vibrating tube filled with seawater samples. The precision achieved is comparable to the pycnometer measurements, both calibrated using distilled water.

The initial data set consisted of 272 measurements of specific gravity, temperature and salinity or chlorinity. Of these, 31 were at 0°C and 241 at higher temperatures. The data set contains only Forch's thermal expansion data for temperatures below 0°C and above 25°C. Other data sources were examined, but none of comparable precision were found.

The measurements of Cox et al. and Kremling are based on the new definition of salinity (UNESCO, 1966) and of temperature (IPTS-68, Barber, 1969). To make the data compatible, the earlier chlorinities (Cl) were converted to salinities S using the formula $S = 1.80655 \times Cl$ (UNESCO, 1966). Temperatures were converted to IPTS-68 using the formula $T_{68} = T - 4.4 \times 10^{-6} T(100 - T)$.* No corrections were made

* Conversion formula constructed from the difference between T_{48} and T_{68} in the range −2 to 30°C by Fofonoff.

Table 1. Comparison of specific gravity data. Means and standard deviations (S.D.) are given in parts per million (PPM) relative to regression formula.

Data Source	Knudsen	Cox	Forch	Kremling	Combined
			SIGMA-0		
Total data points	37	9	–	–	46
Questionable	15	–	–	–	15
Rejected in fit	9	1	–	–	10
Accepted...................	13	8	–	–	21
Mean......................	– 1.21	+ 1.96	–	–	0.0
S.D.......................	2.99	4.11	–	–	3.91
			SIGMA-T		
Total data points	23	77	102	54	256
Questionable	1	–	7	–	8
Rejected in fit	2	7	17	5	31
Accepted...................	20	70	78	49	217
Mean......................	– 1.98	+ .01	– 0.02	+ 2.99	0.0
S.D.......................	6.93	8.20	4.24	8.16	7.08

for earlier changes of the temperature scale. The effect of the redefinition of temperature is apparent primarily at higher temperatures, corresponding to 3 ppm in specific gravity at 30°C.

Specific gravities were converted to absolute densities using a maximum density for pure water at 4°C of 0.999975 gm/cm³ recommended by Girard and Menaché (1972). This value is their best estimate for the maximum density of Standard Mean Ocean Water (SMOW) proposed as a standard of known isotopic composition by Craig (1961). Uncertainty is estimated to be 1 to 3 ppm (UNESCO, 1974, App. 1). Adoption of a particular value for the conversion to absolute density is desirable to maintain a clear distinction between absolute density and specific gravity.

3. Sigma-0

Measurements of specific gravity at 0°C (sigma-0) were considered by Knudsen *et al.* (1902a, b) to be more precise than at other temperatures because of their independence of thermometer calibrations. The separation is retained in the present study to recognize this higher precision.

Knudsen selected a cubic polynomial in chlorinity to represent the 22 measurements at both low and open ocean chlorinities. A recalculation indicated that this cubic form was both necessary and sufficient to represent the data in terms of the statistical criteria given in the Appendix. Millero (1971) in his review of measurements and theory related to molal volumes of electrolytes in solution gave a formula equivalent to

$$\sigma_0 = A + BS + CS^2 + DS^{3/2} \tag{1}$$

as the expected functional dependence on concentration (salinity). The "3/2 power" arises from interaction of water molecules with dissolved ions. The apparent effect

is a decrease or contraction of the water
volume with addition of ions resulting
in a more rapid increase of density with
salinity. The effect is pronounced at low
concentrations ($S < 8^o/_{oo}$).

