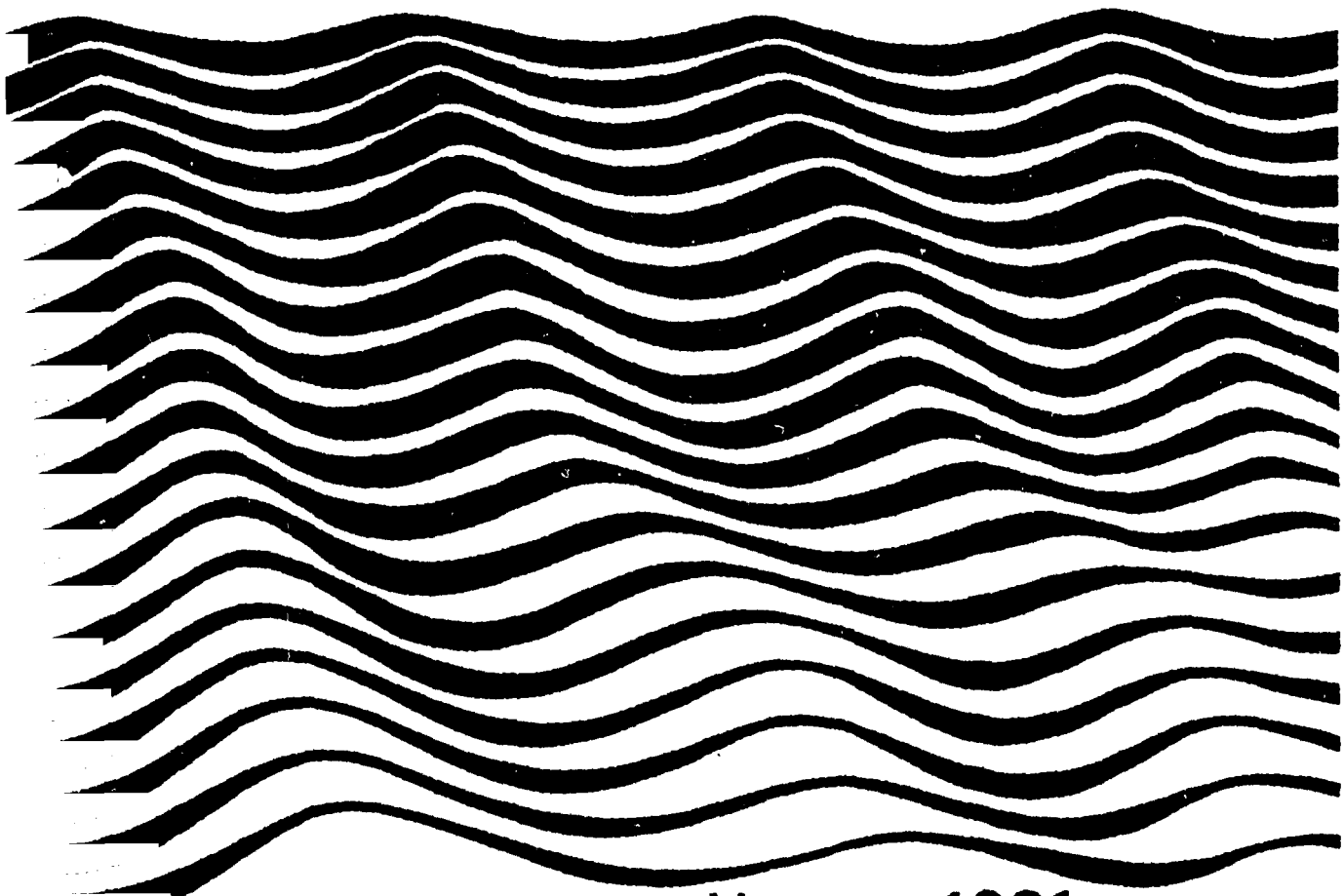


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in marine science 38

**Background papers
and supporting data
on the International Equation
of State of Seawater 1980**

Unesco/ICES/SCOR/IAPSO
joint panel on oceanographic
tables and standards



Unesco, 1981

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PREFACE

This series, the Unesco Technical Papers in Marine Science, is produced by the Unesco Division of Marine Sciences as a means of informing the scientific community of recent developments in oceanographic research and marine science affairs.

Many of the texts published within the series result from research activities of the Scientific Committee on Oceanic Research (SCOR) and are submitted to Unesco for printing following final approval by SCOR of the relevant working group report.

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INTRODUCTION

In 1962, a Joint Panel on the Equation of State of Seawater, appointed by Unesco, ICES, SCOR and IAPSO, brought forward several problems which appeared in the basic relationships used for the determination of density of seawater. In 1964, this committee was replaced by the Joint Panel on Oceanographic Tables and Standards (JPOTS). Since this date, the Panel has been concerned with the precise definition of the equation of state of seawater (Unesco 1965, 1966, 1968, 1970, 1974, 1976, 1978, 1979 and 1981).

The equation of state of seawater is the mathematical expression to calculate density from measurements of temperature, pressure and salinity, or from other parameters dependent on these. Virtually all the computations of density of seawater made since the beginning of the century have been based on the direct measurements of density, chlorinity and salinity, made by Forch, Knudsen and Sørensen, published in 1902, and of compression of seawater, made by Ekman (1908). A new equation of state was considered urgently desirable because newly acquired data indicated slight discrepancies with the Knudsen-Ekman equation of state of seawater (Grasshoff, 1976). This old equation was obtained from measurements of density of natural seawater in which the proportions of the various ions are not exactly constant. To be consistent with the new definition of the Practical Salinity, 1978, the new equation of state is based on measurements of density of standard seawater solutions obtained by weight dilution with distilled water and by evaporation. As the absolute density of pure water is not known with enough accuracy, the density of distilled water used for these measurements was determined from the equation of the SMOW (Standard Mean Ocean Water) whose isotopic composition is well defined (IUPAC, 1976). Intensive work was then carried out in different laboratories with different measuring equipment. This resulted in considerable data on which the new International Equation of State of Seawater is based. The full equation is composed of a one atmosphere equation based on 467 data points, combined with a high pressure expression based on 2 023 data points. The density computed with these equations is relative to the IUPAC (1976) recommended equation for density of SMOW.

The mathematical expression adopted by the Unesco/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards as the International Equation of State of Seawater 1980, gives the density (ρ , kg m⁻³) of seawater as a function of practical salinity (S), temperature (t, °C) and applied pressure (p, bars); its form is :

$$\rho(S,t,p) = \frac{\rho(S,t,o)}{1 - p/K(S,t,p)}$$

where $\rho(S,t,o)$ is the one atmosphere International Equation of State 1980, and $K(S,t,p)$ is the secant bulk modulus, the full expressions of which are reported in the two definitions (p. 9 and 10).

The International Equation of State, 1980 has been formulated and adopted by the Unesco/ICES/SCOR/IAPSO Joint Panel on Oceanographic Tables and Standards, Sidney, B.C., Canada, 1 to 5 September 1980, and endorsed by the International Association for the Physical Sciences of the Ocean (IAPSO) in December 1979, the International Council for the Exploration of the Sea (ICES) in October 1979, the Scientific Committee on Oceanic Research (SCOR) in September 1980 and the Intergovernmental Oceanographic Commission (IOC) of Unesco in June 1981. The new equation is to be used for all values published on and after 1 January 1982.

The present document is a report of all the work and data on which the International Equation of State of Seawater, 1980 is based. This report consists mainly of two published papers from Deep Sea Research, and two unpublished reports on the summary of data treatment for the one atmosphere and the high pressure equations of state of seawater. The cooperation of the publishers of Deep Sea Research in granting permission for reproduction of the two papers is greatly appreciated.

This report is divided into two sections and a conclusion :

- Background papers and supporting data on the one atmosphere International Equation of State of Seawater, 1980.
- Background papers and supporting data on the high pressure International Equation of State of Seawater, 1980.

The International Equation of State of Seawater, 1980 as endorsed by the JPOTS at its last meeting in September 1980, is reported in the Conclusion.

New international oceanographic tables, in replacement of the old Knudsen-Ekman tables, have been prepared by the Division of Marine Sciences, Unesco, as Volume 4 of the International Oceanographic Tables. This volume will be published shortly in the series Unesco Technical Papers in Marine Science, No. 40, and will be available, free of charge, upon request from :

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75700 Paris,
France.

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The One Atmosphere International Equation
of State of Seawater, 1980

Definition

The density (ρ , kg m^{-3}) of seawater at one standard atmosphere ($p = 0$) is to be computed from the practical salinity (S) and the temperature (t , $^{\circ}\text{C}$) with the following equation :

$$\begin{aligned}\rho(S,t,0) = & \rho_w + (8.244\ 93 \times 10^{-1} - 4.0899 \times 10^{-3} t \\ & + 7.6438 \times 10^{-5} t^2 - 8.2467 \times 10^{-7} t^3 + 5.3875 \times 10^{-9} t^4)S \\ & + (-5.724\ 66 \times 10^{-3} + 1.0227 \times 10^{-4} t - 1.6546 \times 10^{-6} t^2)S^{3/2} \\ & + 4.8314 \times 10^{-4} S^2\end{aligned}$$

where ρ_w , the density of the Standard Mean Ocean Water (SMOW) taken as pure water reference, is given by

$$\begin{aligned}\rho_w = & 999.842\ 594 + 6.793\ 952 \times 10^{-2} t - 9.095\ 290 \times 10^{-3} t^2 \\ & + 1.001\ 685 \times 10^{-4} t^3 - 1.120\ 083 \times 10^{-6} t^4 \\ & + 6.536\ 332 \times 10^{-9} t^5\end{aligned}$$

The one atmosphere International Equation of State of Seawater, 1980 is valid for practical salinity from 0 to 42 and temperature from -2 to 40°C .

The High Pressure International Equation
of State of Seawater, 1980

Definition

The density (ρ , kg m⁻³) of seawater at high pressure is to be computed from the practical salinity (S), the temperature (t, °C) and the applied pressure (p, bars) with the following equation :

$$\rho(S,t,p) = \frac{\rho(S,t,o)}{1 - p/K(S,t,p)}$$

where $\rho(S,t,o)$ is the one atmosphere International Equation of State 1980, given on the preceding front page and $K(S,t,p)$ is the secant bulk modulus given by

$$K(S,t,p) = K(S,t,o) + Ap + Bp^2$$

where

$$K(S,t,o) = K_w + (54.6746 - 0.503\ 459\ t + 1.099\ 87 \times 10^{-2}\ t^2 - 6.1670 \times 10^{-5}\ t^3)S + (7.944 \times 10^{-2} + 1.6483 \times 10^{-2}\ t - 5.3009 \times 10^{-4}\ t^2) S^{3/2},$$

$$A = A_w + (2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}\ t - 1.6078 \times 10^{-6}\ t^2)S + 1.910\ 75 \times 10^{-4}\ S^{3/2}$$

$$B = B_w + (-9.9348 \times 10^{-7} + 2.0816 \times 10^{-8}\ t + 9.1697 \times 10^{-10}\ t^2)S$$

the pure water terms K_w , A_w and B_w of the secant bulk modulus are given by

$$K_w = 19\ 652.21 + 148.4206\ t - 2.327\ 105\ t^2 + 1.360\ 477 \times 10^{-2}\ t^3 - 5.155\ 288 \times 10^{-5}\ t^4$$

$$A_w = 3.239\ 908 + 1.437\ 13 \times 10^{-3}\ t + 1.160\ 92 \times 10^{-4}\ t^2 - 5.779\ 05 \times 10^{-7}\ t^3$$

$$B_w = 8.509\ 35 \times 10^{-5} - 6.122\ 93 \times 10^{-6}\ t + 5.2787 \times 10^{-8}\ t^2$$

The high pressure International Equation of State of Seawater, 1980 is valid for practical salinity from 0 to 42, temperature from -2 to 40°C and applied pressure from 0 to 1000 bars.

Note on the symbols, units and nomenclature used in the
background papers on the International Equation of
State of Seawater 1980

With the exception of the paper by Millero and Poisson, Deep Sea Research, 28A, 1981, the papers presented in this report were published or submitted for publication before the meeting of the Joint Panel on Oceanographic Tables and Standards, held in Woods Hole, USA, from 1 to 5 September 1980, during which time the definition of the Practical Salinity 1978, S, was established, and before the IAPSO General Assembly, held at Canberra, Australia, in December 1979. The symbol $S(^{\circ}/_{\infty})$ has been used in these papers for the practical salinity, instead of the adopted symbol S (Sun Report, 1980). The reader must read S instead of $S(^{\circ}/_{\infty})$ and thus ignore the " $^{\circ}/_{\infty}$ " when they appear in the text regarding the practical salinity. For example, $S(^{\circ}/_{\infty}) = 35.238$ or $S = 35.238^{\circ}/_{\infty}$ corresponds to $S = 35.238$.

It should also be borne in mind that in some places, the equation referred to as the Unesco Equation of State of Seawater is now known as the International Equation of State of Seawater.

BACKGROUND PAPERS AND SUPPORTING DATA ON
THE ONE ATMOSPHERE INTERNATIONAL EQUATION
OF STATE OF SEAWATER, 1980

NOTE

International one-atmosphere equation of state of seawater

FRANK J. MILLERO* and ALAIN POISSON†

(Received 21 August 1980; accepted 2 October 1980; final revision received 20 November 1980)

Abstract—The density measurements by MILLERO, GONZALEZ and WARD (1976, *Journal of Marine Research*, 34, 61–93) and POISSON, BRUNET and BRUN-COTTAN (1980, *Deep-Sea Research*, 27, 1013–1028), from 0 to 40°C and 0.5 to 43 salinity, have been used to determine a new 1-atm equation of state for seawater. The equation is of the form (t : °C; S ; ρ kg m⁻³)

$$\rho = \rho_0 + AS + BS^{3/2} + CS^2,$$

where

$$A = 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4$$

$$B = -5.72465 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2$$

$$C = 4.8314 \times 10^{-4}$$

and ρ_0 is the density of water (BIGG, 1967, *British Journal of Applied Physics*, 8, 521–537).

$$\rho_0 = 999.842594 + 6.793952 \times 10^{-2}t - 9.095290 \times 10^{-3}t^2 + 1.001685 \times 10^{-4}t^3 - 1.120083 \times 10^{-6}t^4 + 6.536332 \times 10^{-9}t^5.$$

The standard error of the equation is 3.6×10^{-3} kg m⁻³. This equation will become the new 1-atm equation of state of seawater that has been suggested for use by the UNESCO (United Nations Educational, Scientific and Cultural Organization) joint panel on oceanographic tables and standards.

INTRODUCTION

AT THE UNESCO panel meeting held in Paris, France (UNESCO, 1979), Poisson and Brunet presented some new measurements on the density (ρ) of seawater at 1 atm and $S = 35$ that suggested that the proposed (UNESCO, 1978) equation of state of MILLERO *et al.* (1976) may be in error at temperatures above 25°C. As shown in Fig. 1 the equation of MILLERO *et al.* (1976) does not fit their direct experimental measurements or the new measurements of POISSON *et al.* (1980). Because standard seawater may be used as a density standard, these differences needed to be clarified. The UNESCO panel recommended that we examine these differences and use the data of MILLERO *et al.* (1976) and POISSON *et al.*

* Roesentiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, U.S.A.

† Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, tour 24, 4 Place Jussieu, 75230, Paris Cedex 05, France.

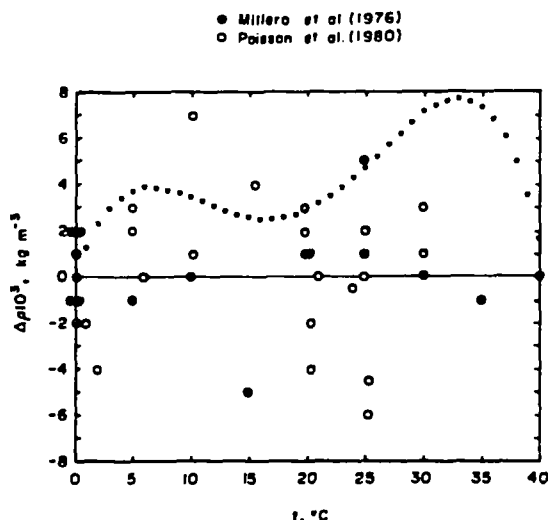


Fig. 1. Comparisons of the measured and calculated (equation 1) relative densities of seawater at $S = 35$. The solid circles are the data of MILLERO *et al.* (1976) and the open circles are the data of POISSON *et al.* (1980). The curve is the equation of state of MILLERO *et al.* (1976).

(1980) to generate a new 1-atm equation of state. This note summarizes our findings and gives the new equation, which was suggested for general use by the UNESCO panel. The full details of the data analysis are given in a UNESCO data report (MILLERO and POISSON, 1981).

DENSITY OF STANDARD SEAWATER ($S = 35$) AS A FUNCTION OF TEMPERATURE

The relative density measurements ($\rho - \rho_0$, where ρ_0 is density of water) at a salinity of 35 consist of 19 points from 0 to 40°C from MILLERO *et al.* (1976) and 20 points from 1.1 to 30°C from POISSON *et al.* (1980) These relative densities were fitted to the equation

$$(\rho - \rho_0) = 28.265 - 1.2247 \times 10^{-1}t + 2.383 \times 10^{-3}t^2 - 3.0775 \times 10^{-5}t^3 + 2.115 \times 10^{-7}t^4 \quad (1)$$

with a $\sigma = 2.6 \times 10^{-3} \text{ kg m}^{-3}$. A comparison of the measured and calculated values of $\rho - \rho_0$ are shown in Fig. 1. Equation (1) and the equation of MILLERO *et al.* (1976) show differences from 26 to 38°C that are as large as $7.7 \times 10^{-3} \text{ kg m}^{-3}$. The cause of the differences is an increase in the salinity of the $S = 40$ samples from 0 to 30°C (MILLERO and POISSON, 1981).

EQUATION OF STATE OF SEAWATER

The relative density data ($\rho - \rho_0$) used to determine the new equation of state consisted of 122 points (0 to 40°C) from MILLERO *et al.* (1976) and 345 points (0 to 30°C) from POISSON *et al.* (1980). Before the data sets could be combined, it was necessary to make some adjustments and normalizations. As the measurements of POISSON *et al.* (1980) were made

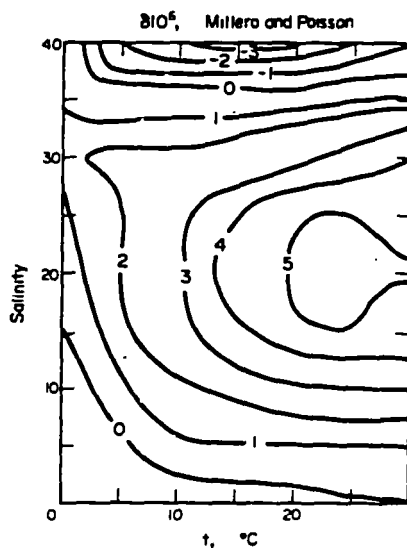


Fig. 2. Comparisons of the smoothed densities by MILLERO *et al.* (1976) and POISSON *et al.* (1980).

relative to a seawater of $S = 35$, this was done by using the values of $(\rho - \rho_0)$ at $S = 35$ at a given temperature calculated from equation (1). The salinities of the $S = 40$ samples of MILLERO *et al.* (1976) have been adjusted by using extrapolated functions of $(\rho - \rho_0)$ vs S and the equations of POISSON *et al.* (1980). The recalculated salinities agreed to ± 0.004 .

The form of the equation of state was (MILLERO *et al.* 1976)

$$(\rho - \rho_0) = AS + BS^{3/2} + CS^2, \quad (2)$$

where A , B , and C are functions of temperature ($t^\circ\text{C}$, IPTS-68). A number of temperature forms for the parameters A , B , and C have been examined (MILLERO and POISSON, 1981). The criterion used for selecting the fewest number of terms was based on an 'F' test analysis of the residuals (FREUND, 1962) and the requirement that $(\rho - \rho_0)$ at $S = 35$ agree (to $\pm 2 \times 10^{-3} \text{ kg m}^{-3}$) with the values calculated from equation (1). A nine-parameter equation, $9(5A, 3B, 1C)$ was found to be necessary for the individual and total data. The data of POISSON *et al.* (1980) gave

$$A = 8.24501 \times 10^{-1} - 4.0639 \times 10^{-3}t + 7.5719 \times 10^{-5}t^2 - 8.8910 \times 10^{-7}t^3 + 6.616 \times 10^{-9}t^4 \quad (3a)$$

$$B = -5.7728 \times 10^{-3} + 9.7437 \times 10^{-5}t - 1.3747 \times 10^{-6}t^2 \quad (3b)$$

$$C = 4.9054 \times 10^{-4} \quad (3c)$$

with a $\sigma = 3.33 \times 10^{-3} \text{ kg m}^{-3}$. The data of MILLERO *et al.* (1976) gave

$$A = 8.23997 \times 10^{-1} - 4.0644 \times 10^{-3}t + 7.6455 \times 10^{-5}t^2 - 8.3332 \times 10^{-7}t^3 + 5.4961 \times 10^{-9}t^4 \quad (4a)$$

$$B = -5.5078 \times 10^{-3} + 9.7598 \times 10^{-5}t - 1.6218 \times 10^{-6}t^2 \quad (4b)$$

$$C = 4.6106 \times 10^{-4} \quad (4c)$$

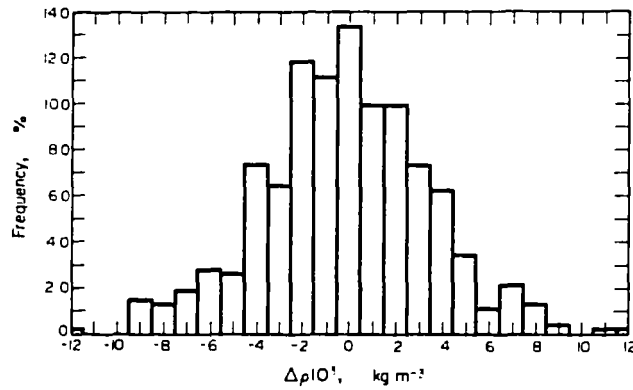


Fig. 3. Frequency of deviations of International equation of state.

with a $\sigma = 3.49 \times 10^{-3} \text{ kg m}^{-3}$. A comparison of the smoothed input data from 0 to 30°C is given in Fig. 2. The differences between the smoothed data of MILLERO *et al.* (1976) and POISSON *et al.* (1980) are within $\pm 5 \times 10^{-3} \text{ kg m}^{-3}$ over the entire salinity and temperature range.

The coefficients for the combined data are

$$A = 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4 \quad (5a)$$

Table 1. The International equation of state for seawater ($\text{m}^3 \text{kg}^{-1}$)

$$v^P = v^0(1 - P/K) \\ = 1/\rho^0(1 - P/K),$$

where

$$\rho^0 = 999.842594 + 6.793952 \times 10^{-2}t - 9.095290 \times 10^{-3}t^2 + \\ 1.001685 \times 10^{-4}t^3 - 1.120083 \times 10^{-6}t^4 + \\ 6.536332 \times 10^{-9}t^5 + (8.24493 \times 10^{-1} - \\ 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 - \\ 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4)S + \\ (-5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}t - \\ 1.6546 \times 10^{-6}t^2)S^{3/2} + 4.8314 \times 10^{-4}S^2 \\ K = 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2}t^3 - \\ 5.155288 \times 10^{-5}t^4 + S(54.6746 - 0.603459t + \\ 1.09987 \times 10^{-2}t^2 - 6.1670 \times 10^{-5}t^3) + S^{3/2}(7.944 \times 10^{-2} + \\ 1.6483 \times 10^{-2}t - 5.3009 \times 10^{-4}t^2) + P[3.239908 + \\ 1.43713 \times 10^{-3}t + 1.16092 \times 10^{-4}t^2 - 5.77905 \times 10^{-7}t^3 + \\ S(2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}t - 1.6078 \times 10^{-6}t^2) + \\ S^{3/2}(1.91075 \times 10^{-4})] + P^2[8.50935 \times 10^{-5} - 6.12293 \times 10^{-6}t + \\ 5.2787 \times 10^{-8}t^2 + S(-9.9348 \times 10^{-7} + \\ 2.0816 \times 10^{-8}t + 9.1697 \times 10^{-10}t^2)]$$

Check values:

S	t	P	ρ	K
35	5°C	0b	1027.67547	22185.93358
		1000	1069.48914	25577.49819

$$B = -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2 \quad (5b)$$

$$C = 4.8314 \times 10^{-4} \quad (5c)$$

with an overall $\sigma = 3.66 \times 10^{-3} \text{ kg m}^{-3}$. The frequency of the deviations shown in Fig. 3 indicate that they have a near normal distribution.

To determine absolute densities from the relative density equation, it is necessary to know the density of SMOW (Standard Mean Ocean Water), which was used in these studies. At present the density of SMOW is based on the calculations of BIGG (1967)

$$\rho_o(\text{kg m}^{-3}) = 999.842594 + 6.793952 \times 10^{-2}t - 9.095290 \times 10^{-3}t^2 + 1.001685 \times 10^{-4}t^3 - 1.120083 \times 10^{-6}t^4 + 6.536332 \times 10^{-9}t^5. \quad (6)$$

The values of ρ_o calculated from equation (6) can be added to $\rho - \rho_o$ calculated from equations (2) and (8) to yield densities (kg m^{-3}) for seawater. Should a new equation for SMOW become available in the future, it can be used in place of equation (6).

The full International equation of state can be obtained by combining our 1-atm results with the high pressure equation of MILLERO, CHEN, BRADSHAW and SCHLEICHER (1980). The resulting equation is

$$v^P = v^0 [1 - P/K] \quad (7)$$

or

$$\rho^P = \rho^0 [1/(1 - P/K)], \quad (8)$$

where $v^P = 1/\rho^P$ is the specific volume at applied pressure P ($P = 0$ is 1 atm) and K is the secant bulk modulus. The coefficients for equations (7) and (8) are given in Table 1. This full equation of state of seawater is the new equation suggested for oceanographic use by the UNESCO panel on oceanographic tables and standards.

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Millero and Poisson :
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ERRATUM

A number of printing errors occurred in this paper that were not detected in proof. These are listed below.

1. The first equation in the abstract should be

$$\rho = \rho_0 + AS + BS^{3/2} + CS^2$$

2. The last term in the density of water equation in the abstract and Table 1 should be 6.536332×10^{-9} .

3. The Pt^2 term of the secant bulk modulus (K) equation in Table 1 should be 1.16092×10^{-4} .

4. A right parenthesis [)] should follow the last term ("... $10^{-10} t^2$)") of the secant bulk modulus (K) equation in Table 1.