For seawater, the increase of σ_0 with
salinity is linear above $8^o/_{oo}$ based on
data of Knudsen and Cox. A linear fit
extrapolated to zero salinity is greater
than pure water specific gravity by 121
ppm. A relatively rapid change in spe-
cific gravity occurs in the low salinity
range as indicated in Figure 1. Both cubic
and "3/2 power" formulas have been
fitted to the sigma-0 data including the
low salinity values and pure water (Til-
ton and Taylor, 1937) for comparison.
The curves are shown as residuals from
a linear fit above $8^o/_{oo}$. The "3/2 power"

Figure 1. A cubic polynomial and a 3/2-power
function (Eqn. 1) fitted by least squares to
the edited σ_0 data (21 values) augmented by
Knudsen's low salinity and Tilton-Taylor
pure water value as residuals from the linear
σ_0 fit (Eqn. 2). The standard deviation of the
data is 11.4 ppm about the cubic and 7.1 ppm
about the 3/2-power function.

formula has significantly lower residuals (standard deviation (S.D.) = 7.1 ppm) than
the cubic polynomial (S.D. = 11.4 ppm). However, because of lack of adequate
measurements in the range $0-8^o/_{oo}$ salinity, neither curve can be considered to re-
present the variation in this range with sufficient accuracy. Further precise measure-
ments are necessary to define the more complex behavior in the low salinity range.
A similar recommendation has already made by the Joint Panel on Oceanographic
Tables and Standards (UNESCO, 1974).

Because only two data points are available between pure water and seawater of
$8^o/_{oo}$, the low salinity data were deleted from the specific gravity data set. In studying
the remaining sigma-0 data, it became evident that a number of Knudsen's data
points were anomalously low in the salinity range $29-36^o/_{oo}$. Both the 0°C and 24.6°C
specific gravities show negative anomalies relative to the data of Cox, Kremling
and Forch. Furthermore, the anomalies at the two temperatures are correlated
indicating that the chlorinities of the samples may be in error. The chlorinities are
too high relative to the specific gravities. It is possible that corrections for evaporation
were underestimated by Knudsen. Because of incompatibility with the more recent
data of Cox and Kremling, seven data points were deleted from Knudsen's data
set. Also, a data point for $S = 20.130^o/_{oo}$ was deleted from Cox's measurements.
This sample has a high positive residual for both 0°C and 24.992°C indicating a
probable error in the salinity.

Thompson and Wirth (1931) concluded that Knudsen's sigma-0 values were too
low in the oceanic range. However, their measurements tend to be higher (mean
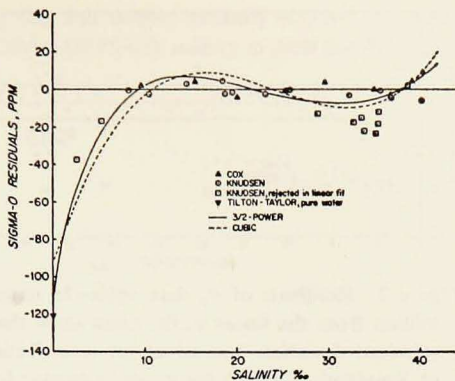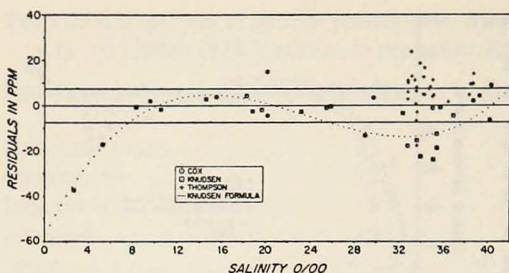= + 7.4 ppm, S.D. = 6.5 ppm n = 30) than the accepted data set.

Figure 2. Residuals of σ_0 data values in parts per million from the linear σ_0 fit. Lines show the two standard deviation interval about zero. Residuals of Knudsen's cubic fit for σ_0 are indicated by the dotted curve. Thompson and Wirth data (+) and residuals exceeding 2.5 standard deviations were rejected in the linear fit.

The edited sigma-0 data, consisting of 13 points from Knudsen's table and 8 points from Cox, was fitted over the salinity range $8-41\,^0/_{00}$ by a linear curve, $\sigma_0 = A + BS$. The quadratic term was not statistically different from zero according to the tests outlined in the Appendix. The resulting formula for Sigma-0 is

$$\left.\begin{array}{l} \sigma_0 = -0.0114 + 0.804296 \times S \\ \text{S.D.} = 3.91 \text{ ppm } n = 21. \end{array}\right\} \quad (2)$$

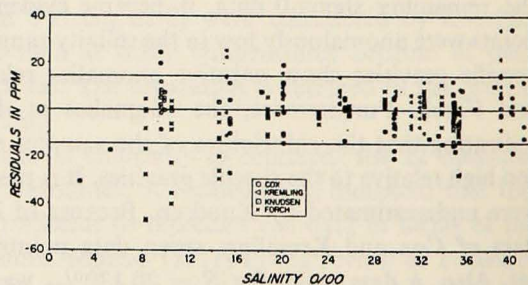Residuals of both accepted and rejected data from the regression curve (2) are shown in Figure 2. The Figure includes data from Thompson and Wirth and Knudsen's cubic regression curve. The maximum deviation for the cubic in the oceanic range of salinity is -13 ppm.

4. Sigma-t

Knudsen constructed an empirical formula for σ_t using the cubic curves in temperature developed by Forch from his thermal expansion measurements. The coefficients were fitted by a quadratic polynomial in σ_0 and adjusted to coincide with the pycnometer measurements at 24.6°C. The negative bias that is present in the σ_0 regression curve at oceanic salinities is also present in the sigma-t formula.

Cox *et al.* (1970) fitted a 10-term polynomial to their data set (S.D. = 11 ppm). However, the selection of terms was not optimized statistically so that the polynomial is not an acceptable representation of their measurements. Forch's thermal expansion data were converted to specific gravities (σ_t), using his cubic fit in temperature to estimate v_0/v_r, the volume v_0 at 0°C relative to the volume v_r at the reference temperature T_r. His ratios v_t/v_r were converted to v_t/v_0 to compute σ_t according to the relationship

Figure 3. Distribution of residuals in parts per million of σ_t and σ_0 data from the polynomial regression surface (Table 2) with salinity. Data with residuals greater than 2.5 standard deviations (about 18 ppm) were rejected. The horizontal lines show the two standard deviation interval about zero.

$$\sigma_t = \sigma_0 \left(\frac{v_0}{v_t}\right) + 10^3 \left(\frac{v_0}{v_t} - 1\right). \quad (3)$$

Table 2. Regression coefficients for specific gravity (σ_t) and density anomaly (σ_ϱ) for sea water at atmospheric pressure. Temperature in degrees Celsius (IPTS-68), salinity in parts per thousand ($^o/_{oo}$).

$$\sigma_t = \Sigma\Sigma\, b_{ij}\, T^i S^j$$
$$\sigma_\varrho = \Sigma\Sigma\, b'_{ij}\, T^i S^j = .999975\,\sigma_t - 0.025$$

i	j	b_{ij}	b'_{ij}	$b_{ij}/\sqrt{V(b_{ij})}$
		σ_0	$\sigma_{\varrho 0}$	
0	0	$-.0114$	$-.0364$	5.1
0	1	.804296	.804276	9943.
		S.D. = 3.91 ppm		
		$\sigma_t - \sigma_0$	$\sigma_\varrho - \sigma_{\varrho 0}$	
1	0	.992488 E-1	.992463 E-1	34.0
1	1	$-.592851$ E-2	$-.592836$ E-2	28.6
1	2	.431145 E-4	.431134 E-4	11.1
2	0	$-.123382$ E-1	$-.123379$ E-1	31.6
2	1	.271588 E-3	.271581 E-3	12.1
2	2	$-.288542$ E-5	$-.288535$ E-5	7.6
3	0	.206066 E-3	.206061 E-3	11.5
3	1	$-.663300$ E-5	$-.663283$ E-5	8.6
3	2	.540236 E-7	.540222 E-7	5.9
4	0	$-.204742$ E-5	$-.204737$ E-5	7.3
4	1	.560566 E-7	.560552 E-7	5.8
		S.D. = 7.08 ppm		
		Higher order terms		
1	3	–	–	.1
2	3	–	–	.1
3	3	–	–	.5
4	2	–	–	.7
5	0	–	–	.5
5	1	–	–	.6
0	2	–	–	.9
		S.D. = 7.20		
CHECKVALUE		23.09274172	23.06716604	$T = 10°C,\ S = 30^o/_{oo}$