These errors have been modified in the preceding reprint of this paper.

SUMMARY OF DATA TREATMENT FOR THE INTERNATIONAL ONE ATMOSPHERE

EQUATION OF STATE FOR SEAWATER

By

Frank J. Millero*

and

Alain Poisson**

(Submitted to Unesco for publication on 22 July 1980)

*Rosenstiel School of Marine and Atmospheric Science
University of Miami
Miami, Florida 33149

**Laboratoire de physique et chimie marines
University Pierre et Marie CURIE
tour 24, 4 Place Jussieu, 75230, PARIS Cedex 05

ABSTRACT

The experimental measurements of Millero et al. (1976) and Poisson et al. (1980) have been used to determine a new 1 atm. equation of state for seawater. The equation is of the form ($t^{\circ}\text{C}$; S ‰; ρ kg m^{-3})

$$\rho = \rho_0 + AS + BS^{3/2} + CS^2$$

where

$$A = 8.24493 \times 10^{-1} - 4.0899 \times 10^{-3}t + 7.6438 \times 10^{-5}t^2 \\ - 8.2467 \times 10^{-7}t^3 + 5.3875 \times 10^{-9}t^4$$

$$B = -5.72466 \times 10^{-3} + 1.0227 \times 10^{-4}t - 1.6546 \times 10^{-6}t^2$$

$$C = 4.8314 \times 10^{-4}$$

and ρ_0 is the density of water (Bigg, 1967).

$$\rho_0 = 999.842594 + 6.793952 \times 10^{-2}t - 9.095290 \times 10^{-3}t^2 + \\ 1.001685 \times 10^{-4}t^3 - 1.120083 \times 10^{-6}t^4 + 6.536336 \times 10^{-9}t^5$$

The standard error of the equation is $3.6 \times 10^{-3} \text{ kg m}^{-3}$. This equation will become the new 1 atm. equation of state of seawater suggested for use by the Joint Panel on Oceanographic Tables and Standards.

INTRODUCTION

At the meeting of the Joint Panel on Oceanographic Tables and Standards in Woods Hole, Massachusetts (UNESCO, 1978), the one atmosphere equation of state of Millero, Gonzalez and Ward (1976) was suggested for use as the basis of a new equation of state for replacement of the earlier equation of Knudsen et al. (1902). At the Panel meeting held in Paris, France, September 1978 (UNESCO, 1979), Poisson and Brunet presented some new measurements on the density of seawater (ρ) at one atmosphere and salinity, $S = 35$, that suggested the equation of state of Millero et al. (1976) may be in error at temperatures above 25°C. A comparison of the measured relative density results (ρ_0 is density of water) of Poisson and Brunet and the values calculated from the equation of Millero et al. (multiplied by 0.999974, the maximum density of Miami water - Millero and Emmet, 1976)

$$(\rho - \rho_0) = AS + BS^{3/2} + CS^2 \quad (1)$$

$$A = 8.25917 \times 10^{-4} - 4.4490 \times 10^{-6}t + 1.0485 \times 10^{-7}t^2 - 1.2580 \times 10^{-9}t^3 + 3.315 \times 10^{-12}t^4$$

$$B = -6.33761 \times 10^{-6} + 2.8441 \times 10^{-7}t - 1.6871 \times 10^{-8}t^2 + 2.83258 \times 10^{-10}t^3$$

$$C = 5.4705 \times 10^{-7} - 1.97975 \times 10^{-8}t + 1.6641 \times 10^{-9}t^2 - 3.1203 \times 10^{-11}t^3$$

$$(\sigma = 3.3 \times 10^{-6})$$

is given in Table I. Between 0 and 20°C the average differences are $\pm 2.1 \times 10^{-6}$; while the values above 25°C indicated that the equation of Millero et al. yields values of density that are $8.4 \pm 1.4 \times 10^{-6}$ too high.

The experimental measurements and the fit of the experimental measurement at $S = 35$ of Millero et al. (1976) to the equation

TABLE I. Comparisons of the measured densities of seawater (ρ) relative to pure water (ρ_0) of Poisson and Brunet and the equation of Millero et al. (1976) at S = 35

<u>Temp.</u>	$(\rho - \rho_0)10^3 \text{ g cm}^{-3}$		
	<u>Measured^a</u>	<u>Calculated^b</u>	<u>$\delta 10^6$</u>
0°C	(28.265)	28.265	(0)
1.169	28.133	28.127	6
1.176	28.128	28.126	2
1.195	28.124	28.124	0
2.373	27.988	27.991	-3
5.0	(27.717)	27.712	(5)
7.120	27.509	27.508	1
	27.509	27.508	1
10.0	(27.257)	27.253	(4)
10.423	27.219	27.219	0
10.498	27.218	27.213	5
15.0	(26.874)	26.873	(1)
15.682	26.829	26.828	1
	26.829	26.828	1
19.695	26.574	26.577	-3
19.715	26.574	26.576	-2
20.0	(26.557)	26.559	(-2)
24.235	26.329	26.336	-7
25.0	(26.294)	26.299	(-5)
25.360	26.276	26.283	-7
25.597	26.261	26.273	-12

TABLE I (Continued)

<u>Temp.</u>	<u>Measured^a</u>	<u>Calculated^b</u>	<u>$\delta 10^6$</u>
30.0	26.075	26.083	-8
	26.075	26.083	-8
	(26.074)	26.083	(-9)

a) Measurements of Poisson and Brunet using a hydrostatic balance.

The values in parenthesis have been calculated from the equation (3b)

$$(\rho - \rho_0)10^3 = 28.265 - .119231t + 1.99189 \times 10^{-3}t^2 - 1.5065 \times 10^{-5}t^3 \quad (\sigma = 2.7 \times 10^{-6} \text{ g cm}^{-3}).$$

b) Calculated from the equation of state of Millero et al. (1976).

$$(\rho - \rho_o)10^3 = 28.2657 - 1.234052 \times 10^{-1}t + 2.480943 \times 10^{-3}t^2 - 3.400130 \times 10^{-5}t^3 + 2.452071 \times 10^{-7}t^4 \quad (2)$$

$$(\sigma = 1.8 \times 10^{-6})$$

supported the contention of Poisson and Brunet (see Table II). At 5 to 35°C the equation of Millero et al. (1976) yields densities that are too high compared to the actual experimental measurements. Although the differences are within $2\sigma = 6 \times 10^{-6}$ at most temperatures, the overall equation does not represent the "best" fit at $S = 35$. Since standard seawater ($S = 35$) may become a density standard, the cause of these differences needed to be examined.

Poisson and Brunet also presented relative measurements of standard seawater diluted with water and evaporated. They fitted their results to the equation

$$10^3(\rho - \rho_o) = S\{1/35[h(t)] + (S - 35)g(t,S)\} \quad (3a)$$

where

$$h(t) = 28.265 - 0.119231t + 1.99189 \times 10^{-3}t^2 - 1.5065 \times 10^{-5}t^3 \quad (3b)$$

$$(\sigma = 2.7 \times 10^{-6})$$

$$g(t,S) = -0.3057 \times 10^{-3} + 0.2054 \times 10^{-4}S + 0.1440 \times 10^{-4}t - 0.5073 \times 10^{-6}S^2 - 0.1966 \times 10^{-6}St - 0.3710 \times 10^{-6}t^2 + 0.4706 \times 10^{-8}S^3 + 0.3111 \times 10^{-8}S^2t + 0.1253 \times 10^{-9}St^2 + 0.5209 \times 10^{-8}t^3 \quad (3c)$$

$$(\sigma = 3.2 \times 10^{-6})$$

TABLE II. Comparisons of the measured and curve fitted values of $(\rho - \rho_0)$ at S=35 of Millero et al. (1976) and the 1 atm. equation of state

Temp.	$10^3(\rho - \rho_0)$		$\delta 10^6$			
	Exp ^a	Fit ^b	Old Eq ^c	New Eq ^d	Exp ^e	Fit ^e
0°C	28.265	28.266	28.265	28.265	0(0)	1(1)
5	27.707	27.707	27.712	27.711	-5 (-4)	-5(-4)
10	27.250	27.248	27.253	27.253	-3(-3)	-5(-5)
15	26.866	26.870	26.873	26.874	-7(-8)	-3(-4)
20	26.557	26.557	26.559	26.560	-2(-3)	-2(-3)
25	26.295	26.296	26.299	26.299	-4(-4)	-3(-3)
30	26.076	26.077	26.083	26.082	-7(-6)	-6(-5)
35	25.894	25.896	25.903	25.901	-9(-7)	-7(-5)
40	25.751	25.751	25.752	25.753	-1(-2)	-1(-2)

a) Magnetic float densities adjusted to S = 35 and converted to g cm⁻³

b) From eq 2 (fit of experimental values of $\rho - \rho_0$).

c) From eq 1 (Millero et al, 1976)

d) New fit of original data of Millero et al (1976) using a non-weighted least squares program.

e) $\delta = \rho(\text{meas. or fit}) - \rho(\text{Eq})$, the values in parenthesis use the new non-weighted fit of the original data.

A comparison of the values of $(\rho - \rho_0)$ calculated from equation (3) of Poisson and Brunet and equation (1) of Millero et al. is given in Table III. The differences at various salinities at a given temperature are similar to those found at $S = 35$. If the differences are normalized to give no error at $S = 35$ (which in affect is making the $h(t)$ term the same as evaluated from eq (1) at $S = 35$), the density differences between the two studies are within $\pm 7 \times 10^{-6} \text{ g cm}^3$ (See Table III). These results indicate that the salinity dependence of density found in the two studies is in excellent agreement.

In order to be sure that some of the differences shown in Table III are not due to the equations used in the two studies, the results of Poisson and Brunet have been fitted to equation (1). The coefficients are given by ($\sigma = 3.33 \times 10^{-6} \text{ g cm}^{-3}$).

$$A = 8.243858 \times 10^{-4} - 0.39703 \times 10^{-5} t + 0.64285 \times 10^{-7} t^2 - 0.4126 \times 10^{-9} t^3 \quad (4a)$$

$$B = -0.5750416 \times 10^{-5} + 0.97209 \times 10^{-7} t - 0.1388477 \times 10^{-8} t^2 \quad (4b)$$

$$C = 0.49002 \times 10^{-6} \quad (4c)$$

The differences between the densities of Poisson and Brunet and Millero et al. using the same equation are shown in Table IV. The results are quite similar to those given in Table III. The two studies agree to within $\pm 5.0 \times 10^{-6} \text{ g cm}^{-3}$ except at higher temperatures and salinities. These differences are related to the differences in density at various temperatures for seawater with $S = 35$. If the two studies are normalized

TABLE III. Comparisons of the density measurements of Poisson and Brunet and Millero et al. (1976)^a

$$\Delta\rho 10^6, \text{ g cm}^{-3}$$

<u>S(°/oo)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>
5	-2	-1	0	-1	-2	-5	-8
10	-1	0	0	-1	-1	-3	-6
15	-2	-1	-2	-1	-1	-2	-9
20	-1	-2	-1	-1	0	-1	-7
25	0	0	-1	0	0	0	-6
30	2	3	2	1	1	-2	-6
35	0	5	4	1	-2	-5	-9
40	-5	6	5	0	-6	-10	-11

(overall average deviation is $\pm 2.77 \times 10^{-6}$)

$$\text{Normalized } \Delta\rho 10^6, \text{ g cm}^{-3}$$

<u>S°/oo</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>
5	-2	-6	-4	-2	0	0	1
10	-1	-5	-4	-2	1	2	3
15	-2	-6	-6	-2	1	3	0
20	-1	-7	-5	-2	2	4	2
25	0	-5	-5	-1	2	5	3
30	2	-2	-2	0	3	3	3
35	0	0	0	0	0	0	0
40	-5	1	1	-1	4	-5	-2

a) $\Delta\rho = \rho(\text{Poisson and Brunet}) - \rho(\text{Millero et al.})$

TABLE IV. Comparisons of the densities of Poisson and Brunet and Millero et al. using the same equation^a

$\Delta\rho 10^6, \text{ g cm}^{-3}$							
<u>S^o/oo</u>	<u>0^oC</u>	<u>5^oC</u>	<u>10^oC</u>	<u>15^oC</u>	<u>20^oC</u>	<u>25^oC</u>	<u>30^oC</u>
5	-2	-1	0	-2	-4	-5	-6
10	-2	0	0	-2	-3	-5	-7
15	-2	1	0	-1	-2	-3	-7
20	-1	1	1	0	-1	-2	-5
25	-1	2	1	0	-1	-2	-5
30	0	3	2	0	-1	-3	-6
35	-2	4	4	0	-3	-6	-9
40	-4	6	5	-1	-7	-10	-12

(overall average deviation is $\pm 3.1 \times 10^{-6}$)

Normalized $\Delta\rho 10^6, \text{ g cm}^{-3}$							
<u>S^o/oo</u>	<u>0^oC</u>	<u>5^oC</u>	<u>10^oC</u>	<u>15^oC</u>	<u>20^oC</u>	<u>25^oC</u>	<u>30^oC</u>
5	0	-5	-4	-2	-1	1	3
10	0	-4	-4	-2	0	1	2
15	0	-3	-4	-1	1	3	2
20	1	-3	-3	0	2	4	4
25	1	-2	-3	0	2	4	4
30	2	-1	-2	0	2	3	3
35	0	0	0	0	0	0	0
40	-2	2	1	-1	-4	-4	-3

a) $\Delta\rho = \rho(\text{Poisson and Brunet}) - \rho(\text{Millero et al.})$

to the same density for $S = 35$ seawater, the maximum differences over the entire temperature and salinity range are within $\pm 5 \times 10^{-6} \text{ g cm}^{-3}$.

The Panel recommended that Millero and Poisson look into the differences in density at $S = 35^{\circ}/\text{oo}$ and use the data of Millero et al. and Poisson et al. to generate a new one atmosphere equation of state for seawater.

This data report summarizes our work in generating a new one atmosphere equation of state for seawater.

Density of $35^{\circ}/\text{oo}$ Salinity Seawater as a Function of Temperature

The summary of all the relative density ($\rho - \rho_0$) measurements at $S = 35^{\circ}/\text{oo}$ of Poisson et al. and Millero et al. are given in Table V. The temperature of earlier measurements of Poisson and Brunet have been corrected after a recalibration of the platinum resistance thermometer. These results are combined with the recent results of Poisson, Brunet and Brun-Cottan (1980). The experimental measurements of Millero et al. (1976) have been corrected to a salinity of $35^{\circ}/\text{oo}$. The data set consist of 19 points from 0 to 40°C from Millero et al. and 20 points from 1.1 to 30°C from Poisson et al. These relative densities were fitted to the equation

$$\begin{aligned} (\rho - \rho_0)10^3 &= 28.264_9 - 1.22473 \times 10^{-1}t + 2.38304 \times 10^{-3}t^2 \\ &- 3.0775 \times 10^{-5}t^3 + 2.11504 \times 10^{-7}t^4 \end{aligned} \tag{5}$$

with a $\sigma = 2.6 \times 10^{-6} \text{ g cm}^{-3}$. A comparison of the measured and calculated values of $\rho - \rho_0$ are shown in Table V. The deviations shown in Figure 1 are reasonably random. The differences between the densities of the equation of Millero et al. and the new equation are given as a dotted line in

TABLE V. The relative densities (g cm^{-3}) of seawater at $S = 35^{\circ}/\text{oo}$
and various temperatures

<u>Temp.</u>	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$		<u>$\Delta 10^6$</u>	<u>Author</u>
	<u>Measured</u>	<u>Calculated^a</u>		
0.000°C	28.266	28.265	1	Millero et al.
	28.263		-2	
	28.264		-1	
	28.264		-1	
	28.267		2	
	28.267		2	
	28.265		0	
	28.267		2	
	28.264		-1	
5.000	27.707	27.708	-1	
10.000	27.250	27.250	0	
15.000	26.866	26.871	-5	
20.000	26.557	26.556	1	
	26.557		1	
25.000	26.295	26.294	1	
	26.299		5	
30.000	26.076	26.076	0	
35.000	25.894	25.895	-1	
40.000	25.751	25.751	0	
1.163	28.124	28.126	-2	Poisson et al.
2.340	27.987	27.991	-4	
5.215	27.690	27.687	3	

TABLE V (Continued)

<u>Temp.</u>	<u>Measured</u>	<u>Calculated</u>	<u>$\Delta 10^6$</u>	<u>Author</u>
5.220	27.688	27.686	2	Poisson et al.
7.100	27.505	27.505	0	
10.412	27.217	27.216	1	
10.478	27.217	27.210	7	
15.681	26.828	26.824	4	
19.697	26.576	26.574	2	
19.717	26.576	26.573	3	
20.725	26.511	26.515	-4	
20.759	26.511	26.513	-2	
20.932	26.504	26.504	0	
24.239	26.330	26.331	-1	
25.368	26.279	26.277	2	
25.423	26.274	26.274	0	
25.435	26.268	26.274	-6	
25.577	26.262	26.267	-5	
30.006	26.079	26.076	3	
30.067	26.075	26.073	2	

a) The calculated values were determined from equation 5. The measured values of Millero et al. from 5 to 40°C were weighted by a factor of three due to the higher precision of the magnetic float density measurements. To obtain the statistically best equation (i.e., using an F-test), we found it necessary to use a five parameter temperature polynomial.

FIGURE 1

● Millero et al. (1976)
○ Poisson et al. (1980)

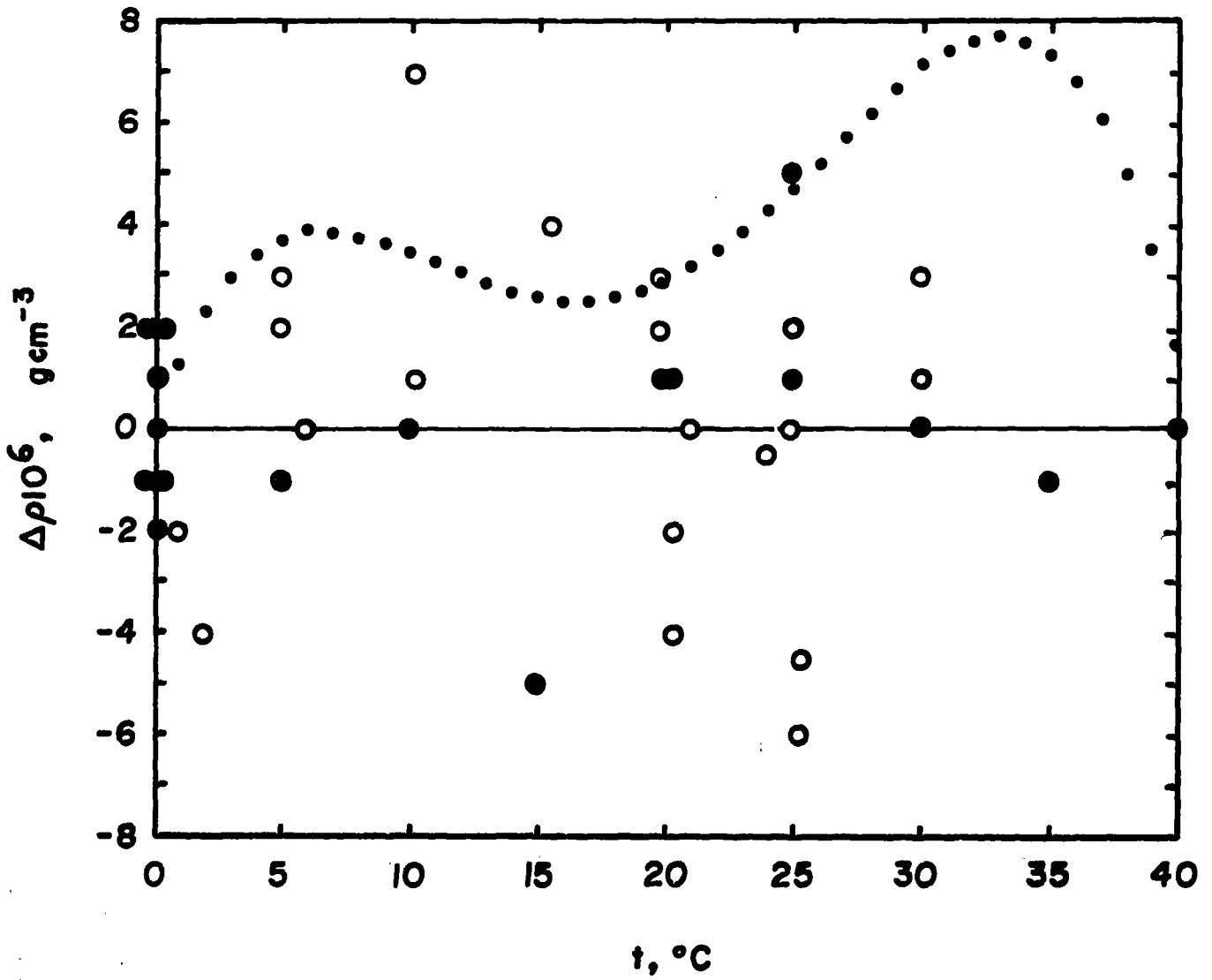


Figure 1. Except for the temperature range between 26 to 38°C the differences are within $5 \times 10^{-6} \text{ g cm}^{-3}$ (the maximum difference is 7.7×10^{-6}). The densities at $S = 35$ calculated from the equation of Millero et al. (1976) are higher than the new equation over the entire temperature range. This is similar to the results shown in Table II. These results indicate that the overall equation of Millero et al. (1976) does not give the "best" fit for seawaters of $S = 35^{\circ}/\text{oo}$ because of either fitting errors or a shift in salinity due to evaporation (especially at $S = 40^{\circ}/\text{oo}$).

Data Set Used to Determine a New Equation of State

The relative density ($\rho - \rho_0$) data used to determine the new 1 atm. equation of state of seawater were taken from the work of Millero et al. (1976) and Poisson et al. (1980). The data consist of 122 points from 0 to 40°C from Millero et al. and 345 points from Poisson et al. from 0 to 30°C.

The various salinity and temperature ranges covered are given in Table VI. About 33% of the data of Millero et al. and about 60% of the data of Poisson et al. are in the oceanographic range of salinity (30 to 42^o/oo). The data of Poisson et al. at most salinities represent two to three duplicate measurements on the same sample; while the measurements of Millero et al. are the averages of at least two duplicate measurements.

Before the two data sets can be combined, it is necessary to make some adjustments and normalizations. Since the measurements of Poisson et al. were made relative to a seawater of 35^o/oo salinity, this can easily be done using the values at a given temperature calculated from equation 5. For the relative densities below a salinity of 35^o/oo, this was done by using the equation (at each temperature)

TABLE VI. Summary of the one atmosphere data set used to derive the UNESCO Equation of State for Seawater

Data of Poisson et al. (1980)

<u>Temp</u>	<u>Salinity (°/oo)</u>										
	<u>5</u>	<u>10</u>	<u>15</u>	<u>20</u>	<u>25</u>	<u>30</u>	<u>35</u>	<u>38</u>	<u>40</u>	<u>42</u>	<u>Sum</u>
0.03°C	-	-	-	-	-	-	4	4	4	4	16
0.3	4	4	3	4	4	5	5	-	-	-	29
2	-	-	-	-	-	-	2	2	2	2	8
5	4	3	4	3	2	2	4	7	5	5	39
10	4	4	4	4	2	4	8	5	5	4	44
15	6	6	6	5	5	4	12	4	4	4	56
20	4	4	4	4	4	4	12	7	5	6	54
25	4	4	4	4	4	4	15	9	7	3	58
30	<u>1</u>	<u>4</u>	<u>4</u>	<u>4</u>	<u>4</u>	<u>4</u>	<u>8</u>	<u>4</u>	<u>4</u>	<u>4</u>	<u>41</u>
Sum	27	29	29	28	25	27	70	42	36	32	345

Data of Millero et al. (1976)

<u>Temp</u>	<u>Salinity (°/oo)</u>									
	<u>0.1-5</u>	<u>5-10</u>	<u>10-15</u>	<u>15-20</u>	<u>20-30</u>	<u>30</u>	<u>35</u>	<u>38</u>	<u>40</u>	<u>Sum</u>
0°C	5	4	2	1	3	2	9	1	2	29
5	5	2	1	-	2	1	1	-	1	13
10	4	2	-	1	1	1	1	-	1	11
15	2	2	1	-	2	1	1	-	1	10
20	2	2	-	-	2	1	2	-	1	10
25	4	3	2	1	3	2	2	1	2	20
30	2	1	-	1	2	-	1	-	1	8
35	4	2	2	-	2	-	1	-	1	12
40	<u>2</u>	<u>2</u>	<u>1</u>	<u>-</u>	<u>2</u>	<u>-</u>	<u>1</u>	<u>-</u>	<u>1</u>	<u>9</u>
Sum	30	20	9	4	19	8	19	2	11	122

$$(\rho - \rho_o)_{S,t}^{\text{Adj}} = (\rho - \rho_o)_{S,t}^{\text{Old}} \times \frac{(\rho - \rho_o)_{35,t}^{\text{new}}}{(\rho - \rho_o)_{35,t}^{\text{old}}} \quad (6)$$

For the samples with salinity above 35^o/oo, the salinities have been redetermined using smoothed equations of $(\rho - \rho_o)$ as a function of S. The values of $(\rho - \rho_o)10^3$ corrected in this manner are given in Table VII.

Before the data of Millero et al. (1976) could be used, it was necessary to determine the cause of the generated equation not giving the "best" temperature fit for S = 35^o/oo. Since Millero et al. (1976) used a weighting method to fit their data, we first examined the fitting procedure. The generalized least squares program used in fitting the high pressure PVT data of seawater was used to refit the data. The differences in the new and the old fit of the same data using the same number of parameters are given in Table VIII. As is quite apparent from this table the differences are all well within the standard error of the fit ($3.3 \times 10^{-6} \text{ g cm}^{-3}$).

The largest source of error in the measurements of Millero et al. (1976) is in the determination of salinity. All of the magnetic float measurements were made on weight diluted or evaporated standard seawater. The salinities for the hydrostatic density measurements were determined on a salinity bridge that had a large off set and required a calibration with samples of known salinity (by weight dilution and evaporation).