His low salinity sample $S = 3.2^o/_{oo}$ was excluded from the data set. Salinities for Forch's samples were computed from the σ_0 values given in his table using the linear formula (2). These estimates are lower than Forch's tabulated salinities by an average of $0.08^o/_{oo}$. The largest difference is $0.28^o/_{oo}$. Because the salinity dependence of the volume ratio v_t/v_0 is small, the precise salinity is required for σ_0 only. Errors of $.08^o/_{oo}$ in salinity correspond to errors of about 1 ppm or less in specific gravity (.001 in σ_t) through the salinity dependence of v_t/v_0. Hence, the replacement of Forch's salinities with the computed salinities removes the large errors that would result from use of both his incompatible salinities and and σ_0 values.
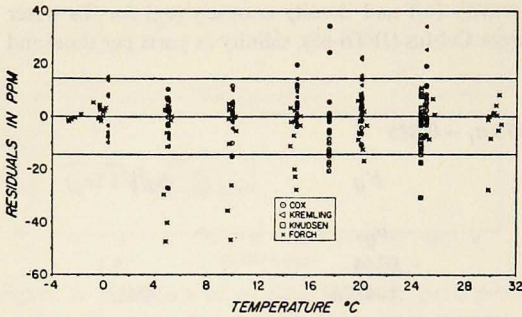
Figure 4. Distribution of residuals of σ_t and σ_0 with temperature. The horizontal lines show the two standard deviation about zero.

A set of $\sigma_t - \sigma_0$ values (σ_0 given by Eq. 2) was computed for 248 measurements from the 4 data sets (Table 1). An initial fit indicated that 11 terms in the polynomial were statistically significant. Thirty-one data points with residuals greater than 2.5 standard deviations were deleted from the data set leaving 217 acceptable values. The regression coefficients were recomputed on the edited data set and tested for significance. The final set of coeffi-

cients is given in Table 2. The table includes coefficients for σ_0 and tests of higher order terms not included in the regression. The residuals of accepted and rejected data are plotted in Figure 3 against salinity and in Figure 4 against temperature. Estimates of sigma-t based on the least squares formula in Table 2 have a standard deviation given by Eq. (6) in the Appendix. A map of the standard deviations is given in Figure 5. Over most of the range, the standard deviation is between 1 and 3 ppm.

Consistency among the four data sources is examined in Table 1. Agreement between Cox *et al.* and Forch is excellent with no systematic difference between the two sets. Cox's data show more scatter. Kremling's measurements are systematically higher by 3 ppm and Knudsen's lower by 2 ppm than the regression surface. Kremling's data is statistically significantly higher than the other sets at the 95% confidence

level but not at the 99% level. Knudsen's data is not distinguishable from the other sets for both sigma-0 and sigma-t. Knudsen's 24.6°C values have residuals that are correlated with those at 0°C suggesting that the errors in the chlorinities are larger than those of specific gravities. The standard deviation for σ_t is too large to reject the 24.6°C points, corresponding to those rejected at 0°C. These points fall marginally within the two standard deviation band and were not excluded from the data set.