Since the initial magnetic float experiments from 0 to 25°C for the samples of S = 30, 35 and 40^o/oo were made in a closed cell, the salinity of the samples could not change during an experiment. It is, thus, possible to examine the internal consistency of these experiments by examining the salinity dependence at a given temperature. If the den-

Table VII
Normalized data used to determine UNESCO Equation of State
Poisson et al. (1980)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{ g cm}^{-3}$	δ^a	δ^b
0.029	35.099	28.340	0	0
0.029	35.099	28.336	-4	-4
0.029	37.842	30.555	-1	-1
0.029	37.842	30.555	-1	-1
0.029	39.715	32.070	0	0
0.029	39.715	32.070	0	0
0.029	41.791	33.746	-4	-3
0.029	41.791	33.747	-3	-2
0.030	34.760	28.068	2	2
0.030	34.760	28.066	0	0
0.030	38.227	30.865	-2	-2
0.030	38.227	30.867	0	0
0.030	39.878	32.201	-1	-1
0.030	39.878	32.199	-3	-3
0.030	41.674	33.650	-5	-5
0.030	41.674	33.653	-2	-2
0.272	5.006	4.068	-2	-2
0.271	5.006	4.069	-1	-1
0.271	5.019	4.083	3	2
0.271	5.019	4.084	4	3
0.271	10.032	8.126	-2	-2
0.271	10.032	8.136	8	8

Table VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{ g cm}^{-3}$	δ^a	δ^b
0.271	10.041	8.132	-3	-3
0.272	10.041	8.139	5	4
0.271	14.976	12.112	3	3
0.272	14.976	12.108	-1	-1
0.271	14.999	12.128	1	0
0.271	19.994	16.142	-3	-5
0.271	19.994	16.141	-4	-6
0.271	20.011	16.155	-4	-5
0.272	20.011	16.152	-7	-8
0.271	24.967	20.147	0	-1
0.272	24.967	20.153	7	5
0.271	24.968	20.156	8	7
0.271	24.968	20.148	1	-1
0.271	29.981	24.186	2	1
0.271	29.981	24.188	4	3
0.271	29.981	24.188	4	3
0.272	29.991	24.194	2	1
0.271	29.991	24.195	3	2
0.271	35.000	28.231	1	0
0.272	35.000	28.229	-1	-2
0.271	35.000	28.233	3	2
0.271	35.000	28.233	3	2
0.271	35.000	28.235	5	4
1.780	34.807	27.900	2	1

Table VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
1.780	37.784	30.292	5	4
1.780	40.034	32.093	-1	-2
1.780	41.863	33.559	-6	-6
1.783	34.796	27.893	4	3
1.783	37.772	30.279	2	1
1.783	40.021	32.080	-4	-4
1.783	41.849	33.550	-3	-3
4.998	36.589	28.970	1	1
4.998	36.589	28.971	2	2
4.998	37.901	30.010	-1	-1
4.998	37.901	30.013	2	2
4.998	39.694	31.438	3	3
4.998	39.694	31.438	3	3
4.998	41.579	32.934	1	1
4.998	41.579	32.934	1	1
5.001	37.986	30.076	-2	-2
5.001	37.986	30.082	4	4
5.001	37.986	30.080	2	2
5.001	39.927	31.619	-1	-1
5.001	39.927	31.622	2	2
5.001	39.927	31.621	1	1
5.001	42.082	33.334	1	1
5.001	42.082	33.334	1	1
5.001	42.082	33.337	4	4

Table VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{ g cm}^{-3}$	δ^a	δ^b
5.055	5.040	4.017	3	4
5.055	5.040	4.017	3	4
5.035	5.051	4.013	-9	-9
5.054	5.051	4.024	2	2
5.054	10.020	7.948	-6	-7
5.055	10.047	7.974	-2	-2
5.055	10.047	7.976	0	0
5.035	14.548	11.525	-7	-8
5.054	14.548	11.523	-9	-9
5.055	14.994	11.884	0	0
5.055	14.994	11.884	0	0
5.054	20.002	15.831	-7	-8
5.055	20.013	15.841	-7	-6
5.055	20.013	15.846	-1	-1
5.035	24.863	19.683	3	2
5.054	24.863	19.680	1	1
5.035	29.904	23.664	-3	-4
5.054	29.904	23.661	-5	-5
5.035	35.000	27.706	1	1
5.054	35.000	27.697	-6	-6
5.055	35.000	27.700	-3	-3
5.055	35.000	27.701	-2	-2
10.018	34.863	27.144	2	2
10.018	34.866	27.145	1	1

Table VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{ g cm}^{-3}$	δ^a	δ^b
10.018	37.992	29.585	-2	-2
10.018	37.992	29.591	4	4
10.018	39.916	31.094	1	1
10.018	39.916	31.098	5	5
10.018	41.779	32.550	-2	-2
10.018	41.779	32.551	-1	-1
10.042	34.648	26.972	0	0
10.042	34.648	26.973	1	1
10.042	37.947	29.543	-7	-7
10.042	37.947	29.557	7	7
10.042	37.947	29.550	0	0
10.042	40.203	31.316	1	1
10.042	40.203	31.319	4	4
10.042	40.203	31.317	2	2
10.042	41.861	32.617	3	3
10.042	41.861	32.612	-2	-2
10.186	5.023	3.922	-3	-3
10.186	5.023	3.918	-7	-7
10.186	10.022	7.810	-1	-1
10.136	10.022	7.804	-7	-7
10.186	14.983	11.663	1	0
10.186	14.983	11.662	0	-1
10.186	20.019	15.574	2	1
10.186	20.019	15.572	0	-1

Table VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
10.186	29.993	23.328	-2	-2
10.186	29.993	23.328	-2	-2
10.186	35.000	27.236	1	1
10.186	35.000	27.233	-2	-2
10.189	5.050	3.951	4	5
10.189	5.050	3.949	2	3
10.189	10.040	7.824	-1	-1
10.189	10.040	7.821	-4	-4
10.189	14.995	11.673	1	1
10.189	14.995	11.671	-1	-1
10.189	20.019	15.569	-3	-4
10.189	20.019	15.569	-3	-4
10.189	24.975	19.424	0	0
10.189	24.975	19.422	-2	-2
10.189	29.986	23.325	1	0
10.189	29.986	23.322	-2	-3
10.189	35.000	27.233	-1	-2
10.189	35.000	27.231	-3	-4
15.034	5.028	3.877	5	6
15.035	5.028	3.872	0	0
15.035	5.029	3.876	4	4
15.035	5.029	3.877	5	5
15.035	10.034	7.707	1	1
15.035	10.034	7.705	-3	-3

Table VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
15.034	10.234	7.864	3	3
15.035	10.34	7.868	7	7
15.035	14.979	11.491	-2	-3
15.035	14.979	11.492	-1	-2
15.034	15.014	11.523	3	2
15.035	15.014	11.526	6	5
15.035	20.018	15.356	3	2
15.034	20.021	15.347	-9	-9
15.035	20.021	15.344	-12	-12
15.035	24.957	19.150	8	7
15.035	24.979	19.162	3	2
15.035	24.979	19.158	-1	-2
15.035	29.964	22.984	-6	-6
15.035	29.964	22.987	-3	-3
15.034	29.971	22.999	4	3
15.035	29.971	22.992	-3	-4
15.034	35.000	26.872	3	3
15.035	35.000	26.866	-3	-3
15.035	35.000	26.867	-2	-2
15.035	35.000	26.867	-2	-2
15.034	35.133	26.974	3	3
15.034	35.133	26.971	0	0
15.034	37.950	29.148	3	3
15.034	37.950	29.147	2	2

Table VII (continued)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
15.034	40.147	30.841	-2	-2
15.034	40.147	30.842	-1	-1
15.034	41.848	32.157	-2	-2
15.034	41.848	32.158	-1	-1
15.143	35.011	26.871	1	1
15.143	35.011	26.870	0	0
15.143	37.581	28.852	0	0
15.143	39.943	30.674	-3	-3
15.143	43.076	33.104	3	4
15.185	34.747	26.666	3	3
15.185	34.747	26.661	-2	-2
15.185	37.950	29.135	1	1
15.185	39.855	30.606	0	0
15.185	42.076	32.321	-3	-2
15.307	5.006	3.854	3	2
15.306	5.006	3.853	2	1
15.307	9.999	7.678	4	3
15.306	9.999	7.675	0	0
15.307	14.981	11.487	0	0
15.306	14.981	11.487	0	0
15.307	20.031	15.360	8	7
15.306	20.031	15.353	1	0
15.307	24.921	19.105	4	4
15.306	24.921	19.104	3	3

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
15.307	35.000	26.849	2	-1
15.306	35.000	26.852	-1	2
20.002	5.008	3.810	3	3
20.002	5.008	3.812	5	5
20.002	5.031	3.827	3	2
20.002	5.031	3.830	6	5
20.002	10.048	7.616	-5	-7
20.002	10.048	7.622	1	-1
20.002	10.058	7.629	0	-1
20.002	10.058	7.630	1	0
20.002	14.995	11.363	-1	-3
20.002	14.995	11.366	2	0
20.002	15.561	11.787	-6	-7
20.002	15.561	11.795	2	1
20.002	20.004	15.153	-4	-6
20.002	20.004	15.157	0	-2
20.002	20.017	15.167	0	-1
20.002	20.017	15.168	1	0
20.002	24.961	18.920	3	2
20.002	24.961	18.920	3	2
20.002	24.965	18.922	2	1
20.002	24.965	18.925	5	4
20.002	29.973	22.723	-3	-4
20.002	29.973	22.724	-2	-3

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
20.002	29.973	22.726	0	-1
20.002	29.973	22.725	-1	-2
20.002	35.000	26.555	-1	-2
20.002	35.000	26.555	-1	-2
20.002	35.000	26.559	3	2
20.002	35.000	26.555	-1	-2
20.060	34.704	26.328	1	1
20.060	34.704	26.325	-2	-2
20.060	37.867	28.743	1	1
20.060	37.867	28.745	3	3
20.060	40.154	30.489	-2	-1
20.060	40.154	30.488	-3	-2
20.060	41.959	31.871	-2	-1
20.060	41.959	31.874	1	2
20.065	34.718	26.336	-2	-2
20.065	34.718	26.342	4	4
20.065	34.750	26.363	1	1
20.065	34.750	26.360	-2	-2
20.065	36.543	27.730	0	0
20.065	37.981	28.826	-3	-3
20.065	38.009	28.847	-3	-3
20.065	40.096	30.448	2	3
20.065	41.944	31.860	-1	0
20.065	42.584	32.351	0	1

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
20.076	34.987	26.543	1	1
20.076	34.987	26.544	2	2
20.076	37.970	28.819	-1	0
20.076	37.970	28.819	-1	0
20.076	40.143	30.480	-1	-1
20.076	40.143	30.479	-2	-2
20.076	41.797	31.746	-2	0
20.076	41.797	31.748	0	2
24.889	34.171	25.669	-4	-5
24.889	34.171	25.671	-2	-3
24.889	39.675	29.843	4	4
24.905	35.001	26.296	-3	-4
24.905	35.001	26.298	-1	-2
24.905	37.465	28.165	1	1
24.905	40.093	30.156	0	1
24.905	42.028	31.626	2	3
24.910	34.925	26.242	0	-1
24.910	34.925	26.243	1	0
24.910	36.986	27.797	-4	-4
24.910	37.882	28.484	5	4
24.910	39.166	29.451	-1	-1
25.009	5.012	3.766	-3	-4
25.009	5.012	3.766	-3	-4
25.009	5.016	3.775	-3	2

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
25.009	5.016	3.771	-1	-2
25.009	10.042	7.540	3	1
25.009	10.042	7.538	1	-1
25.009	10.045	7.537	-2	-4
25.009	10.045	7.537	-2	-4
25.009	14.995	11.245	-2	-4
25.009	14.995	11.247	0	-2
25.009	15.011	11.256	-3	-5
25.009	15.011	11.255	-4	-6
25.009	20.004	15.006	4	1
25.009	20.004	15.002	0	-3
25.009	20.007	15.004	-1	-3
25.009	20.007	15.008	3	1
25.009	24.953	18.729	10	7
25.009	24.953	18.728	9	6
25.009	24.964	18.731	4	1
25.009	24.964	18.730	3	0
25.009	29.969	22.490	-5	-8
25.009	29.969	22.496	1	-2
25.009	29.996	22.513	-3	-5
25.009	29.996	22.509	-7	-9
25.009	35.000	26.293	-1	-2
25.009	35.000	26.293	-1	-2
25.009	35.000	26.295	1	0

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
25.009	35.000	26.292	-2	-3
25.054	34.680	26.050	1	-1
25.054	34.680	26.052	3	1
25.054	34.680	26.046	-3	-5
25.054	37.931	28.514	5	5
25.054	37.931	28.509	0	0
25.054	37.931	28.508	-1	-1
25.054	39.798	29.928	4	5
25.054	39.798	29.921	-3	-2
25.054	39.798	29.920	-4	-3
25.059	35.196	26.438	-1	-2
25.059	35.196	26.438	-1	-2
25.059	37.761	28.381	-1	1
25.059	37.761	28.380	0	0
25.059	39.723	29.865	-2	-1
25.059	39.723	29.864	-3	-2
25.059	41.852	31.485	3	4
25.059	41.852	31.484	2	3
29.903	5.021	3.742	-1	-3
29.903	10.028	7.468	5	2
29.903	10.028	7.460	-3	-6
29.903	10.069	7.494	1	-2
29.903	10.069	7.488	-5	-8
29.903	14.989	11.154	6	2

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{ g cm}^{-3}$	δ^a	δ^b
29.903	14.989	11.146	-2	-6
29.903	14.998	11.157	2	-1
29.903	14.998	11.153	-2	-5
29.903	20.017	14.887	0	-4
29.903	20.017	14.884	-3	-7
29.903	20.018	14.883	-5	-9
29.903	20.018	14.886	-2	-6
29.903	24.955	18.563	-4	-7
29.903	24.955	18.565	-2	-5
29.903	24.968	18.582	6	2
29.903	24.968	18.578	2	-2
29.903	29.981	22.318	-3	-5
29.903	29.981	22.321	0	-2
29.903	29.983	22.323	0	-2
29.903	29.983	22.317	-6	-8
29.903	35.000	26.083	1	2
29.903	35.000	26.078	-4	-3
29.903	35.000	26.079	-3	-2
29.903	35.000	26.080	-2	-1
29.997	34.706	25.863	6	6
29.997	34.706	25.857	0	0
29.997	34.839	25.962	5	5
29.997	34.839	25.954	-3	-3
29.997	38.028	28.348	-4	-2

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{ g cm}^{-3}$	δ^a	δ^b
29.997	38.028	28.352	0	2
29.997	38.096	28.405	2	4
29.997	38.096	28.403	0	2
29.997	39.722	29.626	0	3
29.997	39.722	29.622	-4	-1
29.997	40.235	30.020	8	11
29.997	40.235	30.016	4	7
29.997	41.574	31.021	1	5
29.997	41.574	31.016	-4	0
29.997	41.980	31.327	1	5
29.997	41.980	31.326	0	4

a) $\delta = (\Delta\rho_{\text{meas.}} - \Delta\rho_{\text{calc.}}) 10^6$ where $\rho_{\text{calc.}}$ is from equation for individual data set (eq. 7 for Poisson et al. and eq. 8 for Millero et al.).

b) $\delta = (\Delta\rho_{\text{meas.}} - \Delta\rho_{\text{calc.}}) 10^6$ where $\rho_{\text{calc.}}$ is from final UNESCO equation (eq. 10).

TABLE VII (continued)

Millero et al. (1976)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
0.000	1.386	1.136	2	2
0.000	1.400	1.149	4	3
0.000	1.920	1.569	0	-1
0.000	3.338	2.726	4	3
0.000	3.429	2.796	0	-1
0.000	5.272	4.283	-7	-8
0.000	6.940	5.642	2	1
0.000	7.304	5.926	-8	-9
0.000	9.172	7.441	-3	-3
0.000	14.281	11.560	-5	-4
0.000	14.424	11.678	-2	-1
0.000	19.998	16.171	0	2
0.000	22.488	18.173	-2	-2
0.000	25.249	20.395	-5	-4
0.000	25.973	20.985	2	2
0.000	30.054	24.275	2	2
0.000	30.221	24.409	1	2
0.000	34.993	28.262	4	4
0.000	35.000	28.265	1	1
0.000	35.002	28.264	-1	-1
0.000	35.002	28.265	-1	0
0.000	35.002	28.268	2	3
0.000	35.002	28.268	2	3

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
0.000	35.012	28.274	0	1
0.000	35.013	28.274	0	0
0.000	35.013	28.276	2	2
0.000	37.675	30.422	-3	-3
0.000	40.017	32.314	-4	-4
0.000	40.447	32.668	2	2
5.000	0.611	0.490	0	0
5.000	1.154	0.926	2	2
5.000	2.255	1.802	0	0
5.000	3.546	2.828	0	-1
5.000	4.599	3.667	3	2
5.000	6.925	5.509	1	1
5.000	9.036	7.185	6	7
5.000	14.575	11.564	7	8
5.000	20.291	16.077	5	7
5.000	27.933	22.118	6	7
5.000	30.054	23.792	2	2
5.000	35.002	27.708	-2	-2
5.000	40.017	31.684	-6	-7
10.000	0.477	0.375	0	-1
10.000	1.039	0.816	0	-1
10.000	1.597	1.253	0	-1
10.000	3.673	2.871	-5	-5
10.000	6.569	5.135	3	4

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
10.000	8.637	6.736	-5	-4
10.000	17.775	13.834	-6	-4
10.000	20.696	16.108	-2	0
10.000	30.054	23.390	-2	-1
10.000	35.002	27.251	-1	-1
10.000	40.017	31.172	0	-2
15.000	0.448	0.348	1	1
15.000	2.045	1.582	3	3
15.000	6.368	4.898	-2	-2
15.000	8.865	6.813	-1	0
15.000	11.822	9.081	2	3
15.000	20.181	15.491	8	10
15.000	25.144	19.297	7	9
15.000	30.054	23.062	-1	0
15.000	35.002	26.867	-6	-6
15.000	40.017	30.743	0	-2
20.000	1.064	0.817	4	5
20.000	2.206	1.685	3	4
20.000	4.695	3.576	5	6
20.000	9.788	7.434	6	8
20.000	20.970	15.896	2	5
20.000	27.422	20.789	0	2
20.000	30.054	22.789	-1	0
20.000	35.002	26.558	0	0

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
20.000	35.006	26.561	0	0
20.000	40.017	30.389	2	0
25.000	1.306	0.989	3	3
25.000	1.425	1.078	2	2
25.000	3.017	2.275	1	2
25.000	3.024	2.277	-2	-1
25.000	5.194	3.908	0	1
25.000	6.613	4.970	-2	-1
25.000	8.124	6.098	-6	-5
25.000	13.963	10.478	1	2
25.000	14.408	10.805	-7	-5
25.000	19.632	14.722	-7	-4
25.000	22.107	16.585	-2	1
25.000	24.730	18.554	-3	-1
25.000	25.647	19.244	-3	0
25.000	29.772	22.350	-1	0
25.000	30.054	22.564	0	2
25.000	35.002	26.296	0	-1
25.000	35.137	26.403	4	4
25.000	36.953	27.771	0	-1
25.000	40.017	30.093	3	1
25.000	40.068	30.130	1	-1
30.000	1.064	0.799	-2	2
30.000	4.609	3.438	-2	0

TABLE VII (continued)

$t, ^\circ\text{C}$	$s(^{\circ}/\text{oo})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
30.000	9.752	7.260	-2	0
30.000	16.465	12.256	6	9
30.000	20.891	15.540	-3	1
30.000	27.427	20.416	2	4
30.000	35.006	26.080	-2	-2
30.000	40.054	29.872	3	0
35.000	1.579	1.177	3	3
35.000	3.185	2.367	3	4
35.000	3.680	2.733	3	4
35.000	4.659	3.457	3	5
35.000	6.359	4.709	0	2
35.000	8.550	6.327	1	3
35.000	10.908	8.068	2	5
35.000	14.857	10.984	4	8
35.000	20.591	15.220	5	9
35.000	25.942	19.175	1	4
35.000	35.004	25.897	-3	-4
35.000	40.033	29.652	5	1
40.000	1.445	1.071	2	2
40.000	2.909	2.147	-2	-1
40.000	5.916	4.356	-4	-2
40.000	9.885	7.269	-5	-2
40.000	14.960	11.000	2	6
40.000	21.825	16.044	4	8

TABLE VII (continued)

$t, ^\circ\text{C}$	$S(\text{‰})$	$(\rho - \rho_0)10^3, \text{g cm}^{-3}$	δ^a	δ^b
40.000	27.989	20.579	2	5
40.000	35.006	25.755	2	-2
40.000	40.033	29.481	2	-2

a) $\delta = (\Delta\rho_{\text{meas.}} - \Delta\rho_{\text{calc.}}) 10^6$ where $\rho_{\text{calc.}}$ is from equation for individual data set (eq. 7 for Poisson et al. and eq. 8 for Millero et al.).

b) $\delta = (\Delta\rho_{\text{meas.}} - \Delta\rho_{\text{calc.}}) 10^6$ where $\rho_{\text{calc.}}$ is from final UNESCO equation (eq. 10).

TABLE VIII. Differences between new and old fit of original Millero et al. density data

<u>s(°/∞)</u>	<u>$\Delta\rho 10^6, \text{ g cm}^{-3}$</u>								
	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
5	-3	-1	0	0	0	-1	-1	-1	0
10	-2	0	0	1	1	0	0	-1	1
15	-2	0	0	1	1	1	0	0	1
20	-1	0	0	1	1	2	0	1	2
25	0	0	0	1	1	1	1	1	2
30	1	0	0	1	1	1	1	0	2
35	0	-1	0	1	1	0	1	-1	1
40	0	-1	1	1	0	-1	3	-2	-1

sities below $S = 35$ are fitted to equation (1), it is possible to examine the densities of the samples of $S = 30$ and $40^{\circ}/\text{oo}$. When this is done the experimental values at $S = 30$ were found to agree with the calculated values to within $\pm 4 \times 10^{-6} \text{ g cm}^{-3}$. The salinities determined from the weight dilution equations from 0 to 25°C were equal to 30.051 ± 0.003 which agrees very well with the assigned value (30.054). A similar calculation using the equation of Poisson et al. (1980) gives densities that agree to $\pm 4 \times 10^{-6} \text{ g cm}^{-3}$ and a salinity equal to 30.055 ± 0.003 . These comparisons indicate that the weight dilution runs on $S = 35^{\circ}/\text{oo}$ seawater are internally consistent from 0 to 25°C .

A similar calculation at $S = 40^{\circ}/\text{oo}$ yields densities that are consistently lower than the experimental values. A value for the $S = 40.017 \pm 0.004$ is found by extrapolating our weight dilution runs which is considerably higher than the assigned value (40.004). If the equations of Poisson et al. are used a value of $S = 40.016 \pm 0.003$ is found. A similar analysis of the extrapolated weight dilution density runs at 30°C yielded a $S = 40.056 \pm 0.004$ for the sample with a reported salinity of 40.033. The equation of Poisson et al. gave a value of $S = 40.054$ at 30°C . Although the high salinity seawater used at 35 and 40°C was the same as the sample used at 30°C , the extrapolated weight dilutions are nearly the same as the assigned value ($S = 40.036 \pm 0.005$). This apparently is due to the sequence in which the sample was used (40° , 35° and 30°C) in the individual experiments. We, thus, used the assigned $S = 40.033$ at 35° and 40°C . These calculations indicate that the salinities of the $40^{\circ}/\text{oo}$ samples from 0 to 30°C are slightly higher than reported and caused the overall equation to give a poor fit at $S = 35^{\circ}/\text{oo}$. We will use the corrected salinities in further calculations.

In the hydrostatic experiments the evaporation effects were supposedly accounted for by making conductance experiments on the samples after the density was measured. A comparison of the measured densities with fits of the magnetic float measurements are in good agreement at 0° and 25°C except for the highest salinities (37 to 48⁰/oo). The measured values are $10 \times 10^{-6} \text{ g cm}^{-3}$ higher than expected. Since the differences are higher at 25° than 0°C, this is probably due to evaporation effects. Using the weight dilution extrapolations and the equation of Poisson et al., we determined $S = 40.452 \pm 0.002$ at 0°C compared to the assigned value of 40.447. At 25°C, for the higher salinity samples, we obtain $S = 40.068 \pm 0.002$ and $S = 36.953 \pm 0.002$ compared to the assigned values of 40.049 and 36.944. The salinity differences at 25° are higher than expected ($2\sigma = \pm 0.006^0/\text{oo}$) for conductance calibration. We have thus used the back calculated salinities at 25°C.

Since the measurements of Millero et al. (1976) were made relative to water at 4°C (i.e. specific gravities), it is necessary to multiply the measured values of $(\rho - \rho_3)$ by the absolute density of water at 4°C, $\rho_{\text{max}} = 0.999974 \text{ g cm}^{-3}$ (Millero and Emmet, 1976). An adjustment of the measured densities of Millero et al. to a given density for $S = 35$ is not necessary since the fit of the experimental values (eq. 2) agrees very well (within $\pm 1.6 \times 10^{-6} \text{ g cm}^{-3}$) with the assigned values (eq. 5). The corrected data set of Millero et al. (1976) are given in Table VII.

Before combining the various data sets we have examined them individually to have an idea of the precision of the individual data and differences between the two sets of data (using the equation of state of Millero et al., i.e. equation 1). As in the examinations made by Millero et al. (1976), we have determined a number of temperature forms for the terms

A, B, and C. The criterion for selecting the fewest number of temperature parameters was based on an "F" test analysis of the residuals (Freund, 1962). Since the $S = 35^{\circ}/\infty$ data required a five parameter temperature fit, the minimum terms required in the A parameter was also five (5A). This was necessary to insure the values of $\rho - \rho_0$ at $S = 35\%$ calculated from the overall equation agreed to $\pm 2 \times 10^{-6} \text{ g cm}^{-3}$ with the assigned values obtained from equation (5).