The data points deleted from the combined set on the basis of residuals exceeding 2.5 standard deviations are not all randomly distributed indicating that systematic differences are present in the original data. At low salinities, 8 to 15°/00, Forch's thermal expansion values
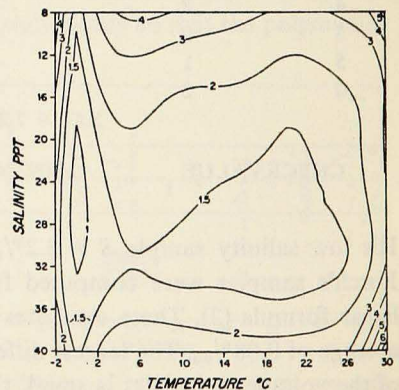

Figure 5. The standard deviation $V(\hat{Y})$ in ppm according to equation 6 in the Appendix of specific gravities estimated from the polynomial formula (Table 2).

are low for temperatures of 5, 10 and 15°C. Nine points in this range fall below the regression polynomial by an average of 34 ppm. This systamatic difference is reflected in Knudsen's equation also. At 6°C and 10°/$_{00}$, the equation is 24 ppm lower than the regression polynomial. Kremling (1972) points out that measurements of more than 200 samples of Baltic water yields specific gravities that averaged 25 ppm higher than Knudsen's equation for salinities of 5°/$_{00}$. It seems likely, therefore, that Forch's values in this range are anomalous.

Points rejected from Cox's data are scattered over the entire range of salinity. Four out of seven points rejected are at 17.494°C, which probably reflects experimental technique rathei than any systematic differences in specific gravities. Kremling's rejected points (higher than the regression polynomial by 20–30 ppm) occur at 20 and 25°C for the low (15.247°/$_{00}$) and high (39.232°/$_{00}$) salinity samples. Kremling (1973) noted particles in the high salinity sample and conjectured that these could have influenced his measurements. No explanation has been offered for the difference for the low salinity sample.

Newton and Kennedy (1965) list 17 values of specific volume at atmospheric pressure with an estimated precision of 70 ppm. The corresponding specific gravities are low by an average of 21 ppm with respect to the present regression foimula. Wilson and Bradley (1968) give 45 values that average 133 ppm higher than the present formula. Neither set was acceptable in terms of the selection criteria.

Millero and Lepple (1973) measured specific gravity of Copenhagen Standard Seawater ovei 0 to 40°C at 35°/$_{00}$. Their values average 20 ppm below the regression polynomial. The standard deviation of the residuals is small (2.5 ppm) indicating that the observed temperature variation is in good agreement with the edited data set used to obtain the regression polynomial. They note that their standard seawater sample may have been diluted with condensed water vapor before the measurements were made.

5. Density

Specific gravity is converted to density (gm/cm³) using 0.999975 gm/cm³ for the reference density ϱ_4 of pure water at 4°C. The density anomaly σ_ϱ is given by

$$\begin{aligned}
\sigma_\varrho &= 10^3 \, (\varrho - 1) \\
&= \varrho_4 \sigma_t + 10^3 \, (\varrho_4 - 1) \\
&= .999975 \, \sigma_t - 0.025 \text{ gm/cm}^3.
\end{aligned}$$

The table of coefficients (Table 2) includes a list of coefficients for computing absolute density anomaly.

6. Conclusions

Densities of seawater calculated from observed temperatures and salinities are limited in accuracy piimarily by the uncertainty in salinity determinations. Using

Table 3. Means and standard deviations of differences of sigma-*t* formulas from the data set in parts per million (PPM).

	Number of empirical constants	Formula – Data n = 238	
		Mean	S.D.
Knudsen (1910)[1]	15	– 7.75	10.17
Cox (1970)	10	2.89	14.41
Kullenberg (1974)[2]	13	– 1.13	9.40
Formula (Table 2)	13	– .10	6.68

[1] Temperature and salinity scales converted.
[2] Temperature scale converted.

3 ppm $(.003^o/_{oo})$ as the standard deviation of individual salinities obtained on ship-board salinometers (Schleicher and Bradshaw, 1956) yields a corresponding standard deviation of 2.4 ppm for sigma-*t* and density. The precision laboratory measurements fitted by a least square polynomial yield estimates with standard deviations ranging from 1 to 3 ppm (Figure 5) over most of the oceanic range. It is concluded that the laboratory measurements are only marginally adequate to define density to an accuracy consistent with present field observations. Comparison of the scatter of modern measurements (Table 1) with those of Knudsen and Forch leads to the conclusion that no improvement in precision of laboratory measurements has been achieved in recent years. Further determinations with similar precision within the range 0 to 25°C and 10 to $40^o/_{oo}$ salinity will not improve knowledge of seawater density appreciably. New determinations in this range must be made using methods capable of higher precision. Useful measurements can, however, be made to extend the range of coverage in both salinity and temperature. Present measurements below $8^o/_{oo}$ salinity are inadequate to define the dependence of density on temperature and salinity. Forch's measurements are the only ones available below 0°C and above 25°C. These need to be verified. Previous empirical formulas for sigma-*t* are not consistent with the present data set edited relative to the least squares polynomial. A comparison with the data set is made in Table 3 of Knudsen's (1901) formula and the more recent formulas of Cox *et al.* (1970) and Kullenberg (UNESCO, 1974). The mean and standard deviation of the formula minus laboratory value is computed at the measurement points. The standard deviation of the differences for Cox's least-squares formula is relatively high because of extrapolation to Forch's 30°C points. The standard deviation of the average differences for each formula is less than 1 ppm so that the means are significantly different from the data set for all three formulas.

It appears likely that the differences among the formulas examined can be attributed to differences in the original data sets used to compute formula coefficients and not to the structure of the formulas. To check this conclusion, values of $\sigma_t - \sigma_0$ were computed from Knudsen's and Kullenberg's formulas at the 217 measurement points used to define the 11-term polynomial in Table 2. In both cases, the 11-term

polynomial could be fitted to the artificially created data sets with standard deviations less than 1 ppm compared with 7.1 ppm for the actual data. Knudsen's and Kullenberg's formulas if optimally fitted to the data would probably coincide with the least squares polynomial with a comparable standard deviation ($\sim$ 1 ppm). It is concluded, therefore, that the present data set is not of sufficient precision to choose objectively among the formula types examined. These formulas would not differ significantly from one another if fitted to the same data set. Over the range of temperature and salinity considered, the least squares polynomial is as simple and precise a fit to the specific gravity measurements of seawater as the nonlinear forms used by Knudsen and Kullenberg. Because of linearity, the least squares polynomial fit can be tested statistically to evaluate objectively the goodness of fit. This cannot be done easily for nonlinear formulas. The least squares formula therefore serves as a useful benchmark to test the quality of fit of other formulas and represents the minimum quality of fit. The choice of a "best" formula cannot be made objectively unless there is agreement on the criteria used for selecting and rejecting the basic laboratory data. Selecting data according to an objective least squares polynomial fitting procedure is one such approach.

Appendix

Regression analysis

Fitting of least-squares polynomials in temperature T and salinity S to the specific gravity data for seawater follows standard multiple regression procedures described, for example, by Brownlee (1965). A minor departure from the procedures consists of considering the constant term as one of the independent regression variables.

Given data Y_ν for T_ν, S_ν; $\nu = 1, 2, \ldots, n$, a regression formula of r terms of the polynomial form $X = T^\alpha S^\beta$, where α, β are positive integer or zero powers, is fitted by minimizing the square residuals with respect to the coefficients of the terms. The estimates for Y_ν at the measured points are

$$\hat{Y}_\nu = \sum_{i=1}^{r} b_i X_{i\nu}; \quad X_{i\nu} = T_\nu^{\alpha_i} S_\nu^{\beta_i} \qquad 1.$$

subject to minimization of the square residuals ε_ν^2, where

$$G_r = \sum_{\nu=1}^{n} \varepsilon_\nu^2 = \sum_{\nu=1}^{n} (Y_\nu - \hat{Y}_\nu)^2. \qquad 2.$$