The summary of the fits of the data of Poisson et al. to equation (1) is given in Table IX. The fewest number of parameters statistically needed to fit the data was the 8(4A, 3B, 1C) equation with a $\sigma = 3.48 \times 10^{-6} \text{ g cm}^{-3}$. To obtain values of $\rho - \rho_0$ at $S = 35^{\circ}/\infty$ that agree to $\pm 2 \times 10^{-6}$ with those calculated from equation (5), the 9(5A, 3B, 1C) equation was needed. This is the equation we have selected as being the best representation of the measurements of Poisson et al. The coefficients for the A, B, and C terms are given below ($\sigma = 3.33 \times 10^{-6} \text{ g cm}^{-3}$)

$$A = 8.24501 \times 10^{-4} - 4.0639 \times 10^{-6}t + 7.5719 \times 10^{-8}t^2 - 8.8910 \times 10^{-10}t^3 + 6.616 \times 10^{-12}t^4 \quad (7a)$$

$$B = -5.7728 \times 10^{-6} + 9.7437 \times 10^{-8}t - 1.3747 \times 10^{-9}t^2 \quad (7b)$$

$$C = 4.9054 \times 10^{-7} \quad (7c)$$

A comparison of the measured and calculated values of $\rho - \rho_0$ is given in Table VII. These deviations shown in Figure 2 are random.

The summary of the fits of the data of Millero et al. to equation (1) is given in Table X. As with the data of Poisson et al., we have selected the 9(5A, 3B, 1C) equation as being the best representation of the measurements of Millero et al. The coefficients for the A, B, and C terms are

Table IX

Summary of the fits of the normalized data of Poisson et al.

to the equation $(\rho - \rho_0) = AS + BS^{3/2} + CS^2$

<u>Parameters</u>	<u>$\sigma 10^6, \text{ g cm}^{-3}$</u>
15(5A, 5B, 5C)	3.21
14(5A, 5B, 4C)	3.21
14(5A, 4B, 5C)	3.24
13(5A, 4B, 4C)	3.25
12(5A, 4B, 3C)	3.24
12(5A, 3B, 4C)	3.27
12(4A, 4B, 4C)	3.43
11(5A, 4B, 2C)	3.25
11(5A, 3B, 3C)	3.34
11(5A, 2B, 4C)	3.26
10(5A, 4B, 1C)	3.26
10(5A, 1B, 4C)	3.36
10(5A, 3B, 2C)	3.34
9(5A, 3B, 1C)	3.33
9(5A, 1B, 3C)	3.43
9(5A, 2B, 2C)	4.04
8(4A, 3B, 1C)	3.48
8(5A, 2B, 1C)	4.05
8(4A, 2B, 2C)	4.15
8(5A, 3B, 0C)	11.10
7(4A, 3B, 0C)	11.06
6(4A, 2B, 0C)	11.76

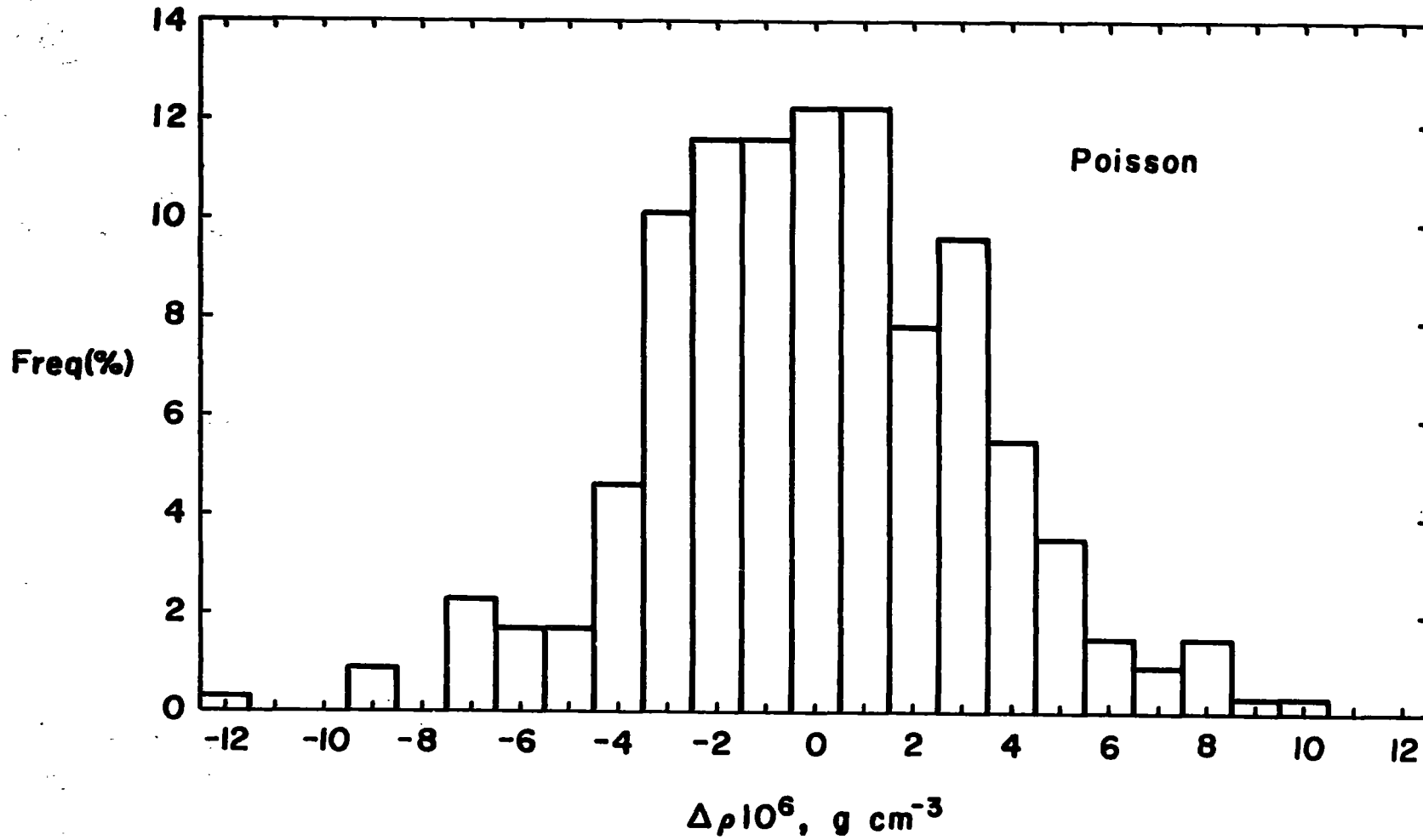


FIGURE 2

Table X

Summary of the fits of the normalized data of Millero et al.

to the equation $(\rho - \rho_0) = AS + BS^{3/2} + CS^2$

<u>Parameters</u>	<u>$\sigma 10^6, \text{ g cm}^{-3}$</u>
15(5A, 5B, 5C)	3.22
14(5A, 5B, 4C)	3.21
14(5A, 4B, 5C)	3.21
13(5A, 4B, 4C)	3.34
12(5A, 4B, 3C)	3.38
12(5A, 3B, 4C)	3.36
12(4A, 4B, 4C)	3.80
11(5a, 4B, 2C)	3.45
11(5A, 3B, 3C)	3.48
11(5A, 2B, 4C)	3.35
10(5A, 4B, 1C)	3.43
10(5A, 1B, 4C)	3.50
10(5A, 3B, 2C)	3.55
9(5A, 3B, 1C)	3.50
9(5A, 1B, 3C)	3.65
9(5A, 2B, 2C)	5.88
8(4A, 3B, 1C)	3.95
8(5A, 3B, 0C)	10.95
8(5A, 2B, 1C)	5.86
8(4A, 2B, 2C)	6.12

given below ($\sigma = 3.50 \times 10^{-6} \text{ g cm}^{-3}$).

$$A = 8.23997 \times 10^{-4} - 4.0644 \times 10^{-6} t + 7.6455 \times 10^{-8} t^2 - 8.3332 \times 10^{-10} t^3 + 5.496 \times 10^{-12} t^4 \quad (8a)$$

$$B = -5.5078 \times 10^{-6} + 9.7598 \times 10^{-8} t - 1.6218 \times 10^{-9} t^2 \quad (8b)$$

$$C = 4.6106 \times 10^{-7} \quad (8c)$$

A comparison of the measured and calculated values of $\rho - \rho_0$ is given in Table VII. These deviations shown in Figure 3 are random.

A comparison of the densities of Millero et al. and Poisson et al. determined from the smoothed equations 7 and 8 is given in Table XI and Figure 4. Over most of the temperature and salinity range the differences are within $\pm 5 \times 10 \text{ g cm}^{-3}$. The maximum difference is $7.8 \times 10^{-6} \text{ g cm}^{-3}$ between 15 to 20^o/oo salinity and 30°C. These differences are larger than expected and were examined further by comparing an equation generated from the data of Millero et al. excluding the 35 and 40°C data. The coefficients found for this data are given below ($\sigma = 3.4 \times 10^{-6} \text{ g cm}^{-3}$)

$$A = 8.23725 \times 10^{-4} - 3.9986 \times 10^{-6} t + 7.4386 \times 10^{-8} t^2 - 8.8622 \times 10^{-10} t^3 + 6.421 \times 10^{-12} t^4 \quad (9a)$$

$$B = -5.42528 \times 10^{-6} + 8.5107 \times 10^{-8} t - 1.08996 \times 10^{-9} t^2 \quad (9b)$$

$$C = 4.5502 \times 10^{-7} \quad (9c)$$

A comparison of the smoothed densities of Millero et al. (eq. 9) and Poisson et al. (eq. 7) using only the 0 to 30°C is given in Table XI, b, and shown in Figure 5. These comparisons demonstrate that the 0 to 30°C data of Millero et al. and Poisson et al. are internally consistent to

- 65 -

Freq (%)

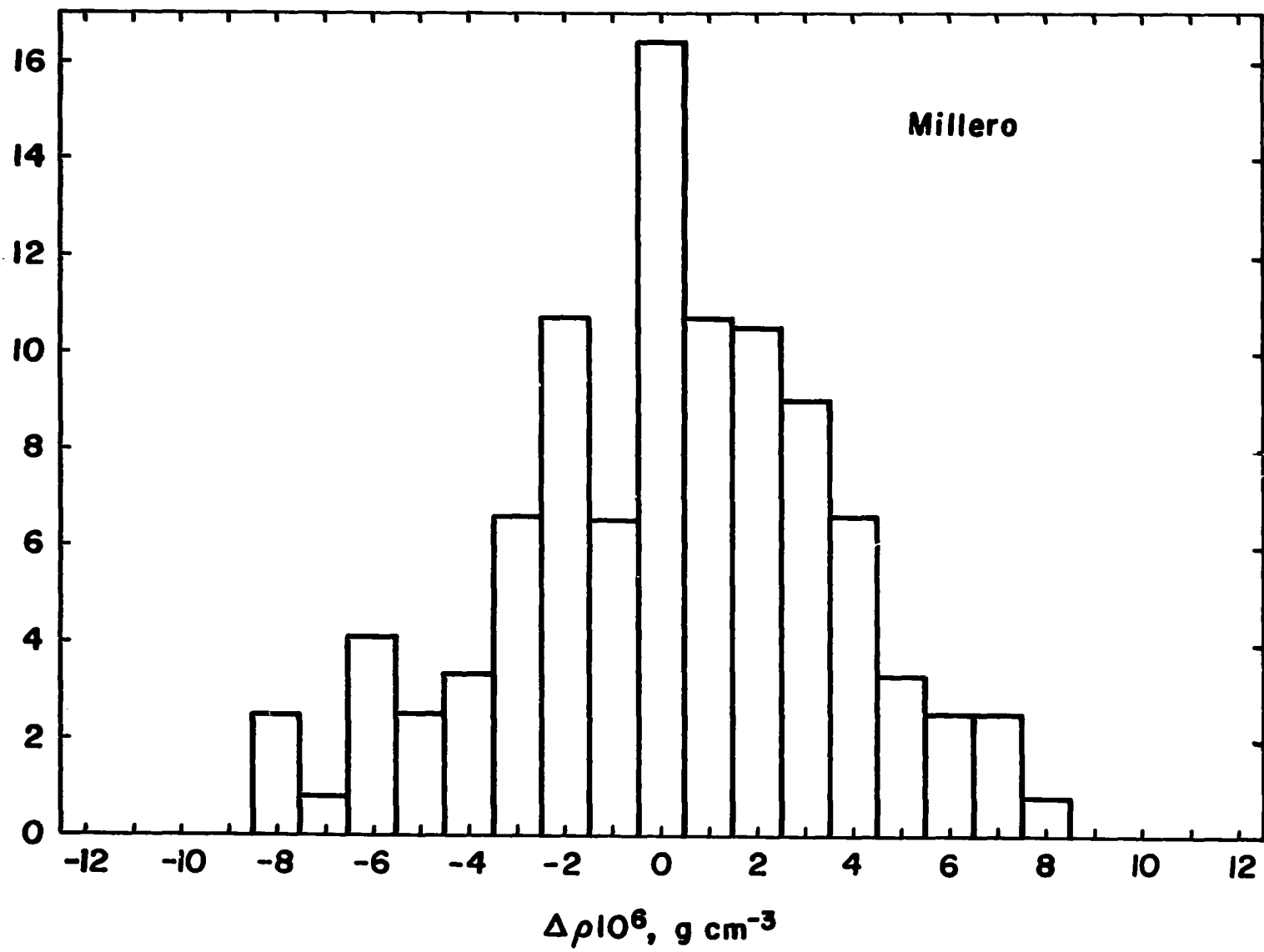


FIGURE 3

TABLE XI. Comparisons of the smoothed fitted data of Millero et al. and Poisson et al.

(a) $\Delta\rho 10^6, \text{ g cm}^{-3}$

Temp.	$5^\circ/\text{oo}$	$10^\circ/\text{oo}$	$15^\circ/\text{oo}$	$20^\circ/\text{oo}$	$25^\circ/\text{oo}$	$30^\circ/\text{oo}$	$35^\circ/\text{oo}$	$40^\circ/\text{oo}$
0°C	0	0	1	2	2	2	1	.0
5	-1	1	1	2	2	2	1	-1
10	0	1	1	2	2	1	1	-2
15	0	2	2	3	3	1	0	-2
20	1	3	4	4	4	3	1	-3
25	2	4	6	6	5	3	1	-3
30	3	6	7	8	6	4	-1	-5

(b) $\Delta\rho 10^6, \text{ g cm}^{-3}$

Temp.	$5^\circ/\text{oo}$	$10^\circ/\text{oo}$	$15^\circ/\text{oo}$	$20^\circ/\text{oo}$	$25^\circ/\text{oo}$	$30^\circ/\text{oo}$	$35^\circ/\text{oo}$	$40^\circ/\text{oo}$
0°C	-1	-1	0	1	1	2	1	1
5	0	1	2	2	2	2	0	-2
10	1	2	3	3	3	2	0	-3
15	1	3	3	4	4	2	0	-3
20	1	3	4	5	5	3	1	-3
25	1	3	5	5	5	3	1	-2
30	1	3	4	5	4	4	1	-1

(a) Using fit of 0 to 40°C data of Millero et al. (eq. 8).

(b) Using fit of 0 to 30°C data of Millero et al. (eq. 9).

FIGURE 4

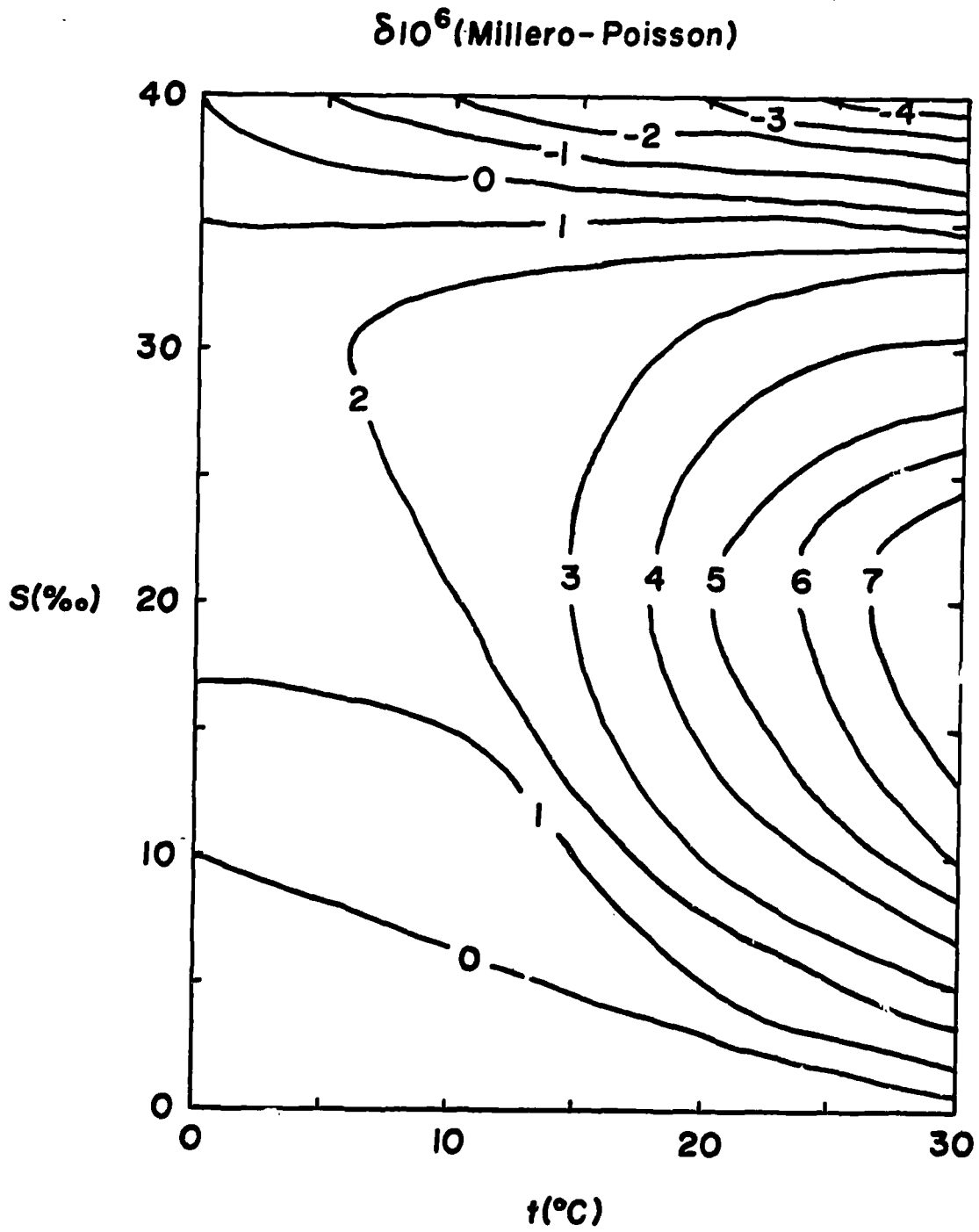
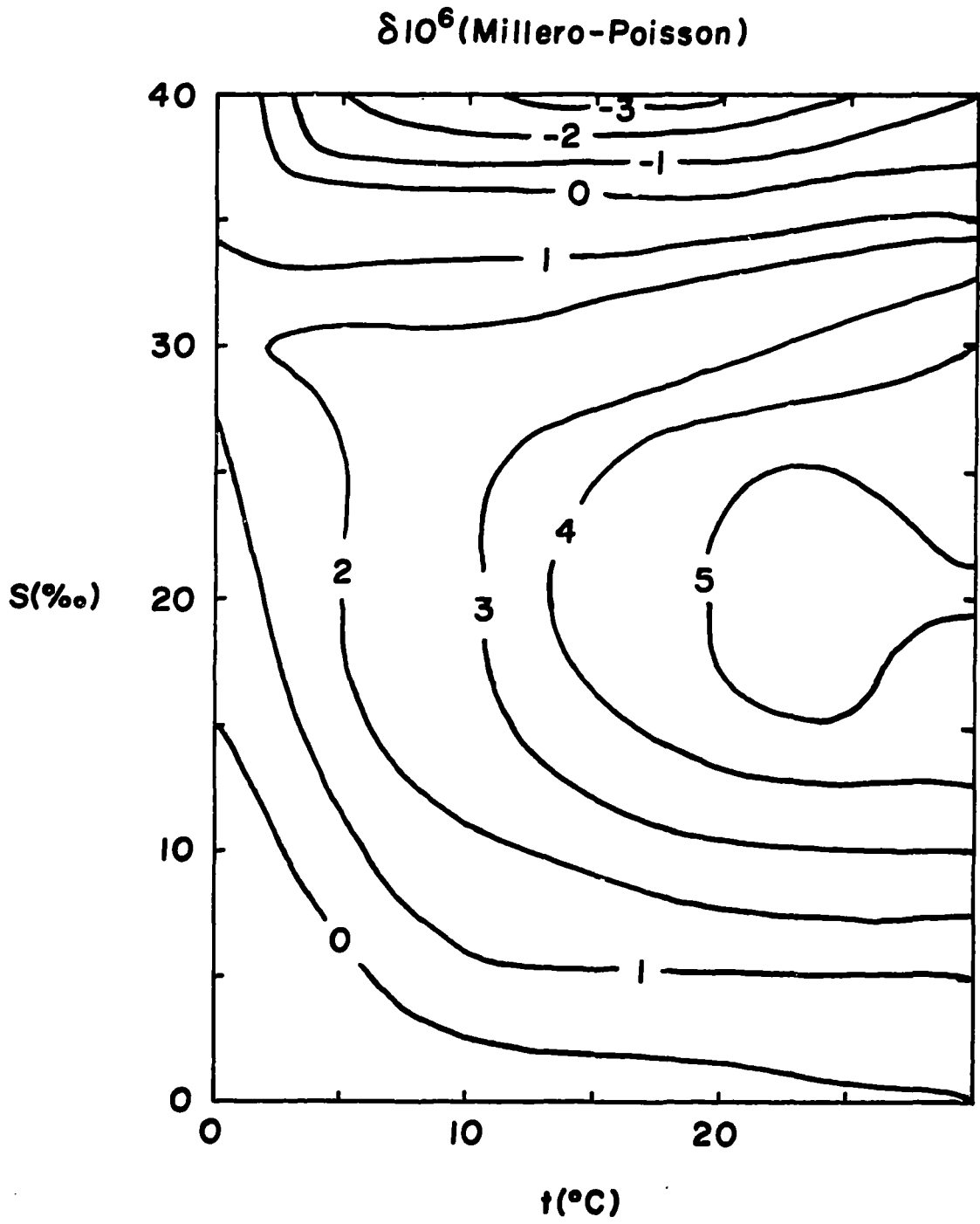


FIGURE 5



$\pm 5 \times 10^{-6} \text{ g cm}^{-3}$. The inclusion of the 35 and 40°C of Millero et al. causes larger deviations at 30°. These larger deviations apparently are caused by fitting errors (i.e. end effects). Since most of the world oceans are below 30°C, we have given less weight to the 35 and 40°C when fitting the total data.

We have fitted the total data set to a number of temperature forms for the terms A, B, and C. As with the individual data we have selected the 9(5A, 3B, 1C) equation as being the best representation. We have also examined various weighting techniques. Since the data of Poisson et al. consists of about three times more data than Millero et al., we have used a 3 to 1 weighting factor. The differences between using 1 to 1, 2 to 1 and 3 to 1 weighting factors caused a maximum difference in $\rho - \rho_0$ of $1 \times 10^{-6} \text{ g cm}^{-3}$ from 0 to 30°C. Since the Millero data at 35 and 40°C appears to be slightly inconsistent with the 0 to 30°C data, we have not weighted this data. The coefficients of the combined equation (herein called UNESCO) given below

$$A = 8.24493 \times 10^{-4} - 4.0899 \times 10^{-6}t + 7.6438 \times 10^{-8}t^2 - 8.2467 \times 10^{-10}t^3 + 5.3875 \times 10^{-12}t^4 \quad (10a)$$

$$B = -5.72466 \times 10^{-6} + 1.0227 \times 10^{-7}t - 1.6546 \times 10^{-9}t^2 \quad (10b)$$

$$C = 4.8314 \times 10^{-7} \quad (10c)$$

The differences between the measured and calculated values of $\rho - \rho_0$ for the data are given in Table VII. The overall standard error is $3.60 \times 10^{-6} \text{ gm cm}^{-3}$ (3.6×10^{-6} for the data of Poisson et al. and $3.8 \times 10^{-6} \text{ g cm}^{-3}$ for the data of Millero et al). As shown in Figure 6 the de-

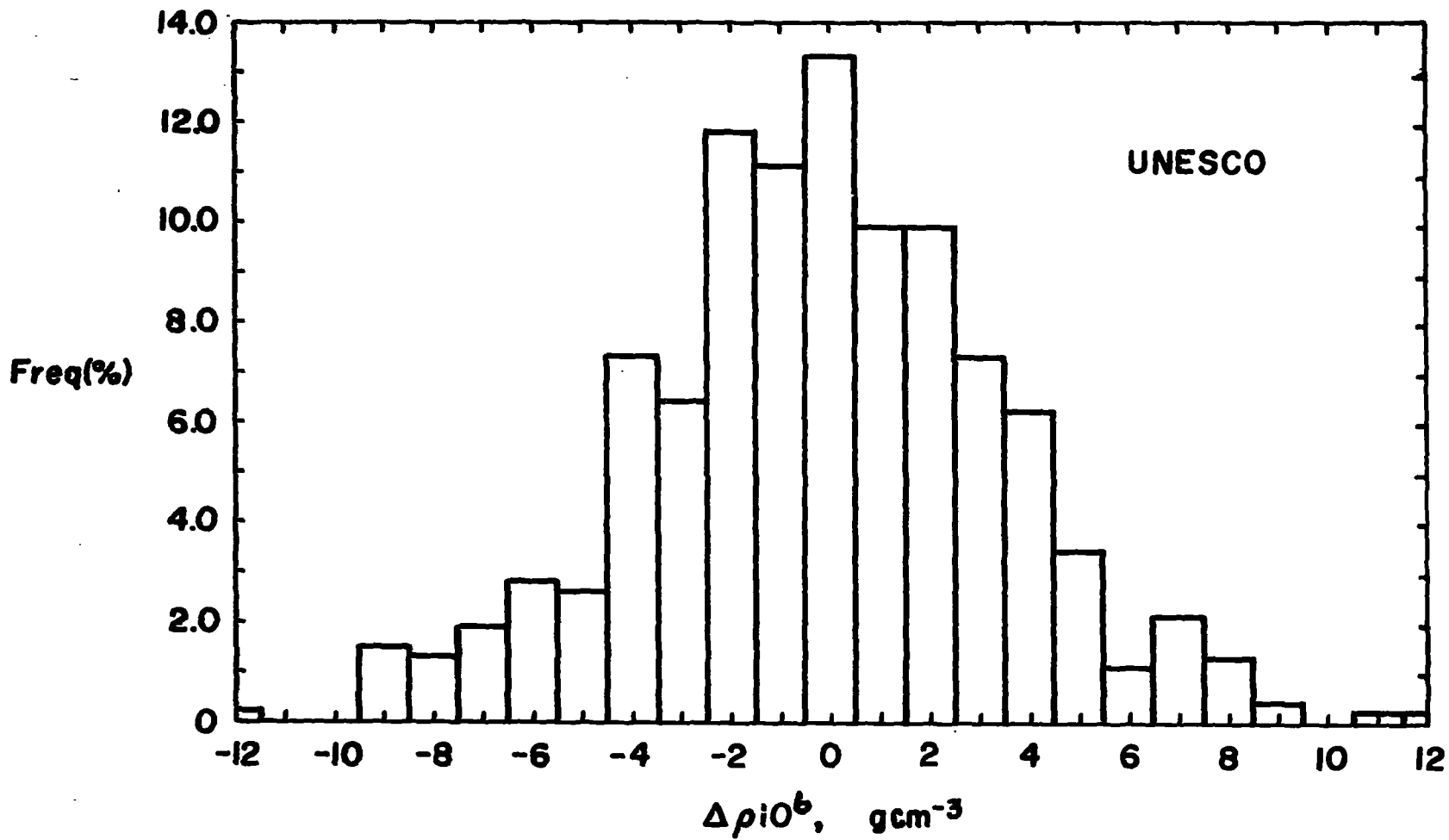


FIGURE 6

viations are random. A comparison of the UNESCO equation with the smoothed data of Poisson et al. and Millero et al. is given in Table XII and shown in Figures 7 and 8. The maximum difference between the UNESCO equation and the smoothed input data is $5 \times 10^{-6} \text{ g cm}^{-3}$. Over most of the oceanographic range of temperature (0 to 30°C) and salinity (30 to 40‰) the differences are less than $3 \times 10^{-6} \text{ g cm}^{-3}$.

To determine absolute densities (ρ) from the relative density equation, it is necessary to know the density of SMOW (Standard Mean Ocean Water) used in these studies. At present the density of SMOW is based on the equation of Bigg (1967)

$$\begin{aligned} \rho_0 (\text{g cm}^{-3}) = & 0.999842594 + 6.793952 \times 10^{-5} t - 9.095290 \times 10^{-6} t^2 + \\ & 1.001685 \times 10^{-7} t^3 - 1.120083 \times 10^{-9} t^4 + 6.536332 \times \\ & 10^{-12} t^5 \end{aligned} \quad (11)$$

The values of ρ determined from equations (10) and (11) are given in Table XIII.

The thermal expansibilities of seawater solutions

$$\alpha = -1/\rho[\partial\rho/\partial T] \quad (12)$$

can be obtained by differentiating equations (10) and (11) with respect to temperature. The differential $\partial\rho/\partial T$ is given by

$$\begin{aligned} (\partial\rho/\partial T) = & 6.793952 \times 10^{-5} - 2 \times 9.095290 \times 10^{-6} t + 3 \times 1.001685 \times \\ & 10^{-7} t^2 - 4 \times 1.120083 \times 10^{-9} t^3 + 5 \times 6.536332 \times 10^{-12} t^4 + \\ & S(-4.0899 \times 10^{-6} + 2 \times 7.6438 \times 10^{-8} t - 3 \times 8.2467 \times \\ & 10^{-10} t^2 + 4 \times 5.3875 \times 10^{-12} t^3) + S^{1.5}(1.0227 \times 10^{-7} - 2 \times \\ & 1.6546 \times 10^{-9} t) \end{aligned} \quad (13)$$

TABLE XII. Comparisons of the UNESCO equation and the smoothed input data of Poisson and Millero

(a) $\Delta\rho 10^6, \text{ g cm}^{-3}$

Temp.	5°/oo	10°/oo	15°/oo	20°/oo	25°/oo	30°/oo	35°/oo	40°/oo
0°C	1	0	1	1	1	1	1	1
5	0	1	0	0	0	1	1	0
10	0	0	0	0	0	0	0	-1
15	0	0	0	1	0	0	0	0
20	0	1	2	2	2	2	1	1
25	1	2	3	3	3	1	1	-1
30	2	3	4	4	3	2	-1	-2

(b) $\Delta\rho 10^6, \text{ g cm}^{-3}$

Temp.	5°/oo	10°/oo	15°/oo	20°/oo	25°/oo	30°/oo	35°/oo	40°/oo
0°C	1	0	0	-1	-1	-1	0	1
5	1	0	-1	-2	-2	-1	0	1
10	0	-1	-1	-2	-2	-1	-1	1
15	-1	-2	-2	-2	-3	-1	0	2
20	-1	-2	-2	-2	-2	-1	0	2
25	-1	-2	-3	-3	-2	-2	0	2
30	-1	-3	-3	-4	-3	-2	0	3
35	-2	-3	-4	-4	-3	-1	1	3
40	-2	-3	-4	-4	-3	-2	1	3

(a) $\Delta\rho = \rho(\text{UNESCO}) - \rho(\text{Poisson})$

(b) $\Delta\rho = \rho(\text{UNESCO}) - \rho(\text{Millero})$

FIGURE 7

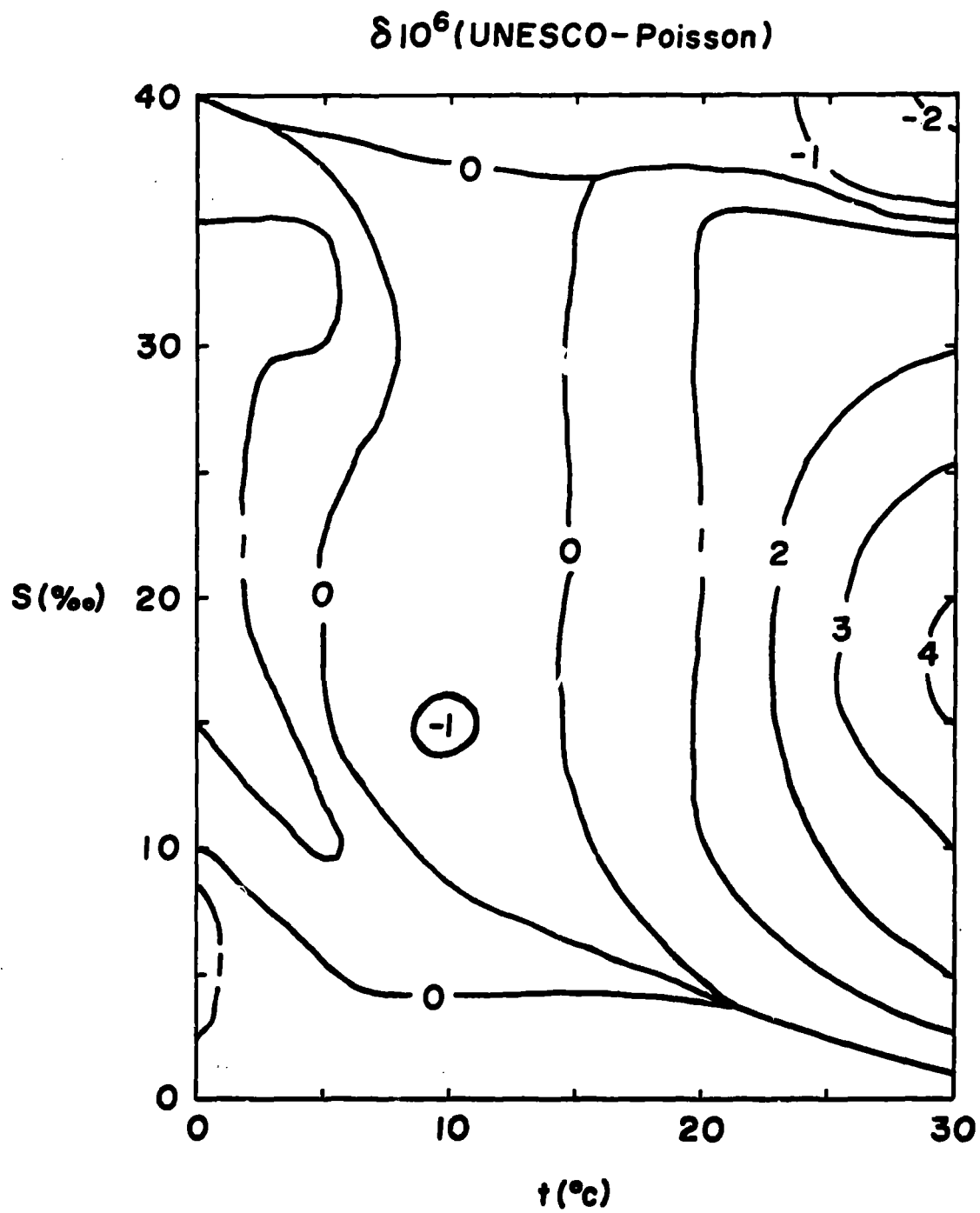


FIGURE 8

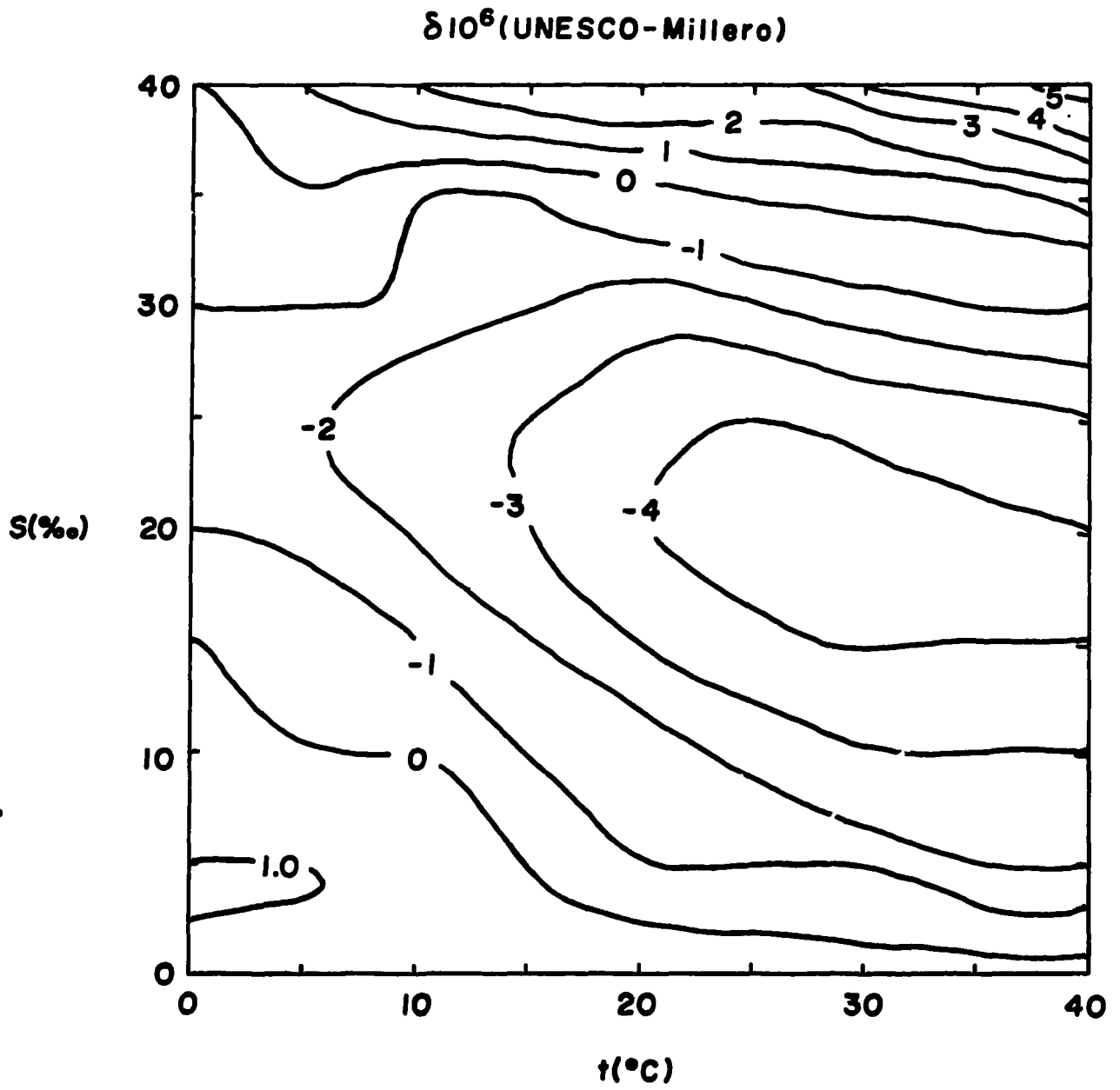


TABLE XIII. The densities (g cm^{-3}) of seawater as a function of temperature and salinity

<u>Temp.</u>	<u>S = 0</u>	<u>S = 5</u>	<u>S = 10</u>	<u>S = 15</u>	<u>S = 20</u>
0°C	0.999843	1.003913	1.007955	1.011986	1.016014
5	0.999967	1.003949	1.007907	1.011858	1.015807
10	0.999702	1.003612	1.007501	1.011385	1.015269
15	0.999102	1.002952	1.006784	1.010613	1.014443
20	0.998206	1.002008	1.005793	1.009576	1.013362
25	0.997048	1.000809	1.004556	1.008301	1.012050
30	0.995651	0.999380	1.003095	1.006809	1.010527
35	0.994036	0.997740	1.001429	1.005118	1.008810
40	0.992220	0.995906	0.999575	1.003244	1.006915
<u>Temp.</u>	<u>S = 25</u>	<u>S = 30</u>	<u>S = 35</u>	<u>S = 40</u>	
0°C	1.020041	1.024072	1.028106	1.032147	
5	1.019758	1.023714	1.027675	1.031645	
10	1.019157	1.023051	1.026952	1.030862	
15	1.018279	1.022122	1.025973	1.029834	
20	1.017154	1.020954	1.024763	1.028583	
25	1.015806	1.019569	1.023343	1.027127	
30	1.014252	1.017985	1.021729	1.025483	
35	1.012509	1.016217	1.019934	1.023662	
40	1.010592	1.014278	1.017973	1.021679	

The values of α for seawater solutions calculated from equations (10), (11), (12) and (13) are given in Table XIV. These values are precise to $\pm 0.5 \times 10^{-6} \text{ K}^{-1}$.

Comparisons With Other Equations of State

Since the new equation will replace the Knudsen equation (1902), it is appropriate to compare the results of the two equations. In Figure 9 we give the differences in the densities obtained from the UNESCO equation and the Knudsen equation. Similar comparisons are made with the equation proposed by Cox et al. (1970) and Millero et al. (1976) in Figures 10 and 11. In the low salinity range both the work of Knudsen and Cox et al. show large deviations. As discussed elsewhere (Millero et al., 1976; Millero and Kremling, 1976) these differences are due to the salts that are present in Baltic river waters. The low salinity waters used in both Knudsen and Cox et al. work were Baltic waters, while in our studies we used seawater diluted with water. At a salinity of 35‰ the densities of Knudsen are $6 \pm 1 \times 10^{-6} \text{ g cm}^{-3}$ lower than the new equation from 0 to 25°C. This is in general agreement with the findings of other workers (Cox et al., 1970, Kremling 1972, Millero et al. 1976 and Poisson et al. 1980). The fact that this difference is independent of temperature (as the differences at other salinities) indicates that the differences are due to errors in salinities not the densities. The internal precision of the Knudsen work is very good.

The UNESCO equation agrees with the equation of Millero et al. to within $\pm 5 \times 10^{-6} \text{ g cm}^{-3}$ except at high salinities between 25 to 35°C. As discussed earlier this is due to errors in the assigned salinities at $S = 40$ ‰ and the resultant overfitting of the data. The differences of the UNESCO eq. and the work of Cox et al. at $S = 35$ are quite low at 0 and 25°C but show large temperature variations (-13 to $7 \times 10^{-6} \text{ g cm}^{-3}$ differences

TABLE XIV. The thermal expansivities (K^{-1}) of seawater solutions as a function of temperature and salinity

$\alpha 10^6, K^{-1}$					
<u>Temp.</u>	<u>S = 0</u>	<u>S = 5</u>	<u>S = 10</u>	<u>S = 15</u>	<u>S = 20</u>
0°C	-68.0	-48.4	-30.0	-12.4	4.6
5	16.0	31.9	46.8	61.1	74.9
10	88.1	100.9	112.9	124.4	135.6
15	150.9	161.1	170.8	180.0	188.9
20	206.7	214.7	222.4	229.7	236.9
25	257.0	263.2	269.2	275.0	280.7
30	303.1	307.7	312.2	316.7	321.1
35	345.7	348.8	352.0	355.3	358.6
40	384.9	386.6	388.6	390.7	393.0

<u>Temp.</u>	<u>S = 25</u>	<u>S = 30</u>	<u>S = 35</u>	<u>S = 40</u>
0°C	21.1	37.1	52.6	67.6
5	88.2	101.1	113.6	125.8
10	146.3	156.7	166.8	176.6
15	197.6	206.0	214.1	222.1
20	243.8	250.6	257.2	263.6
25	286.2	291.7	297.0	302.2
30	325.5	329.8	334.1	338.4
35	362.0	365.3	368.7	372.1
40	395.4	397.8	400.4	403.0

FIGURE 9

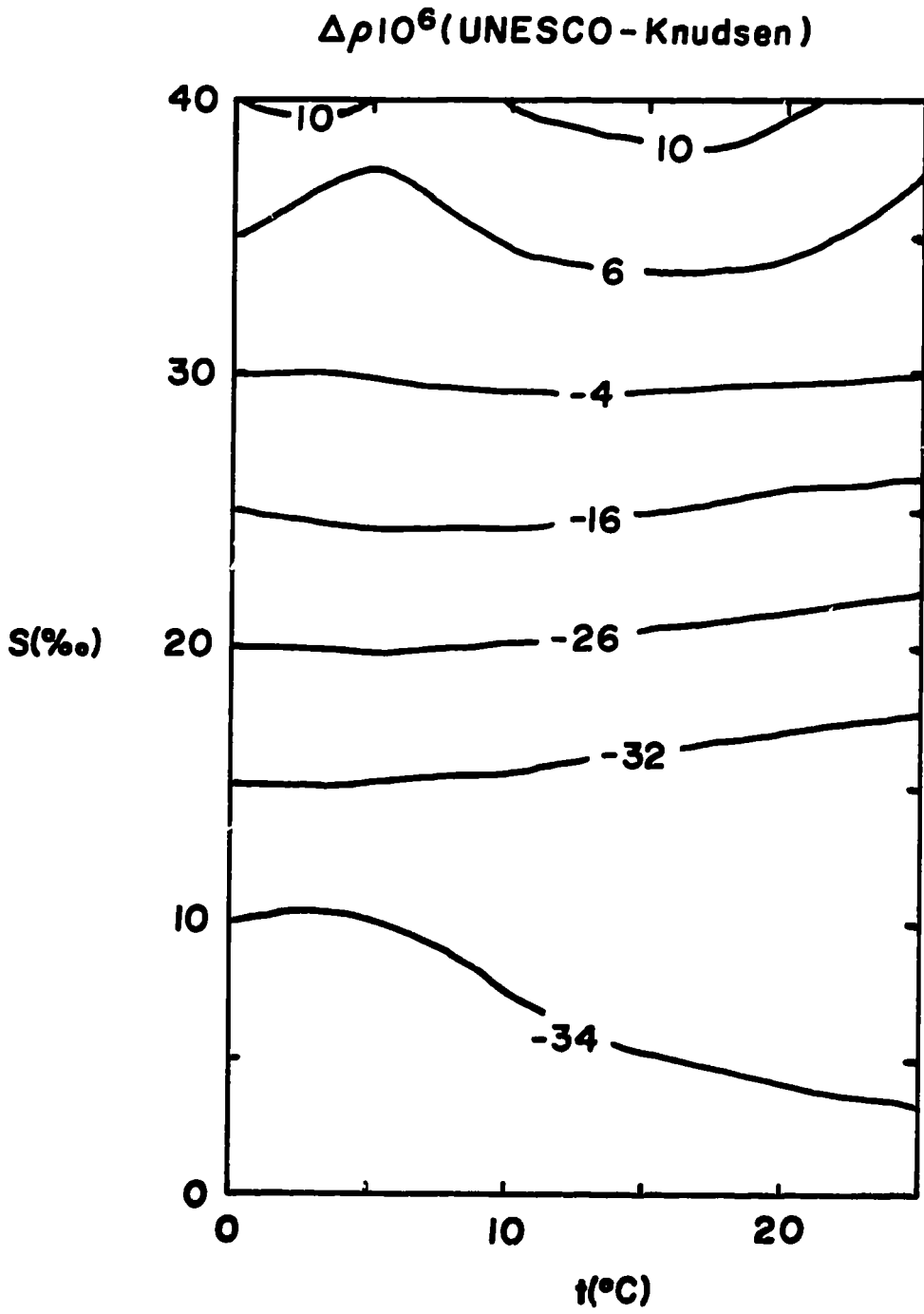


FIGURE 10

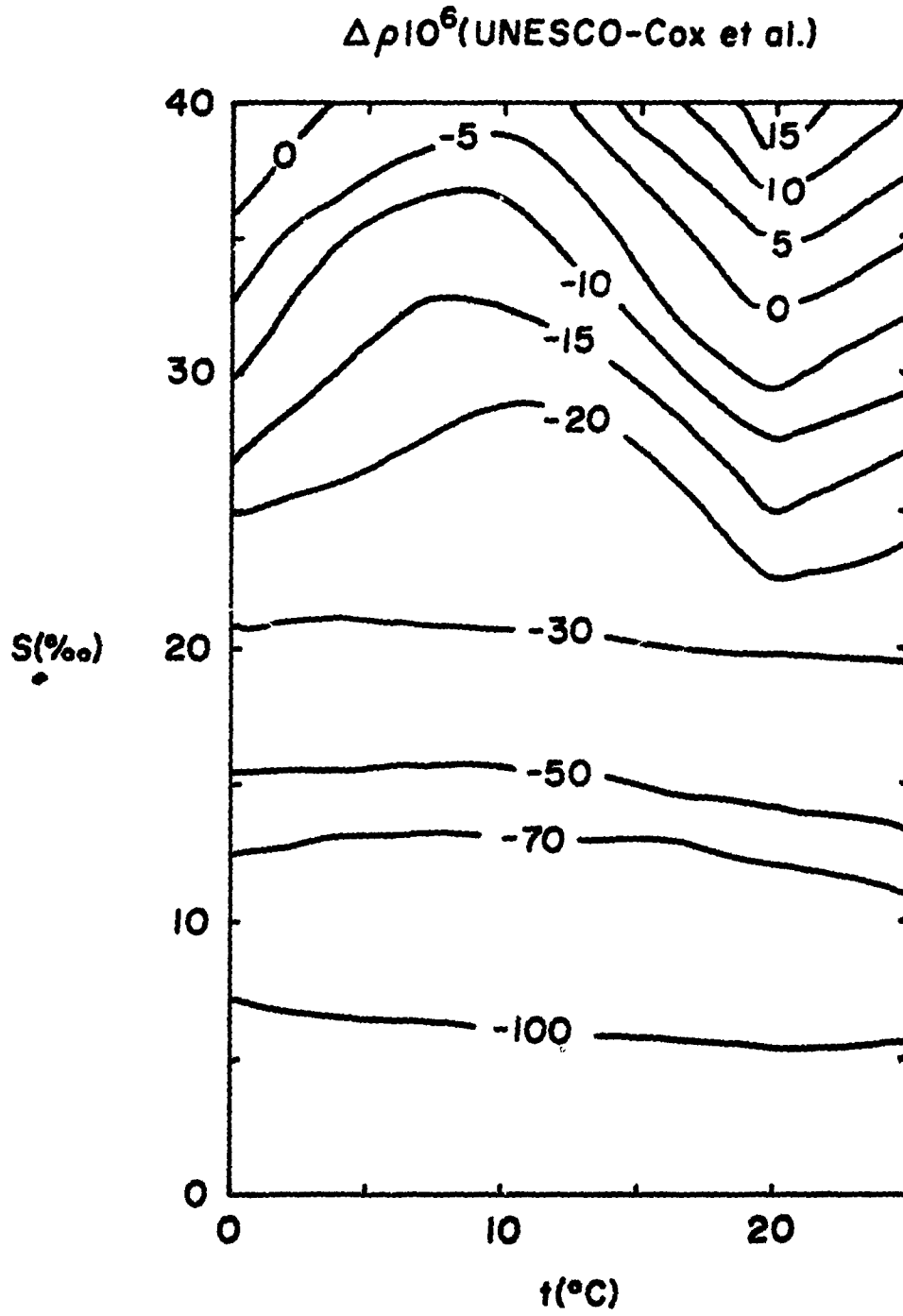
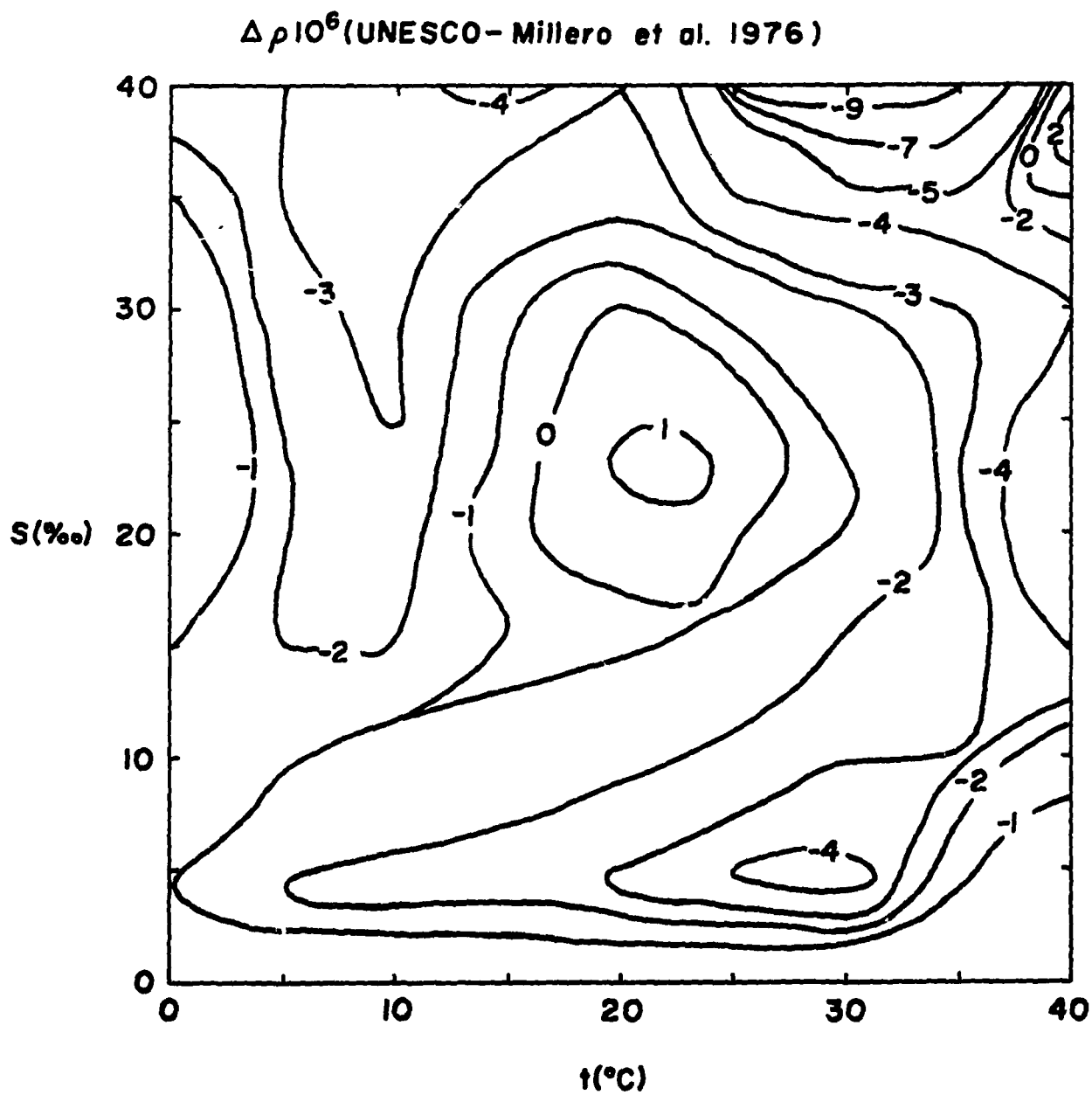


FIGURE 11



from 5 to 20°C). These differences are related to uncertainties in the density measurements of Cox et al. as a function of temperature.