Minimization of G_r with respect to the coefficients b_i yields the normal equations

$$\sum_{j=1}^{r} R_{ij} b_j = Z_i \qquad 3.$$

where

$$R_{ij} = \sum_{\nu=1}^{n} X_{i\nu} X_{j\nu} \qquad\qquad Z_i = \sum_{\nu=1}^{n} X_{i\nu} Y_\nu.$$

The normal equations are solved to yield

$$b_i = \sum_{j=1}^{r} C_{ij} Z_j = \sum_{j=1}^{r} \sum_{\nu=1}^{n} C_{ij} X_{j\nu} Y_\nu \qquad 4.$$

where C_{ij} are elements of the inverse matrix $R^{-1} = (R_{ij})^{-1}$.

If Y_ν is assumed to be a random variable normally distributed about a true value Y_ν^0 with variance $V(Y) = \sigma^2$, the coefficients b_i will also be random variables with variance $V(b_i)$ given by

$$V(b_i) = \sum_{\nu=1}^{n} \left[\sum_{j=1}^{r} C_{ij} X_{j\nu} \right]^2 V[Y] = C_{ii} \sigma^2. \qquad 5.$$

Because the regression coefficients are random variables the estimates $\hat{Y}$ are also randomly distributed about a true value Y^0 with variance

$$\left. \begin{aligned} V(\hat{Y}) &= \sum_{i=1}^{r} \sum_{j=1}^{r} \mathrm{Cov}\,(b_i, b_j) X_i X_j \\ &= \sigma^2 \sum_{i=1}^{r} \sum_{j=1}^{r} C_{ij} X_i X_j. \end{aligned} \right\} \qquad 6.$$

The covariance appears in (6) because b_i, b_j do not have independent distributions.

The formula

$$\hat{Y} = \sum_{i=1}^{r} b_i X_i \qquad 7.$$

is used to interpolate the function over the range of the independent variables T, S. The standard deviation of the estimated function $\hat{Y}$ is given from (6) by $\sqrt{V(\hat{Y})}$.

The variance σ^2 is estimated from the residuals at the measured points

$$Y_\nu - Y_\nu^0 = \hat{Y}_\nu - Y_\nu^0 + \varepsilon_\nu \qquad 8.$$

which have expected values for sums of squares of

$$\left. \begin{aligned} n\sigma^2 &= \sum_{\nu=1}^{n} \sum_{i=1}^{r} \sum_{j=1}^{r} \mathrm{Cov}\,(b_i, b_j) X_{i\nu} X_{j\nu} + G_r \\ &= r\sigma^2 + G_r. \end{aligned} \right\} \qquad 9.$$

Hence, the expected value (unbiased) for σ^2 is

$$\sigma^2 \sim \sigma_r^2 = G_r/(n - r). \qquad 10.$$

Significance tests

For a normal distribution, the ratio $b_i/\sqrt{C_{ii}\sigma^2}$ has a Student's t-distribution with $n-r$ degrees of freedom under the null hypothesis. Hence, b_i can be considered significantly different from zero (at the 95% confidence level) if the ratio exceeds $t_{.05}(n-r) > 1.96$. Brownlee gives another convenient test for determining the significance of adding additional terms in reducing the square residuals G_r. At the 95% confidence level, an additional term X_{r+1} is significant if $G_r - G_{r+1} > \sigma_{r+1}^2 F_{.05}$ $(1, n-r-1) > 3.84 \cdot \sigma_{r+1}^2$, where $F_{.05}$ $(1, n-r-1)$ is the F-distribution for 1 and $n-r-1$ degrees of freedom.

The polynomial fitting procedure consists of identifying all terms in the formula for $\hat{\gamma}$ that are significant according to the objective criteria given above.

REFERENCES

Barber, C. B. 1969. The international practical temperature scale of 1968. Metrologia *5*: 35–44.