The comparisons of the expansibilities derived from the UNESCO equation of state and the work of Knudsen et al. (1902), Cox et al. (1970) and Millero et al. (1976) are shown in Figures 12, 13 and 14. The expansibilities from UNESCO agree to $\pm 2.3 \times 10^{-6} \text{ K}^{-1}$ with Knudsen, $\pm 1.5 \times 10^{-6} \text{ K}$ with Millero et al. and $\pm 5.0 \times 10^{-6} \text{ K}^{-1}$ with Cox et al. These comparisons show the very good precision of the density measurements of Knudsen et al. and the large temperature errors of Cox et al. (1970).

ACKNOWLEDGEMENTS

Frank J. Millero wishes to acknowledge the Office of Naval Research (N00014-75-C-0173) and the Oceanographic Section of the National Science Foundation (GA-40532) for supporting his PVT research. Alain Poisson wishes to acknowledge the support of the C.N.R.S., contract A.T.P. "Chimie marine 76", No. 1661. Both authors wish to acknowledge the computer help of Don Schreiber.

FIGURE 12

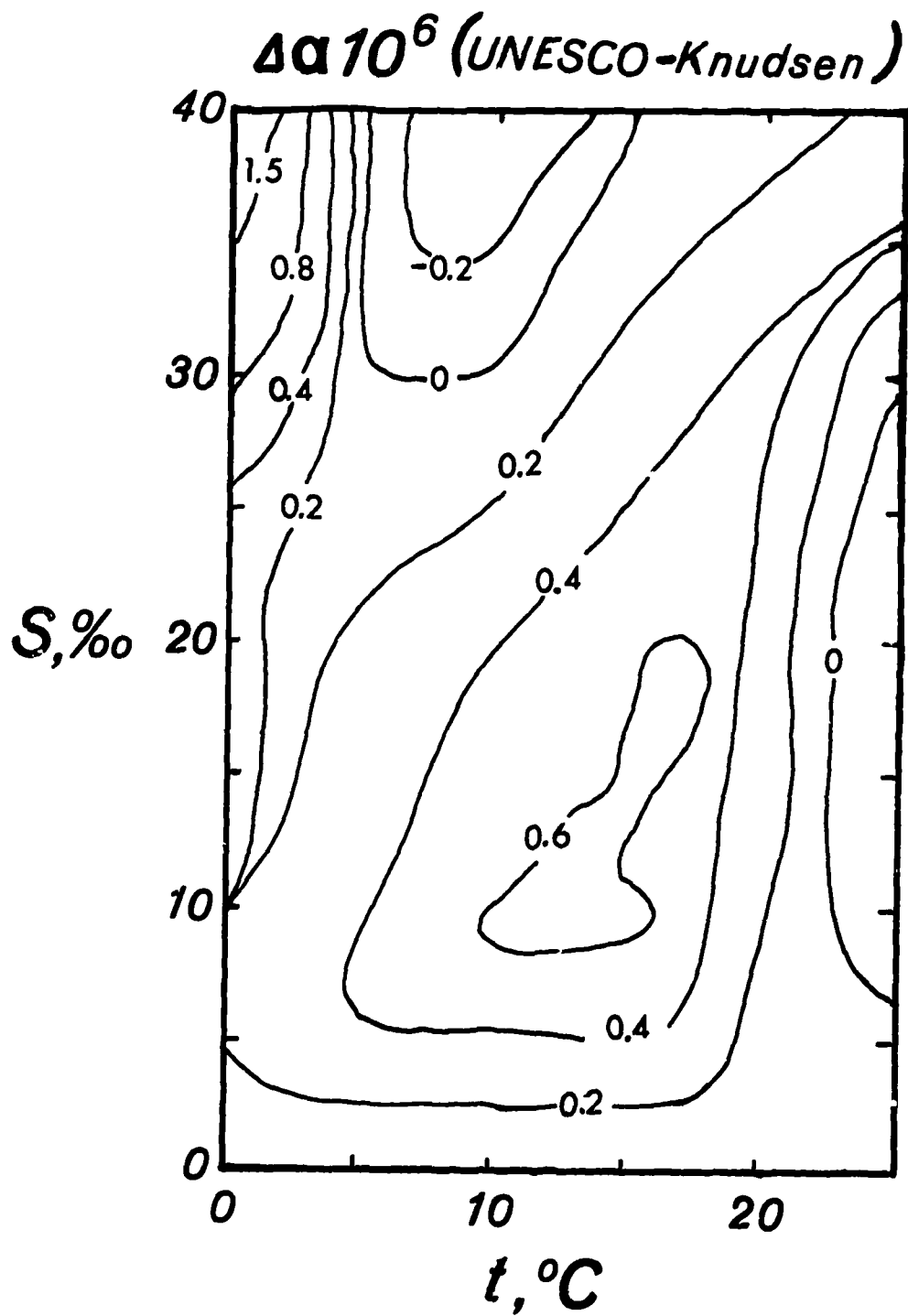


FIGURE 13

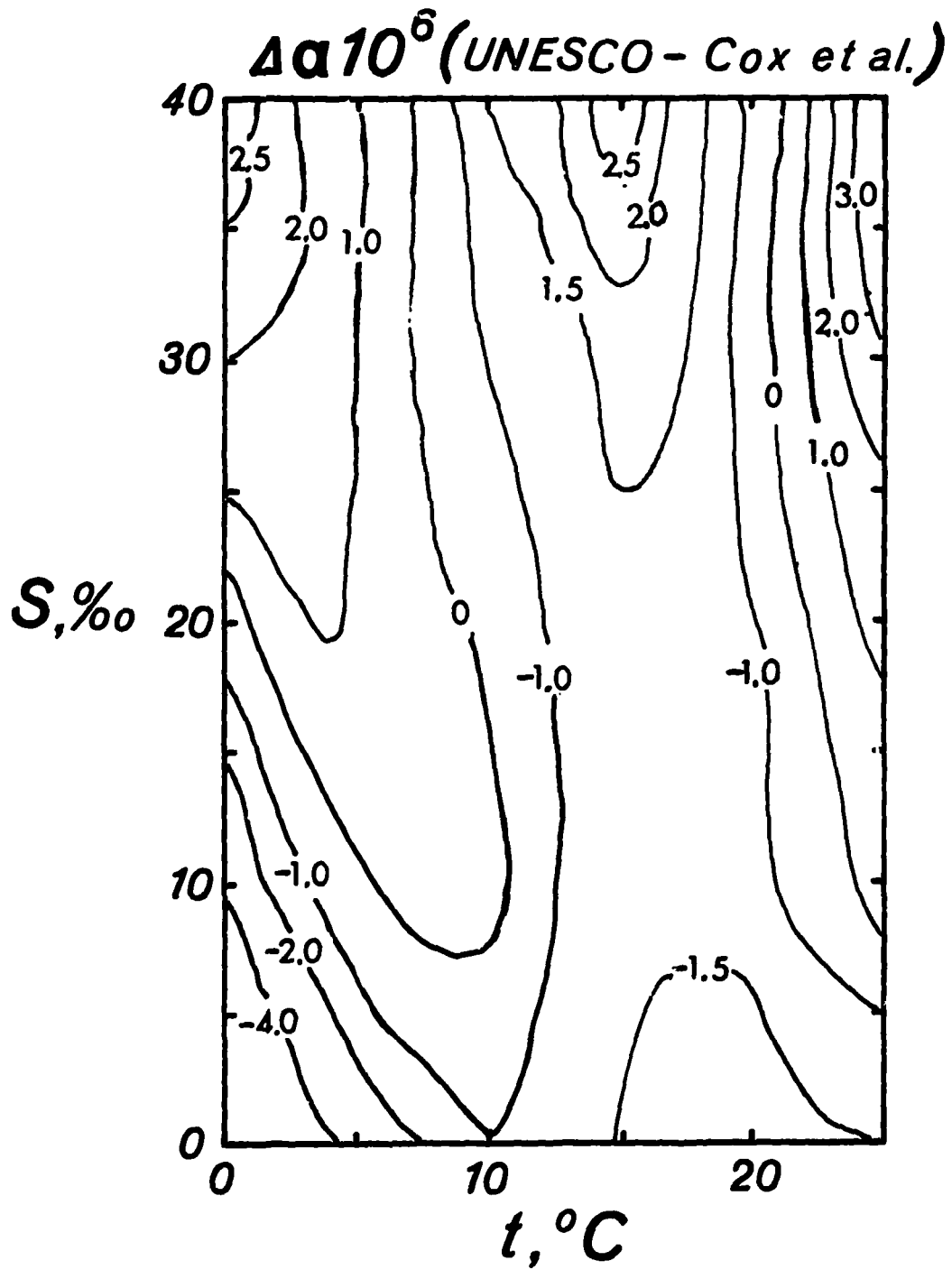
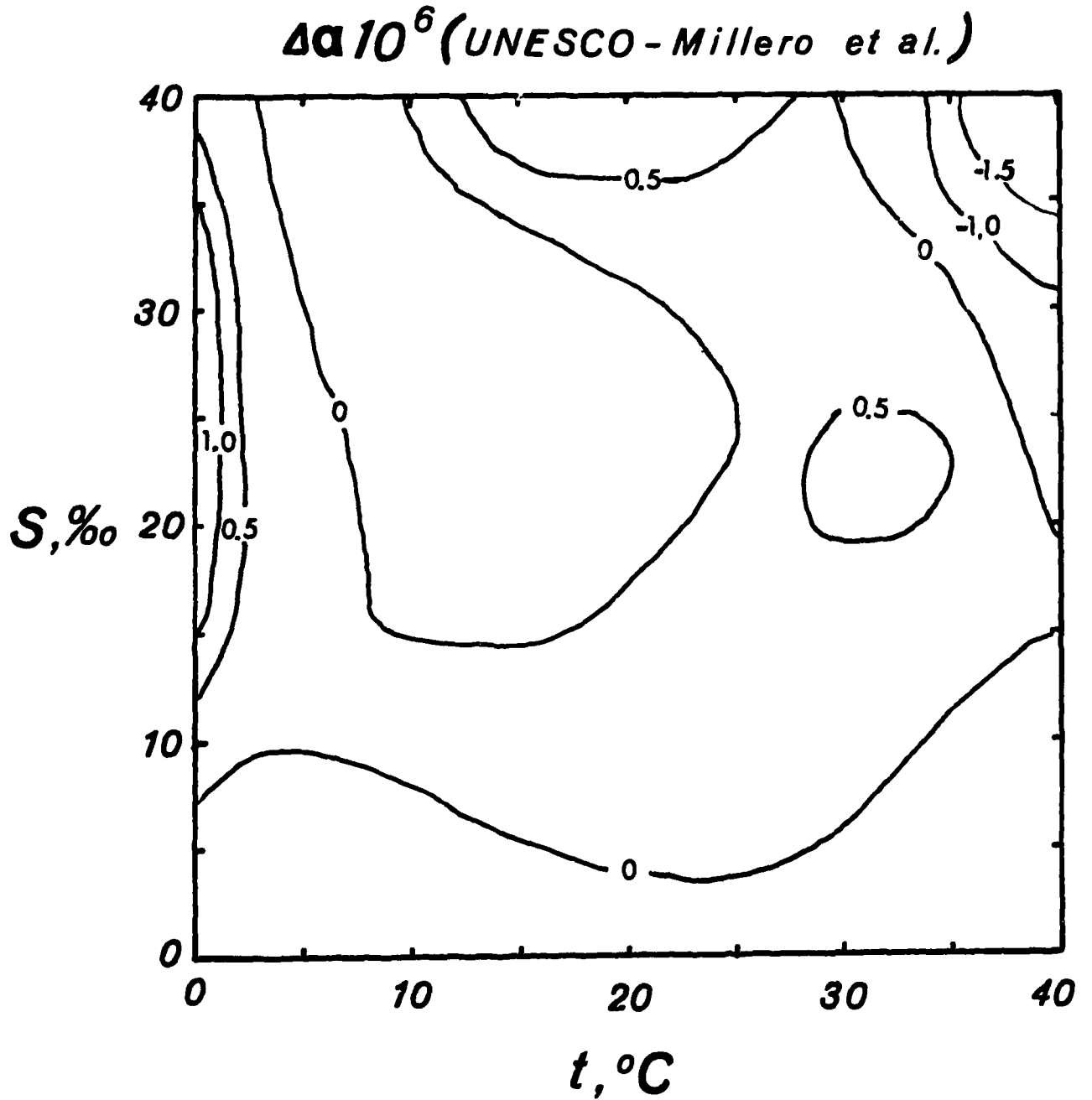


FIGURE 14



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**BACKGROUND PAPERS AND SUPPORTING DATA ON
THE HIGH PRESSURE INTERNATIONAL EQUATION
OF STATE OF SEAWATER, 1980**

NOTE TO THE READERS

In the published paper "A New High Pressure Equation of State for Seawater" by Millero, Chen, Bradshaw and Schleicher (Deep Sea Research, 27A, 1980) as well as in "Summary of Data Treatment for the International High Pressure Equation of State for Seawater", by Millero, Chen, Bradshaw and Schleicher (submitted to Unesco in September 1978), which both appear in this section, the one atmosphere equation of state of Millero, Gonzalez and Ward (1976) was used to normalize the various data sets. Since the values of $v^0 - v^P$ come directly from the experimental data, the values of the secant bulk modulus fitted are not strongly affected by the values of v^0 . For example, at 0°C , $P = 1000\text{b}$, $S = 35$ and $K = 28\,080.74$. An error of $\pm 5 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ in $v^0 - v^P$ yields an error of ± 4.07 in K , while a similar error in v^0 yields an error of $\pm .15$ in K . The maximum error in the new equation of state of Millero and Poisson (1981) is $10 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$, or an error of ± 0.3 in K which is well within the experimental error of $K(\pm 4.1)$.

NOTE

A new high pressure equation of state for seawater

FRANK J. MILLERO*, CHEN-TUNG CHEN†,
ALVIN BRADSHAW‡ and KARL SCHLEICHER‡

(Received 29 November 1978; in revised form 15 November 1979; accepted 20 November 1979)

Abstract—A new high pressure equation of state for water and seawater has been derived from the experimental results of Millero and coworkers in Miami and Bradshaw and Schleicher in Woods Hole. The form of the equation of state is a second degree secant bulk modulus

$$K = Pv^0/(v^0 - v^P) = K^0 + AP + BP^2$$

$$K^0 = K_w^0 + aS + bS^{3/2}$$

$$A = A_w + cS + dS^{3/2}$$

$$B = B_w + eS$$

where v^0 and v^P are the specific volume at 0 and P applied pressure and S is the salinity (‰). The coefficients K_w^0 , A_w , and B_w for the pure water part of the equation are polynomial functions of temperature. The standard error of the pure water equation of state is $4.3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v_w^0 . The temperature dependent parameters a , b , c , d , and e have been determined from the high pressure measurements on seawater. The overall standard error of the seawater equation of state is $9.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . Over the oceanic ranges of temperature, pressure, and salinity the standard error is $5.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . This new high pressure equation of state has recently (1979) been recommended by the UNESCO Joint Panel on Oceanographic Tables and Standards for use by the oceanographic community.

INTRODUCTION

AT THE 8th meeting of the Joint Panel on Oceanographic Tables and Standards (UNESCO, 1978) a recommendation was made to formulate a new equation of state for seawater based on the high pressure specific volume data (v) of CHEN and MILLERO (1976, 1978), CHEN, FINE and MILLERO (1977), and BRADSHAW and SCHLEICHER (1970, 1976, unpublished data). A thorough summary of the formulation of this new equation of state has been completed (MILLERO, CHEN, BRADSHAW and SCHLEICHER, 1979). In this short note, we will briefly outline how the new equation of state was formulated and present the new high pressure equation of state.

The form of the high pressure equation of state is the second degree secant bulk modulus (K) (CHEN and MILLERO, 1976)

$$K = Pv^0/(v^0 - v^P) = K^0 + AP + BP^2, \quad (1)$$

where v^0 and v^P are the specific volumes at zero and P applied pressure, $K^0 = 1/\beta^0$ is the reciprocal of the 1 atmosphere compressibility [$\beta^0 = -(1/v^0)(\partial v^P/\partial P)_T$], and A and B are

* Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, FL 33149, U.S.A.

† Oregon State University, School of Oceanography, Corvallis, OR 97311, U.S.A.

‡ Woods Hole Oceanographic Institution, Woods Hole, MA 02543, U.S.A.

Table 1. Summary of the data used for the equation of state

S(‰)	Pressure range (bar)	Temperature range (°C)	No. of points	Reference
0	100-1000	-4-40	282	* , †
5	100-1000	0-40	135	‡ , §
10	100-1000	0-40	134	‡ , §
15	100-1000	-2-40	186	‡ , §
20	100-1000	0-40	134	‡ , §
25	100-1000	0-40	135	‡ , §
30	100-1000	-2-40	228	‡ , § , ¶
35	100-1000	-4-40	366	‡ , § , ¶
40	100-1000	-2-40	229	‡ , § , ¶
			1829	

* CHEN, FINE and MILLERO (1977).

† BRADSHAW and SCHLEICHER (1976, unpublished results).

‡ CHEN and MILLERO (1976).

§ BRADSHAW and SCHLEICHER (1970, 1976, unpublished results).

¶ CHEN and MILLERO (1978).

temperature- and salinity-dependent parameters. The salinity (S in ‰) dependence of K^0 , A , and B is given by

$$K^0 = K_w^0 + aS + bS^{3/2} \quad (1a)$$

$$A = A_w + cS + dS^{3/2} \quad (1b)$$

$$B = B_w + eS. \quad (1c)$$

The terms K_w^0 , A_w , and B_w are temperature-dependant parameters for pure water, while the terms a , b , c , d , and e are temperature-dependent parameters for seawater. The advantage of formulating the high pressure equation of state in this manner arises from the ability to adjust the pure-water terms, the 1-atmosphere terms, or the high-pressure terms at a future time without affecting the other terms.

A summary of the data used to formulate the equation of state is given in Table 1. A total of 1908 values of v^p for water (298) and seawater (1610) over the temperature range of -4 to 40°C , the pressure range of 0 to 1000 bars applied pressure, and 0 to 40‰ salinity make up the data. To make the various sets of data for water and seawater self-consistent, it was necessary to make some adjustments to the published results (MILLERO *et al.*, 1979). In the next section we will outline the 1-atmosphere data treatment.

One-atmosphere data treatment

To calculate the secant bulk modulus of water and seawater

$$K = v^0 P / (v^0 - v^p) \quad (2)$$

it was necessary to have specific volume data at 1 atm. (v^0) over the entire temperature and salinity range of the measurements. The relative density measurements (d) of MILLERO, GONZALEZ and WARD (1976) satisfy this need. To be consistent with the maximum density assigned to distilled standard mean ocean water ($\rho_{\text{max}} = 0.999975 \text{ g cm}^{-3}$) and the maximum density of Miami (MILLERO and EMMET, 1976) water ($\rho_{\text{max}} = 0.999974 \text{ g cm}^{-3}$), some adjustments had to be made to the relative density

measurements ($d = \rho/\rho_{\max}$) by MILLERO *et al.* (1976). The absolute differences in the density of seawater (ρ) and pure water (ρ_0), ($\rho - \rho_0$) can be obtained by multiplying the relative densities ($d - d_0$) by $\rho_{\max} = 0.999974$. As the 1-atm seawater equation of state of MILLERO *et al.* (1976) is given by

$$d - d_0 = AS + BS^{3/2} + CS^2, \quad (3)$$

the coefficients can be adjusted by multiplying A , B , and C by $\rho_{\max} = 0.999974$. The density of pure water ρ_w was taken from the interim equation of Menaché for standard mean ocean water (SMOW) (UNESCO, 1976). This equation is based on the work of BIGG (1967—see also WAGENBRETH and BLANKE, 1971). The equation has been adjusted by $1 \times 10^{-6} \text{ g cm}^{-3}$ at 0°C to account for the differences between ion-exchanged Miami and distilled SMOW (MILLERO and EMMET, 1976).

$$\begin{aligned} \rho = & (0.999841594 + 6.793952 \times 10^{-5}t - 9.095290 \times 10^{-6}t^2 \\ & + 1.001685 \times 10^{-7}t^3 - 1.120083 \times 10^{-9}t^4 + 6.536332 \times 10^{-12}t^5) \\ & + (8.25917 \times 10^{-4} - 4.4490 \times 10^{-6}t + 1.0485 \times 10^{-7}t^2 \\ & - 1.2580 \times 10^{-9}t^3 + 3.315 \times 10^{-12}t^4)S \\ & + (-6.33761 \times 10^{-6} + 2.8441 \times 10^{-7}t - 1.6871 \times 10^{-8}t^2 \\ & + 2.83258 \times 10^{-10}t^3)S^{3/2} + (5.4705 \times 10^{-7} \\ & - 1.97975 \times 10^{-8}t + 1.6641 \times 10^{-9}t^2 \\ & - 3.1203 \times 10^{-11}t^3)S^2. \end{aligned} \quad (4)$$

The standard error of this equation is $3.3 \times 10^{-6} \text{ g cm}^{-3}$ in ρ from 0 to 40°C and 0 to 40‰ salinity. The 1-atm density measurements by CHEN and MILLERO (1976) agree on the average with the values determined from equation (4) to $\pm 4.5 \times 10^{-6} \text{ g cm}^{-3}$. As the values of $v^0 - v^P$ come directly from the experimental data, the secant bulk modulus is not strongly affected by the values selected for v^0 . For example, at 0°C , $P = 1000$, and $S = 35$, $K = 28080.74$, a ± 5 ppm error in $v^0 - v^P$ yields an error of ± 4.07 in K while a ± 5 ppm error in v^0 yields an error of ± 0.15 in K .

The 1-atm values of the secant bulk modulus of water and seawater have been determined from the sound speed measurements by DEL GROSSO (1970) and DEL GROSSO and MADER (1972) for water and MILLERO and KUBINSKI (1975) for seawater. KELL (1975) determined the isothermal compressibilities of water at 1 atm from the sound speed (U) measurements of DEL GROSSO (1970) and DEL GROSSO and MADER (1972)

$$\beta = \frac{1}{\rho U^2} + \frac{T\alpha^2}{\rho c_p}, \quad (5)$$

where T is the absolute temperature ($^\circ\text{K}$), $\alpha = (1/v)(\partial v/\partial T)$ is the thermal expansibility and c_p is the heat capacity. Kell's compressibility results for water from 0 to 40°C were used to determine $K_w^0 = 1/\beta_w^0$ and fit to

$$K_w^0 = 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2}t^3 - 5.155288 \times 10^{-5}t^4 \quad (6)$$

with $\sigma = 0.1$ bar.

The 1-atm compressibilities for seawater were determined from the relative sound speed measurements of MILLERO and KUBINSKI (1975), which have been refitted by CHEN and

MILLERO (1977). The heat capacities were taken from the work of MILLERO, PERRON and DESNOYERS (1973) and the densities and expansibilities were obtained from equation (4). The secant bulk modulus for seawater at 1 atm ($K^0 = 1/\beta^0$) determined from equation (5) are reliable to ± 2.0 bar. The K^0 values for seawater were fitted to the equation

$$K^0 - K_w^0 = aS + bS^3, \quad (7)$$

where K_w^0 is given by equation (6) and

$$a = 54.6746 - 0.603459t + 1.09987 \times 10^{-2}t^2 - 6.1670 \times 10^{-5}t^3 \quad (7a)$$

$$b = 7.944 \times 10^{-2} + 1.6483 \times 10^{-2}t - 5.3009 \times 10^{-4}t^2. \quad (7b)$$

The standard error in the fit is 1.9 bar in K^0 and 0.004×10^{-6} bar $^{-1}$ in β^0 .

High pressure data treatment

To make the various high pressure data sets self-consistent, it was necessary to make some adjustments to the published results. BRADSHAW and SCHLEICHER's (1976) compression measurements were made at 10°C for water and seawater. These results have been fitted to a function of salinity and pressure $f(S, P)$, the specific volume compression relative to $P = 6.38b$. The specific volumes at 10°C were calculated from this function by using the equation

$$v^P(10^\circ\text{C}) = v^0(10^\circ\text{C}) + f(S, 0) - f(S, P), \quad (8)$$

where $f(S, 0)$ is evaluated at $P = 0$, and $v^0(10^\circ\text{C}) = 1/\rho^0(10^\circ\text{C})$ can be determined from equation (4). Equation (8) was used to convert the expansion measurements of BRADSHAW and SCHLEICHER (1970) to specific volumes at a given pressure (MILLERO *et al.*, 1979).

The specific volumes for water from the sound derived equation of CHEN *et al.* (1977) and the expansion results of BRADSHAW and SCHLEICHER (unpublished results) have been used to calculate the secant bulk modulus

$$K_w^P = v_w^0 P / (v_w^0 - v_w^P). \quad (9)$$

These values of K_w^P have been fitted to an equation of the form

$$K_w^P - K_w^0 = A_w P + B_w P^2, \quad (10)$$

where K_w^0 is given by equation (6). The results of the various fits are given in Table 2. The seven-parameter equation (4A, 3B) gives the best fit with the fewest number of parameters. An evaluation of the six- and seven-parameter equations using the *F*-test indicates that at the 95% confidence level seven parameters are needed. The values of A_w and B_w are given by

$$A_w = 3.239908 + 1.43713 \times 10^{-3}t + 1.16092 \times 10^{-4}t^2 - 5.77905 \times 10^{-7}t^3 \quad (10a)$$

$$B_w = 8.50935 \times 10^{-5} - 6.12293 \times 10^{-6}t + 5.2787 \times 10^{-8}t^2 \quad (10b)$$

The standard error is 4.3×10^{-6} cm 3 g $^{-1}$ in v_w^P . The differences in the values of v_w^P calculated from equation (10) and the values measured by BRADSHAW and SCHLEICHER (unpublished results) and CHEN *et al.* (1977) are shown in Figs 1 and 2.

The high pressure specific volume data for seawater of various workers (CHEN and MILLERO, 1976, 1978 and BRADSHAW and SCHLEICHER, 1970, 1976, unpublished results) must be normalized to the same 1-atm specific volumes and the same values of v_w at each

Table 2. Summary of the bulk modulus fit of pure water data by BRADSHAW and SCHLEICHER and CHEN, FINE and MILLERO*

$K_w^P = K_w^0 + A_w P + B_w P^2$		
Parameters	$\sigma(K)$	$10^6 \sigma(v)$
10(5A, 5B)	5.93	4.33
9(5A, 4B)	5.91	4.32
8(5A, 3B)	5.91	4.32
7(5A, 2B)	5.95	4.45
6(5A, B)	9.00	8.45
8(4A, 4B)	5.91	4.34
7(4A, 3B)	5.91	4.33
6(4A, 2B)	5.94	4.46
5(4A, B)	9.06	8.46

* The data were weighted by $P/200+1$. The results of Bradshaw and Schleicher at $P = 8.3$ bar were not used due to the large uncertainty in K_w .

pressure and temperature. The need for this normalization can be demonstrated by comparing the differences in v^P for 35‰ seawater at 10°C of BRADSHAW and SCHLEICHER (1976) and CHEN and MILLERO (1977). The differences are shown in Table 3. The maximum difference is $14 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . By comparing the differences between seawater and water ($v - v_w$), the deviations are decreased to $1 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in $(v^P - v_w^P)$. These comparisons clearly demonstrate that the relative specific volumes for seawater are in excellent agreement.

As the measurements of CHEN and MILLERO (1976, 1978) were made relative to pure water, the easiest way to normalize the data was to use an equation of state for pure water determined from the measurements by BRADSHAW and SCHLEICHER (unpublished results). The equation of state for water generated from the measurements [equation (10)] has a standard deviation of $2.3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v_w^P (MILLERO *et al.*, 1979).

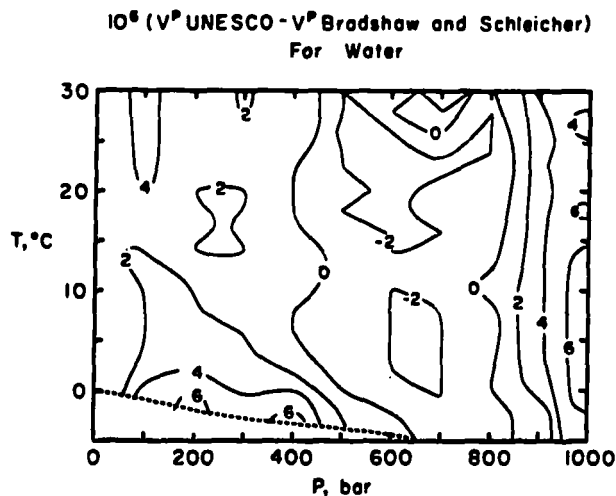


Fig. 1. Differences in the values of v^P for water calculated from equation (10) and the measured values of Bradshaw and Schleicher vs pressure at several temperatures.

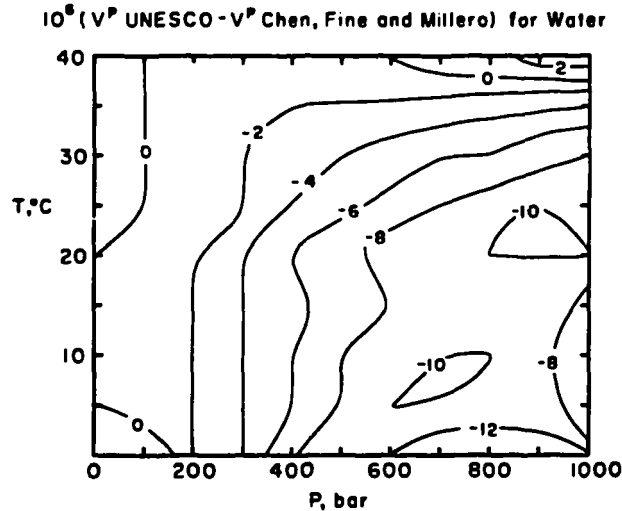


Fig. 2. Differences in the values of v^P for water calculated from equation (10) and the measured values of Chen, Fine and Millero vs pressure at several temperatures.

The individual normalized data sets of CHEN and MILLERO (1976, 1978) and BRADSHAW and SCHLEICHER (1970, 1976, unpublished results) have been fitted to the equation (MILLERO *et al.*, 1979)

$$K^P - K_w^0 - (K^0 - K_w^0) = [cS + dS^{3/2}]P + [eS]P^2. \quad (11)$$

The individual data sets were found statistically to give the 'best' fit for a seven-parameter equation (3C, D, 3E). A comparison of the individual equations at $S = 35\text{‰}$ is shown in Figs 3 and 4. The sound-derived data of CHEN and MILLERO (1978) are in excellent agreement with the results of Bradshaw and Schleicher for low temperatures but appear to deviate at high temperatures. The comparisons of Bradshaw and Schleicher's results with

Table 3. Comparisons of the specific volume measurements of BRADSHAW and SCHLEICHER and CHEN and MILLERO at 10°C

$P(\text{bar})$	$\Delta v 10^6$ *	$\Delta(v - v_w) 10^6 \dagger$
0	0	0
100	2	-1
200	4	0
300	6	1
400	6	0
500	7	0
600	7	1
700	9	0
800	10	0
900	12	1
1000	14	0

* $\Delta v 10^6 = v^P$ (Chen and Millero) - v^P (Bradshaw and Schleicher).

† $\Delta(v - v_w) 10^6 = v - v_w$ (Chen and Millero) - $v - v_w$ (Bradshaw and Schleicher).

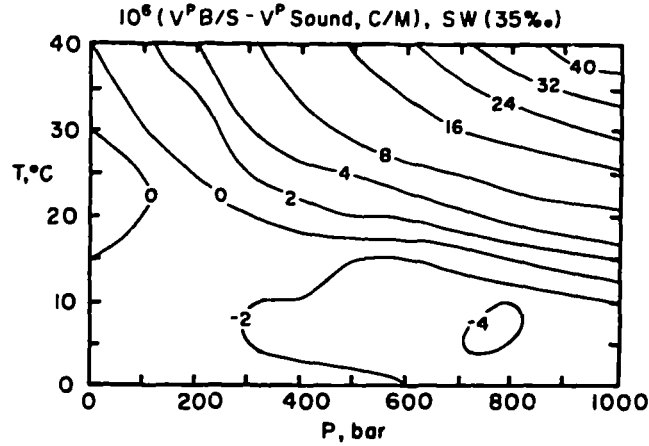


Fig. 3. A comparison of the individual equations at 35‰ seawater for v^P of Bradshaw and Schleicher and v^P sound of Chen and Millero vs pressure at several temperatures.

the direct measurements of Chen and Millero show the opposite trend. Over most of the oceanic range of temperature and pressure the three studies are in good agreement.

The combined results from the three independent data sets were fit to equation (11) and gave

$$c = 2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}t - 1.6078 \times 10^{-6}t^2 \quad (11a)$$

$$d = 1.9107_3 \times 10^{-4} \quad (11b)$$

$$e = -9.9348 \times 10^{-7} + 2.0816 \times 10^{-8}t + 9.1697 \times 10^{-10}t^2. \quad (11c)$$

The overall standard deviation is $9.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The standard deviation is 4.0×10^{-6} for Bradshaw and Schleicher's data, 9.6×10^{-6} for the direct measurements by Chen and Millero, and $5.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the sound measurements by Chen and

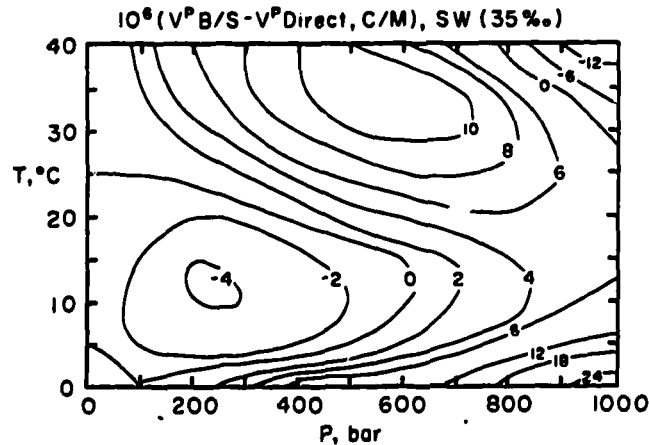


Fig. 4. A comparison of the individual equations at 35‰ seawater for v^P of Bradshaw and Schleicher and v^P direct of Chen and Millero vs pressure at several temperatures.

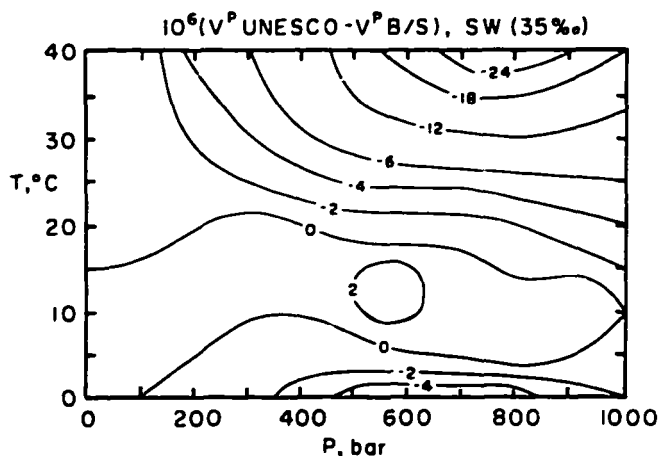


Fig. 5. A comparison of the new equation v^P and v^P of Bradshaw and Schleicher vs pressure for 35‰ seawater at several temperatures.

Millero. Over the oceanic ranges of P , T , and S the three independent data sets give an overall standard error of $5 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P .

Comparisons of the new equation with the equations generated from the three data sets are shown in Figs 5, 6, and 7. The full equation of state [equation (1)] is given in Table 4. The specific volume of seawater at pressure P can be determined from the secant bulk modulus equation using

$$v^P = v^0(1 - P/K). \quad (12)$$

The thermal expansibility [$\alpha^P = (1/v^P)(\partial v^P/\partial T)_P$] can be determined from

$$\alpha^P = \frac{1}{v^P} \left[\frac{\partial v^0}{\partial T} (1 - P/K) + \frac{v^0 P}{K^2} \frac{\partial K}{\partial T} \right]. \quad (13)$$

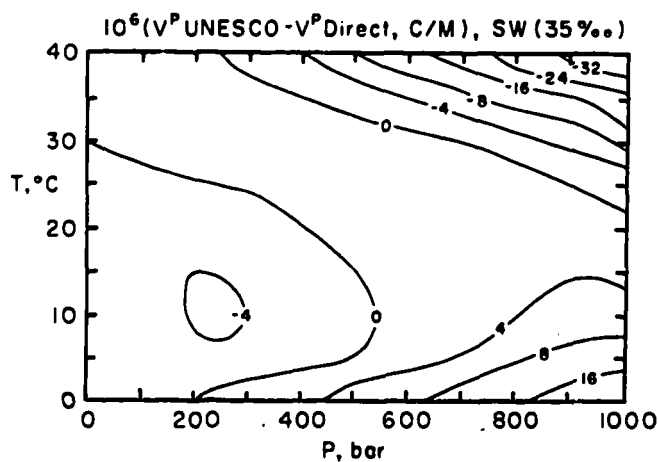


Fig. 6. A comparison of the new equation v^P and v^P direct of Chen and Millero vs pressure for 35‰ seawater at several temperatures.

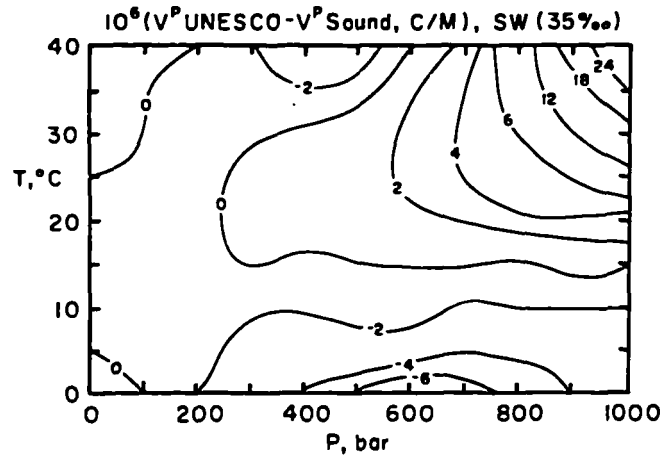


Fig. 7. A comparison of the new equation v^P and v^P sound of Chen and Millero vs pressure for 35‰ seawater at several temperatures.

Table 4. New UNESCO high pressure equation of state for seawater

$$\begin{aligned}
 K &= v^0 P / (v^0 - v^P) = K^0 + AP + BP^2 \\
 K^0 &= K_w^0 + aS + bS^{3/2} \\
 A &= A_w + cS + dS^{3/2} \\
 B &= B_w + eS \\
 K_w^0 &= 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2}t^3 - 5.155288 \times 10^{-5}t^4 \\
 A_w &= 3.239908 + 1.43713 \times 10^{-3}t + 1.16092 \times 10^{-4}t^2 - 5.77905 \times 10^{-7}t^3 \\
 B_w &= 8.50935 \times 10^{-5} - 6.12293 \times 10^{-6}t + 5.2787 \times 10^{-8}t^2 \\
 a &= 54.6746 - 0.603459t + 1.09937 \times 10^{-2}t^2 - 6.1670 \times 10^{-5}t^3 \\
 b &= 7.944 \times 10^{-2} + 1.6483 \times 10^{-2}t - 5.3009 \times 10^{-4}t^2 \\
 c &= 2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}t - 1.6078 \times 10^{-6}t^2 \\
 d &= 1.9107_3 \times 10^{-4} \\
 e &= -9.9348 \times 10^{-7} + 2.0816 \times 10^{-8}t + 9.1697 \times 10^{-10}t^2
 \end{aligned}$$

Check values:

For $t = 0, S = 0, P = 1000, K = 22977.21$;
 For $t = 0, S = 35, P = 1000, K = 24992.00$;
 For $t = 25, S = 0, P = 1000, K = 25405.10$;
 For $t = 25, S = 35, P = 1000, K = 27108.95$.

The isothermal compressibility [$\beta^P = -(1/v^P)(\partial v^P / \partial P)_T$] can be determined from

$$\beta^P = -\frac{1}{v^P} \left[\frac{v^0 P}{K^2} \frac{\partial K}{\partial P} \right]. \quad (14)$$

Values of v^P , α^P , and β^P calculated for seawater of various salinities are given elsewhere (MILLERO *et al.*, 1979).

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SUMMARY OF DATA TREATMENT FOR THE INTERNATIONAL HIGH PRESSURE
EQUATION OF STATE FOR SEAWATER

By

Frank J. Millero¹, Chen-Tung Chen²,
Alvin Bradshaw³ and Karl Schleicher³

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1. Rosenstiel School of Marine and Atmospheric Science, University of Miami, Miami, Florida 33149.
2. School of Oceanography, Oregon State University, Corvallis, Oregon 97331.
3. Woods Hole Oceanographic Institution, Woods Hole, Mass. 02543.

ABSTRACT

This data report gives a thorough summary of the formulation of a new international high pressure equation of state for seawater. The results of Chen and Millero (1976, 1978), Chen, Fine and Millero (1977) and Bradshaw and Schleicher (1970, 1976, unpublished results) were used as a data source. The form of the equation of state is a second degree secant bulk modulus equation

$$K = Pv^0 / (v^0 - v^P) = K^0 + AP + BP^2$$

$$K^0 = K_W^0 + aS + bS^{3/2}$$

$$A = A_W + cS + dS^{3/2}$$

$$B = B_W + eS$$

where v^0 and v^P are the specific volume at 0 and P applied pressure and S is the salinity (‰). The coefficients K_W^0 , A_W and B_W for the pure water part of the equation of state are given by

$$K_W^0 = 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2}t^3 \\ - 5.155288 \times 10^{-5}t^4$$

$$A_W = 3.239908 + 1.43713 \times 10^{-3}t + 1.16092 \times 10^{-4}t^2 \\ - 5.77905 \times 10^{-7}t^3$$

$$B_W = 8.50935 \times 10^{-5} - 6.12293 \times 10^{-6}t + 5.2787 \times 10^{-8}t^2$$

The standard error of the pure water part of the equation of state is $4.33 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v_W^P . The coefficients a, b, c, d and e are given by

$$a = 54.6746 - 0.603459t + 1.09987 \times 10^{-2}t^2 - 6.167 \times 10^{-5}t^3$$

$$b = 7.944 \times 10^{-2} + 1.6483 \times 10^{-2}t - 5.3009 \times 10^{-4}t^2$$

$$c = 2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}t - 1.6078 \times 10^{-6}t^2$$

$$d = 1.9107_5 \times 10^{-4}$$

$$e = -9.9348 \times 10^{-7} + 2.0816 \times 10^{-8}t + 9.1697 \times 10^{-10}t^2$$

The overall standard error of the seawater equation of state is $9.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . Over the oceanic ranges of temperature, pressure and salinity ($t = -4$ to 30°C , $P = 0$ to 1000 bars, $S = 30$ to 40 ‰) the standard error is $5.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . Tables of the specific volume v^P , the thermal expansibility, $\alpha^P = (1/v^P)(\partial v^P/\partial T)_P$, and $\beta^P = -(1/v^P)(\partial v^P/\partial P)_T$ for seawater from 0 to 40 ‰ salinity (5 ‰ intervals), 0 to 40°C (5° intervals) and 0 to 1000 bars (100 bar intervals) have been generated from the new equation of state and are given elsewhere (UNESCO 1981).

INTRODUCTION

At the eighth meeting of the Joint Panel on Oceanographic Tables and Standards (UNESCO, 1978) a recommendation was made to formulate a new equation of state for seawater based on the high pressure specific volume data (v) of Chen and Millero (1976, 1978), Chen, Fine and Millero (1977) and Bradshaw and Schleicher (1970, 1976, unpublished data). This data report gives a thorough summary of the formulation of this new international equation of state for seawater.

The form of the high pressure equation of state is the second degree secant bulk modulus (K)

$$K = Pv^0 / (v^0 - v^P) = K^0 + AP + BP^2 \quad (1)$$

$$K^0 = K_W^0 + aS + bS^{3/2} \quad (1a)$$

$$A = A_W + cS + dS^{3/2} \quad (1b)$$

$$B = B_W + eS \quad (1c)$$

where K_W^0 , A_W and B_W are temperature dependent parameters for pure water (W) and a , b , c , etc., are temperature dependent parameters for seawater (the superscript zero or P are applied pressure and S is the salinity in ‰). It should be pointed out that the pure water (K_W^0 , A_W , and B_W) and the 1 atm specific volume (v^0) parts of the equation of state are independent of the high pressure terms (a , b , c , d and e). It is thus, possible to use the high pressure part of the equation of state with other values for the pure water terms (K_W^0 , A_W , and B_W) and the 1 atm terms (v^0).

Data Set For The Equation of State

As agreed upon at the 8th meeting of the Joint Panel on Oceanographic Tables and Standards, the data set for the equation of state of seawater will include :

1. The 1 atm seawater density data of Millero, Gonzalez, and Ward (J. Mar. Res., 34: 61-93, 1976). The data consist of 115 points from 0.5 to 40^o/oo salinity and 0 to 40°C.
2. The high pressure specific volume data of Chen and Millero (Deep-Sea Res., 23: 595-612, 1976). The data consist of 486 points from 0 to 40°C, 5 to 40^o/oo salinity, and 100 to 1000 bars.
3. The high pressure compression data of Bradshaw and Schleicher (Deep-Sea Res., 23: 583-593, 1976). The data consist of 40 points at 10°C, 0 to 40^o/oo salinity, and 8 to 1000 bars. This data will be used to convert the relative expansibility measurements to absolute values of specific volume.
4. The high pressure expansibility data of Bradshaw and Schleicher (Deep-Sea Res., 17: 691-706, 1970; and the results to be published). The data consist of 612 points from -4 to 30°C, 0 to 40^o/oo salinity, and 8 to 1000 bars (208 for H₂O and 404 for seawater).
5. The sound derived specific volumes for water (Chen, Fine, and Millero, J. Chem. Phys., 66: 2142-2144, 1977), and seawater (Chen and Millero, J. Mar. Res., in press). The data consist of 810 points from 0 to 40°C, 0 to 40^o/oo salinity, and 0 to 1000 bars (90 for H₂O and 720 for seawater).

A summary of the data set is given in Table 1.

TABLE 1
SUMMARY OF THE DATA USED FOR THE EQUATION OF STATE

1 atm Data

<u>S(°/oo)</u>	<u>Temperature Range</u>	<u>Number of Points</u>	<u>Reference</u>
0.5 to 22	0 to 40°C	73	Millero, Gonzalez, and Ward (1976)
24 to 40	0 to 40°C	<u>42</u>	
		115	

Pressure Data

<u>S(°/oo)</u>	<u>Pressure Range</u>	<u>Temperature Range</u>	<u>Number of Points</u>
0	8 to 1000 bars	-4 to 40°C	298
5	100 to 1000	0 to 40	135
10	100 to 1000	0 to 40	134
15	8 to 1000	-2 to 40	202
20	100 to 1000	0 to 40	134
25	100 to 1000	0 to 40	135
30	8 to 1000	-2 to 40	244
35	8 to 1000	-4 to 40	381
40	8 to 1000	-2 to 40	<u>245</u>
			1908

One Atmosphere Data Treatment

This section summarizes the data treatment on the 1 atm part of the equation of state (v^0 and K^0). The density of water at 1 atm for standard mean ocean water (SMOW) at various temperatures (0 to 40°C) were determined from the equation of Bigg (1967). Since the Miami water used to dilute the standard seawater has a density of $1 \times 10^{-6} \text{ g cm}^{-3}$ lower than SMOW, (Millero and Emmet, 1976) the values to be used with the 1 atm equation of state of ρ for water should be lower by 1×10^{-6} . This adjustment was made by subtracting 1×10^{-6} from the first term of the Bigg equation giving

$$\begin{aligned} \rho(\text{MIAMI}), \text{ g cm}^{-3} &= 0.999841594 + 6.793952 \times 10^{-5} t \\ &\quad - 9.025290 \times 10^{-6} t^2 + 1.001685 \times 10^{-7} t^3 \\ &\quad - 1.120083 \times 10^{-9} t^4 + 6.536332 \times 10^{-12} t^5 \end{aligned} \quad (2)$$

Values of the density and specific volume calculated from equation (2) at various temperatures are given in Table 2. It should be pointed out that the densities calculated from the Bigg equation agree with the wider range equation of Kell (1975) to $\pm 2 \times 10^{-6} \text{ g cm}^{-3}$ from 0 to 40°C. The thermal expansibilities agree to within $\pm 0.4 \times 10^{-6} \text{ deg}^{-1}$ from 0 to 40°C. The density equation of seawater solutions at 1 atm of Millero, Gonzalez and Ward (1976) were expressed as differences in the specific gravities (or densities expressed with $\rho_{\text{MAX}} = 1.000000 \text{ g ml}^{-1}$). To convert these values to absolute differences ($\rho - \rho^0$) in density (g cm^{-3}), it is necessary to multiply the values of ($d - d_0$) by $0.999974 \text{ g cm}^{-3}$. Since the maximum value of $d - d_0$ is $\sim 32.3 \times 10^{-3}$, this decreases the value of $d - d_0$ by only 1×10^{-6} , which is approximately the precision of the measurements. Since the 1 atm

TABLE 2

THE DENSITIES AND SPECIFIC VOLUMES OF MIAMI WATER

FROM THE BIGG EQUATION

<u>Temp(°C)</u>	<u>$\rho(\text{g cm}^{-3})$</u>	<u>$\nu(\text{cm}^{-3} \text{g}^{-1})$</u>
-4	0.999418	1.000583
-2	0.999669	1.000332
-1	0.999764	1.000236
0	0.999842	1.000158
2	0.999942	1.000058
4	0.999974	1.000026
5	0.999966	1.000034
6	0.999942	1.000058
8	0.999950	1.000150
10	0.999701	1.000299
12	0.999499	1.000502
14	0.999245	1.000755
15	0.999101	1.000900
16	0.998944	1.001057
18	0.998597	1.001405
20	0.998205	1.001798
22	0.997772	1.002233
24	0.997298	1.002709
25	0.997047	1.002962
26	0.996786	1.003224
28	0.996236	1.003778
30	0.995650	1.004369
32	0.995029	1.004996
34	0.994375	1.005657
35	0.994035	1.006001
40	0.992219	1.007842

seawater equation of state is given by the function

$$d - d_0 = A S + B S^{3/2} + C S^2 \quad (3)$$

where A, B, and C are temperature dependent parameters, the coefficients can be adjusted by multiplying by 0.999974.

$$A = 8.25917 \times 10^{-4} - 4.4490 \times 10^{-6} t + 1.0485 \times 10^{-7} t^2 - 1.2580 \times 10^{-9} t^3 + 3.315 \times 10^{-12} t^4 \quad (4)$$

$$B = -6.33761 \times 10^{-6} + 2.8441 \times 10^{-7} t - 1.6871 \times 10^{-8} t^2 + 2.83258 \times 10^{-10} t^3 \quad (5)$$

$$C = 5.4705 \times 10^{-7} - 1.97975 \times 10^{-8} t + 1.6641 \times 10^{-9} t^2 - 3.1203 \times 10^{-11} t^3 \quad (6)$$

The densities of seawater solutions at 1 atm (g cm^{-3}) can be calculated from

$$\begin{aligned} \rho = & (0.999841594 + 6.793952 \times 10^{-5} t - 9.095290 \times 10^{-6} t^2 \\ & + 1.001685 \times 10^{-7} t^3 - 1.120083 \times 10^{-9} t^4 + 6.536332 \times 10^{-12} t^5) \\ & + (8.25917 \times 10^{-4} - 4.4490 \times 10^{-6} t + 1.0485 \times 10^{-7} t^2 \\ & - 1.2580 \times 10^{-9} t^3 + 3.315 \times 10^{-12} t^4) S \\ & + (-6.33761 \times 10^{-6} + 2.8441 \times 10^{-7} t - 1.6871 \times 10^{-8} t^2 \\ & + 2.83258 \times 10^{-10} t^3) S^{3/2} + (5.4705 \times 10^{-7} \\ & - 1.97975 \times 10^{-8} t + 1.6641 \times 10^{-9} t^2 \\ & - 3.1203 \times 10^{-11} t^3) S^2 \end{aligned} \quad (7)$$

The values of ρ determined from equation (7) are given in Table 3. The values of the specific volume, v , determined from $1/\rho$ are given in Table 4.