Brownlee, K. A. 1965. *Statistical Theory and Methodology in Science and Engineering.* J. Wiley & Sons, New York, 590 pp.

Bryden, H. L. 1973. New polynomials for thermal expansion, adiabatic temperature gradient and potential temperature of seawater. Deep-Sea Res., *20*: 401–408.

Cox, R. A., M. J. McCartney, and F. Culkin. 1970. The specific gravity/salinity/temperature relationship in natural seawater. Deep-Sea Res. *17*: 679–689.

Craig, H. 1961. Standard for reporting concentrations of Deuterium and Oxygen-18 in natural waters. Science, *133*: 1833–1834.

Ekman, V. W. 1908. Die Zusammendrueckbarkeit des Meerwassers nebst einigen werten fuer Wasser und Quecksilber. Pub. de Circ. *43*: 1–47.

Girard, G., and M. Menaché. 1972. Sur le calcul de la masse volumique de l'eau. C. R. Acad. Sci., Paris *274*: 337–339.

Knudsen, M. 1901. *Hydrographical Tables.* G. E. C. Gad, Copenhagen, 63 p.

Knudsen, M., C. Forch, and S. P. L. Sørensen. 1902a. Berichte über die Konstantenbestimmungen zur Aufstellung der hydrographischen Tabellen. D. Kgl. Danske Vidensk. Selsk. Skrifter, 6 Raekke, naturvidensk. og mathem. Afd. XII 1: 1–151.

Knudsen, M., C. Forch, and S. P. L. Sørensen. 1902b. Bericht über die chemische und physikalische Untersuchung des Seewassers und die Aufstellung der neuen Hydrographischen Tabellen. Wissenshaftliche Meersuntersuchungen herausgegeben von der Komission zur Untersuchung der deutschen Meere in Kiel, Band NF 6: 125–184.

Kremling, K. 1972. Comparison of specific gravity in natural seawater from hydrographic tables and measurements by a new density instrument. Deep-Sea Res., *19*: 377–383.

McDonald, J. R. 1969. Review of some experimental and analytical equations of state. Rev. Mod. Phys., *41*: 316–349.

Millero, F. J. 1971. The molal volumes of electrolytes. Chem. Rev., *71*: 147–176.

Millero, F. J., and F. K. Lepple. 1973. The density and expansibility of artificial seawater solutions from 0 to 40°C and 0 to 21 ⁰/₀₀ chlorinity. Mar. Chem., *1*: 89–104.

Newton, M. S., and G. C. Kennedy. 1965. An experimental study of the P-V-T-S relations of seawater. J. Mar. Res., *23*: 88–103.

Schleicher, K. E., and A. Bradshaw. 1956. A conductivity bridge for measurement of the salinity in seawater. J. Cons. Perm. Int. Explor. Mer., *22*: 9–20.

Thompson, T. G., and H. E. Wirth. 1931. The specific gravity of seawater at zero degrees in relation to the chlorinity. J. Cons. Perm. Int. Explor. Mer., *6*: 232–240.

Tilton, L. W., and J. K. Taylor. 1937. Accurate representation of the refractivity and density of distilled water as a function of temperature. J. Res. Nat. Bur. Stand., *18*: 205–214.

UNESCO. 1966. Second report of the Joint Panel on Oceanographic Tables and Standards. UNESCO Tech. Pap. Mar. Sci. No. 4.

UNESCO. 1974. Sixth report of the Joint Panel on Oceanographic Tables and Standards. UNESCO Techn. Pap. Mar. Sci. No. 16.

Wang, Dong-Ping, and F. J. Millero. 1973. Precise representation of the P-V-T properties of water and seawater determined from sound speeds. Jour. Geoph. Res. *78*: 7122–7128.

Wilson, W., and D. Bradley. 1968. Specific volume of seawater as a function of temperature, pressure and salinity. Deep-Sea Res., *15*: 355–363.