TABLE 3

THE DENSITIES OF SEAWATER SOLUTIONS AT 1 ATM

<u>ρ (g cm⁻³)</u>					
<u>S(°/oo)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	0.999842	0.999966	0.999701	0.999101	0.998205
5	1.003914	1.003949	1.003612	1.002952	1.002009
10	1.007955	1.007908	1.007502	1.006784	1.005793
15	1.011985	1.011859	1.011386	1.010612	1.009575
20	1.016012	1.015809	1.015271	1.014443	1.013360
25	1.020039	1.019760	1.019159	1.018279	1.017152
30	1.024070	1.023716	1.023053	1.022122	1.020953
35	1.028107	1.027678	1.026954	1.025974	1.024764
40	1.032150	1.031647	1.030864	1.029837	1.028588

<u>S(°/oo)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	0.997047	0.995650	0.994035	0.992219
5	1.000812	0.999383	0.997742	0.995906
10	1.004557	1.003097	1.001432	0.999577
15	1.008300	1.006810	1.005120	1.003247
20	1.012048	1.010526	1.008812	1.006919
25	1.015803	1.014251	1.012511	1.010596
30	1.019569	1.017986	1.016219	1.014280
35	1.023346	1.021733	1.019938	1.017972
40	1.027136	1.025493	1.023669	1.021672

TABLE 4
THE SPECIFIC VOLUMES OF SEAWATER SOLUTIONS AT 1 ATM

<u>S(°/oo)</u>	<u>v(cm³ g⁻¹)</u>				
	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	1.000158	1.000034	1.000299	1.000900	1.001798
5	0.996101	0.996066	0.996401	0.997057	0.997995
10	0.992108	0.992154	0.992554	0.993262	0.994240
15	0.988157	0.988280	0.988742	0.989499	0.990516
20	0.984240	0.984437	0.984959	0.985763	0.986816
25	0.980354	0.980623	0.981201	0.982050	0.983137
30	0.976496	0.976834	0.977467	0.978357	0.979477
35	0.972662	0.973068	0.973753	0.974684	0.975834
40	0.968851	0.969324	0.970060	0.971028	0.972206

<u>S(°/oo)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	1.002962	1.004369	1.006001	1.007842
5	0.999189	1.000617	1.002263	1.004111
10	0.995464	0.996912	0.998570	1.000423
15	0.991768	0.993236	0.994906	0.996763
20	0.988096	0.989583	0.991265	0.993128
25	0.984443	0.985949	0.987644	0.989515
30	0.980807	0.982332	0.984040	0.985921
35	0.977187	0.978729	0.980452	0.982346
40	0.973580	0.975140	0.976878	0.978787

The expansibilities of seawater solutions at 1 atm can be calculated from the temperature dependency of ρ , $\alpha = -1/\rho (\partial\rho/\partial T)_P = 1/v (\partial v/\partial P)_P$. The values of $(\partial\rho/\partial T)$ at 1 atm can be calculated from

$$\begin{aligned} \left(\frac{\partial\rho}{\partial T}\right) &= \left(\frac{\partial\rho^0}{\partial T}\right) + \left(\frac{\partial A}{\partial T}\right) S + \left(\frac{B}{T}\right) S^{1/2} \\ &+ \left(\frac{\partial C}{\partial T}\right) S^2 \end{aligned} \quad (8)$$

$$\begin{aligned} \frac{\partial\rho^0}{\partial T} &= 6.793952 \times 10^{-5} - 18.19058 \times 10^{-6} t \\ &+ 3.005055 \times 10^{-7} t^2 - 4.480332 \times 10^{-9} t^3 \\ &+ 32.68166 \times 10^{-12} t^4 \end{aligned} \quad (9)$$

$$\begin{aligned} \frac{\partial A}{\partial T} &= -4.4490 \times 10^{-6} + 2.0970 \times 10^{-7} t \\ &- 3.7740 \times 10^{-9} t^2 + 13.260 \times 10^{-12} t^3 \end{aligned} \quad (10)$$

$$\frac{\partial B}{\partial T} = 2.8441 \times 10^{-7} - 3.3742 \times 10^{-8} t + 8.49774 \times 10^{-10} t^2 \quad (11)$$

$$\frac{\partial C}{\partial T} = -1.9797_5 \times 10^{-8} + 3.3282 \times 10^{-9} t - 9.3609 \times 10^{-11} t^2 \quad (12)$$

These values of $(\partial\rho/\partial T)$ are tabulated in Table 5. The thermal expansibility calculated from equations (7) and (8) are tabulated in Table 6.

TABLE 5
THE VALUES OF $(\partial\rho/\partial T)$ FOR SEAWATER SOLUTIONS AT 1 ATM

$\frac{\partial\rho}{\partial T} \times 10^6 \text{ (g cm}^{-3}\text{K}^{-1}\text{)}$					
<u>s(°/oo)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	67.94	-16.04	-88.07	-150.77	-206.28
5	48.38	-32.11	-101.19	-161.43	-214.91
10	30.46	-47.19	-113.81	-171.91	-223.53
15	13.27	-61.72	-126.03	-182.12	-232.00
20	-3.52	-75.85	-137.88	-192.03	-240.24
25	-20.11	-89.69	-149.40	-201.62	-248.23
30	-36.61	-103.28	-160.59	-210.87	-255.95
35	-53.14	-116.68	-171.46	-219.77	-263.37
40	-69.75	-129.92	-182.03	-228.31	-270.49
<u>s(°/oo)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	
0	-256.25	-301.82	-343.66	-381.95	
5	-263.23	-307.49	-348.32	-385.82	
10	-270.22	-313.04	-352.54	-388.79	
15	-277.14	-318.57	-356.78	-391.81	
20	-283.96	-324.13	-361.22	-395.21	
25	-290.64	-329.74	-365.95	-399.20	
30	-297.18	-335.43	-371.04	-403.90	
35	-303.58	-341.19	-376.53	-409.42	
40	-309.82	-347.06	-382.46	-415.82	

TABLE 6
THE THERMAL EXPANSIBILITIES (K^{-1}) OF SEAWATER SOLUTIONS AT 1 ATM

<u>S($^{\circ}/\infty$)</u>	<u>$\alpha 10^6 (K^{-1})$</u>				
	<u>0$^{\circ}$C</u>	<u>5$^{\circ}$C</u>	<u>10$^{\circ}$C</u>	<u>15$^{\circ}$C</u>	<u>20$^{\circ}$C</u>
0	-67.95	16.04	88.10	150.91	206.65
5	-48.19	31.99	100.83	160.95	214.48
10	-30.22	46.82	112.96	170.75	222.25
15	-13.12	61.00	124.61	180.21	229.80
20	3.47	74.67	135.81	189.30	237.08
25	19.71	87.95	146.59	198.00	244.05
30	35.75	100.89	156.97	206.30	250.70
35	51.68	113.54	166.96	214.20	257.01
40	67.57	125.93	176.58	221.69	262.97

<u>S($^{\circ}/\infty$)</u>	<u>25$^{\circ}$C</u>	<u>30$^{\circ}$C</u>	<u>35$^{\circ}$C</u>	<u>40$^{\circ}$C</u>
0	257.01	303.14	345.73	384.95
5	263.02	307.68	349.11	387.41
10	269.00	312.07	352.03	388.96
15	274.86	316.41	354.96	390.54
20	280.58	320.75	358.07	392.50
25	286.12	325.11	361.43	395.02
30	291.48	329.50	365.12	398.22
35	296.65	333.94	369.17	402.19
40	301.63	338.43	373.62	407.00

The 1 atm values of the secant bulk modulus (K^0) have been determined from the sound speed measurements of Del Grosso (1970) and Del Grosso and Mader (1972) for pure water and Millero and Kubinski (1975) for seawater. Kell (1975) has determined the isothermal compressibilities of water at 1 atm (β_T^0) from the sound speed measurements of Del Grosso (1970) and Del Grosso and Mader (1972), and the heat capacities of de Haas (1950),

$$\beta_T^0 = \frac{1}{\rho U^2} + \frac{T\alpha^2}{\rho C_p} \quad (13)$$

where U is the sound velocity, $\alpha = 1/v(\partial v/\partial T)_p$ is the thermal expansibility and C_p is the specific heat capacity (at constant P). He represented the values from 0 to 95°C (based on 148 data points) by

$$\begin{aligned} 10^6 \beta_T^0 = & (50.88496 + 0.6163813t + 1.459187 \times 10^{-3}t \\ & + 20.08438 \times 10^{-6}t^3 - 58.47727 \times 10^{-9}t^4 \\ & + 410.4110 \times 10^{-12}t^5)/(1 + 19.67348 \times 10^{-3}t) \end{aligned} \quad (14)$$

with a standard error of $0.3 \times 10^{-9} \text{ bar}^{-1}$. The values of β_T^0 from 0 to 40°C determined from this equation are given in Table 7. Also given in Table 7 are the values of $K^0 = 1/\beta_T^0$ at various temperatures. An error of $0.3 \times 10^{-9} \text{ bar}^{-1}$ in β_T^0 yields an error of ~ 0.15 in K . Chen, Fine and Millero (1977) refitted the values of $K^0 = 1/\beta_T^0$ for pure water determined by Kell (1975) from 0 to 100°C by

$$\begin{aligned} K_W^0 = & 19652.17 + 148.18t - 2.29995t^2 + 0.012810t^3 \\ & - 4.91564 \times 10^{-5}t^4 + 1.03553 \times 10^{-7}t^5 \end{aligned} \quad (15)$$

From 0 to 40°C this equation yields values of K_W^0 that are within 0.80 with those given in Table 7, which is equivalent to a difference of \sim

TABLE 7

VALUES OF β_T^0 AND K_W^0 FOR WATER AT 1 ATMOSPHERE FROM 0 TO 40°C

Temp	$\beta_T^0 10^6$	$\Delta\beta_T 10^6$ ^a	K_W^0	ΔK_W ^b
0	50.8850	0.0001	19652.16	-0.05
2	50.1505	-0.0003	19939.98	0.13
4	49.4812	-0.0004	20209.70	0.18
5	49.1692	-0.0003	20337.94	0.14
6	48.8712	-0.0003	20461.95	0.12
8	48.3152	-0.0001	20697.42	0.03
10	47.8086	0.0001	20916.74	-0.05
12	47.3474	0.0002	21120.48	-0.11
14	46.9280	0.0002	21309.24	-0.10
15	46.7331	0.0003	21398.11	-0.12
16	46.5475	0.0003	21483.43	-0.12
18	46.2029	0.0001	21643.66	-0.07
20	45.8918	0.0000	21790.39	0.02
22	45.6122	-0.0001	21923.96	0.03
24	45.3619	-0.0001	22044.93	0.07
25	45.2472	-0.0002	22100.82	0.10
26	45.1392	-0.0002	22153.69	0.11
28	44.9427	-0.0001	22250.55	0.05
30	44.7707	-0.0001	22336.04	0.04
35	44.4404	0.0002	22502.05	-0.12
40	44.2391	-0.0001	22604.44	0.04

a) $\Delta\beta_T 10^6 = 10^6 \beta_T^0(\text{Kell}) - 10^6 \beta_T^0(\text{calc. from equation 16})$

b) $\Delta K = K_W^0(\text{Kell}) - K_W^0(\text{calc. from equation 16})$

$0.002 \times 10^{-6} \text{ bar}^{-1}$ in β_T^0 . By refitting the values of $K_W^0 = 1/\beta_W^0$ from Kell's results from 0 to 40°C, we have been able to eliminate one temperature term and improved the standard error. The equation is

$$K_W^0 = 19652.21 + 148.4206t - 2.327105t^2 + 1.360477 \times 10^{-2}t^3 - 5.155288 \times 10^{-5}t^4 \quad (16)$$

and the standard deviation is 0.10 bar in K_W^0 ($0.0002 \times 10^{-6} \text{ bar}^{-1}$ in β_W^0). The maximum deviation in K_W^0 is 0.18 bar (which is equivalent to $\sim 0.0004 \times 10^{-6} \text{ bar}^{-1}$ in β_T^0).

The most reliable estimates of β_T^0 for seawater at 1 atm are those determined from sound velocities. Chen and Millero (1977) have refitted the relative sound speed measurements of Millero and Kubinski (1975) to an equation of the form

$$U^0 - U_W^0 (\text{m sec}^{-1}) = A_U S + B_U S^{3/2} + C_U S^2 \quad (17)$$

where the coefficients A_U , B_U and C_U are given by

$$A_U = 1.389 - 1.262 \times 10^{-2}t + 7.164 \times 10^{-5}t^2 + 2.006 \times 10^{-6}t^3 - 3.21 \times 10^{-8}t^4 \quad (17a)$$

$$B_U = -1.922 \times 10^{-2} - 4.42 \times 10^{-5}t \quad (17b)$$

$$C_U = 1.727 \times 10^{-3} \quad (17c)$$

The standard deviation of the fit was 0.03 m sec^{-1} (which is equivalent to an error of $\sim 0.002 \times 10^{-6} \text{ bar}^{-1}$ in $\beta_S = 1/\rho U^2$). The values of $U^0 - U_W^0$ calculated from equation (17) agree to within 0.05 m sec^{-1} with the measurements of Del Grosso (1972, 1974) and Kroebel and Mahrt (1976) and to within 0.03 m sec^{-1} with the equation of Millero and Kubinski (1975). The values of β_S calculated from

$$\beta_S = 1/\rho U^2 \quad (18)$$

are given in Table 8. To convert these values of β_S to isothermal compressibilities, it is necessary to have specific heat data (equation 13) for seawater solutions. Millero, Perron and Desnoyers (1973) have made precise measurements on the relative specific heat of seawater solutions from 5 to 35°C . They fitted their results to equations of the form (to a standard error of $0.0008 \text{ J K}^{-1} \text{ g}^{-1}$)

$$C_p = C_{pW} + A_{Cp} Cl + B_{Cp} Cl^{3/2} \quad (19)$$

where C_{pW} is given by

$$C_{pW} = 4.2174 - 3.720283 \times 10^{-3} t + 1.412855 \times 10^{-4} t^2 - 2.654387 \times 10^{-6} t^3 + 2.093236 \times 10^{-8} t^4 \quad (19a)$$

and the coefficients A_{Cp} and B_{Cp} are given by

$$A_{Cp} = -1.38085 \times 10^{-2} + 1.938 \times 10^{-4} t - 2.50 \times 10^{-6} t^2 \quad (19b)$$

TABLE 8

VALUES OF β_S FOR SEAWATER SOLUTIONS AT 1 ATM CALCULATED FROM SOUND SPEEDS^a

<u>S(°/oo)</u>	<u>$10^6 \beta_S$</u>								
	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	50.854 ₇	49.167 ₅	47.756 ₃	46.576 ₂	45.591 ₆	44.773 ₅	44.100 ₁	43.553 ₂	43.117 ₈
5	50.163	48.531	47.167	46.024	45.071	44.279	43.627	43.098	42.676
10	49.491	47.913	46.593	45.489	44.566	43.798	43.167	42.655	42.248
15	48.835	47.309	46.032	44.963	44.069	43.327	42.716	42.220	41.827
20	48.189	46.715	45.479	44.446	43.581	42.863	42.271	41.792	41.413
25	47.556	46.130	44.936	43.936	43.100	42.405	41.833	41.370	41.004
30	46.932	45.554	44.400	43.433	42.625	41.953	41.399	40.952	40.600
35	46.317	44.986	43.871	42.937	42.156	41.506	40.971	40.538	40.200
40	45.711	44.426	43.349	42.446	41.691	41.063	40.546	40.129	39.804

a) $\beta_S = 1/\rho U^2$, where ρ is the density (g cm^{-3}) Millero, Gonzalez and Ward (1976) and U is the speed of sound (cm sec^{-1}) Chen and Millero (1977).

$$B_{Cp} = 4.29875 \times 10^{-4} - 9.90 \times 10^{-6} t + 1.250 \times 10^{-7} t^2 \quad (19c)$$

Equation (19) can be converted to a function of $S(^{\circ}/\infty)$

$$Cp = Cp_W + A_{Cp}' S + B_{Cp}' S^{3/2} \quad (20)$$

by dividing the coefficient A_{Cp} by 1.80655 and B_{Cp} by $(1.80655)^{3/2}$

$$A_{Cp}' = -7.64357_5 \times 10^{-3} + 1.07276_3 \times 10^{-4} t - 1.3838_5 \times 10^{-6} t^2 \quad (20a)$$

$$B_{Cp}' = 1.77038_3 \times 10^{-4} - 4.0771_8 \times 10^{-6} t + 5.148 \times 10^{-8} t^2 \quad (20b)$$

The values of Cp calculated from equations (19a) and (20) are tabulated in Table 9. The values of Cp determined by Millero et al. (1973) agree with the measurements of Cox and Smith (1959) and Bromley et al. (1967, 1968, 1970) to within $\pm 0.002 \text{ J K}^{-1} \text{ g}^{-1}$ from 0 to 40°C and 0 to 40^o/∞ salinity. (Comparisons at 35^o/∞ are given in Table 10.) An error of ± 0.002 in Cp is equivalent to a maximum error of 0.001×10^{-6} in $T\alpha^2/\rho Cp$ (see Table 11). The largest source of errors in determining $T\alpha^2/\rho Cp$ is uncertainties in the expansibilities, α . The values of α determined from the equation of state of Millero, Gonzalez and Ward (1976) agree with those calculated from Knudsen's equation (1901) to $0.6 \times 10^{-6} \text{ K}^{-1}$. The errors in $T\alpha^2/\rho Cp$ at various temperatures, due to an error of $0.6 \times 10^{-6} \text{ K}^{-1}$ in α , are shown in Table 11. The largest errors of $0.003_7 \times 10^{-6}$ occur at the highest temperatures. The maximum error in $T\alpha^2/\rho Cp$ at 1 atm is $\sim 0.004 \times 10^{-6} \text{ bar}^{-1}$ at the high temperatures and salinities.

The values of $(T\alpha^2/\rho Cp)10^6$ calculated from the equation of state of

TABLE 9

SPECIFIC HEAT OF SEAWATER SOLUTIONS, C_p , AT 1 ATM ($J g^{-1} K^{-1}$)

<u>S(°/oo)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	4.2174	4.2020	4.1919	4.1855	4.1816
5	4.1812	4.1681	4.1599	4.1552	4.1526
10	4.1466	4.1356	4.1293	4.1261	4.1248
15	4.1130	4.1041	4.0995	4.0977	4.0976
20	4.0804	4.0733	4.0704	4.0700	4.0710
25	4.0484	4.0432	4.0418	4.0428	4.0448
30	4.0172	4.0137	4.0139	4.0161	4.0191
35	3.9865	3.9847	3.9864	3.9898	3.9938
40	3.9564	3.9563	3.9593	3.9639	3.9689

<u>S(°/oo)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	4.1794	4.1782	4.1779	4.1784
5	4.1515	4.1510	4.1511	4.1516
10	4.1245	4.1247	4.1251	4.1258
15	4.0982	4.0990	4.0998	4.1005
20	4.0725	4.0738	4.0749	4.0757
25	4.0471	4.0491	4.0505	4.0513
30	4.0222	4.0247	4.0264	4.0272
35	3.9977	4.0007	4.0026	4.0035
40	3.9735	3.9769	3.9792	3.9801

TABLE 10

COMPARISONS OF THE MEASURED AND CALCULATED SPECIFIC HEATS OF SEAWATER

OF 35⁰/∞ SALINITY

<u>Temp</u>	<u>Cp(smooth)</u>	<u>Cox and Smith</u>	<u>Δ10⁴</u>	<u>Bromley</u>	<u>Δ10⁴</u>
0°C	3.9865	3.985	15	3.9871	-6
5	3.9847	3.986	-13	---	---
10	3.9864	3.988	-16	3.9880	-16
15	3.9898	3.990	-2	---	---
20	3.9938	3.993	8	3.9940	-2
25	3.9977	3.995	17	---	---
30	4.0007	3.999		4.0002	5
35	4.0026	---	---	---	---
40	4.0035	---	---	4.0051	<u>-16</u>
			<u>+ 12</u>		<u>+ 9</u>

TABLE 11

ERROR IN β_T FOR 35^o/oo SALINITY SEAWATER CALCULATED FROM SOUND SPEEDS,
HEAT CAPACITIES, AND EXPANSIBILITIES

Temp	$\Delta\beta_T 10^6 (\text{bar}^{-1})$			
	<u>From Sound Speed^a</u>	<u>From Heat Capacity^b</u>	<u>From Expansibility^c</u>	<u>Total^d</u>
0°C	0.0026	0.0000	0.0004	0.0026
10	0.0024	0.0001	0.0014	0.0028
20	0.0023	0.0002	0.0022	0.0032
30	0.0022	0.0004	0.0030	0.0037
40	0.0021	0.0006	0.0037	0.0043

a) Error due to $\pm 0.04 \text{ m sec}^{-1}$ in sound speed.

b) Error due to $\pm 0.004 \text{ j K}^{-1} \text{ g}^{-1}$ in heat capacity.

c) Error due to $\pm 0.6 \times 10^{-6} \text{ K}^{-1}$ in expansibility.

d) Total error = $\sqrt{\Sigma \Delta^2}$

Millero et al. (1976) and the heat capacities of Millero et al. (1973) are given in Table 12. The values of the isothermal compressibilities (β_T^0) calculated from equation (13) are given in Table 13. The results agree on the average to $\pm 0.002 \times 10^{-6}$ with the earlier calculations of Millero and Kubinski from 0 to 35°C. Larger errors of as much as 0.016×10^{-6} occur at 40°C due to errors in the values of α calculated from the earlier density measurements of Millero and Gonzalez. The results agree on the average to $\pm 0.02 \times 10^{-6}$ with the direct measurements of Lepple and Millero (1971). The total error in β_T^0 due to the errors in U and $T\alpha^2/\rho C_p$ is $\sim 0.004 \times 10^{-6} \text{ bar}^{-1}$ which is equivalent to an overall standard error of $\sim 2.0 \text{ bar}$ in K^0 .

The values of K^0 (Table 14) have been fitted to equations of the form

$$K^0 - K_W^0 = a S + b S^{3/2} + c S \quad (21)$$

where K_W^0 is given by equation (16).

A summary of the residuals and standard errors of the various forms of equation (21) are given in Table 15. To fit the values of K^0 to a σ better than 1.9, the S^2 term is needed. Since the expected standard error in K^0 is 2.0, the 8 parameter equations (with the S^2 term) are an overfit of the data. The analyses of the variance of the 6 and 7 parameter equations using the F-test

$$F = (\sigma_1^2)/(\sigma_2^2) \quad (22)$$

[where σ_1 and σ_2 are the standard errors of samples with size N_1 and N_2 (where N is the degree of freedom)], indicate that at 95% confidence level the 7 parameter equations are more reliable. Since the 7 parameter equations (4A, 2B, C) and (4A, 3B) are equivalent at the 95% confidence level, we have selected the equation without the S^2 term to represent K^0 .

The equation for K^0 at 1 atm for seawater is given by

$$K^0 = K_W^0 + a S + b S^{3/2} \quad (23)$$

TABLE 12

VALUES OF $T\alpha^2/\rho C_p \times 10^6$ FOR SEAWATER SOLUTIONS AT 1 ATM^a (bar⁻¹)

<u>s(°/oo)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	0.030 ₃	0.001 ₇	0.052 ₃	0.156 ₉	0.300 ₂
5	0.016	0.007	0.069	0.179	0.324
10	0.006	0.015	0.087	0.202	0.349
15	0.002	0.025	0.106	0.226	0.375
20	0.001	0.037	0.126	0.250	0.399
25	0.003	0.052	0.148	0.274	0.425
30	0.009	0.069	0.170	0.299	0.449
35	0.018	0.087	0.193	0.323	0.473
40	0.031	0.108	0.216	0.347	0.497

<u>s(°/oo)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	0.473 ₇	0.670 ₆	0.887 ₂	1.121 ₃
5	0.498	0.693	0.907	1.139
10	0.522	0.715	0.925	1.151
15	0.546	0.736	0.943	1.163
20	0.571	0.759	0.961	1.178
25	0.595	0.781	0.982	1.196
30	0.619	0.804	1.004	1.218
35	0.643	0.828	1.029	1.245
40	0.666	0.852	1.056	1.278

a) The values have been normalized by a maximum of 0.0006×10^{-6} to be consistent with the pure water values of Kell (1975).

TABLE 13

VALUES OF β_T^0 FOR SEAWATER SOLUTIONS CALCULATED FROM SOUND SPEEDS AT 1 ATM

$10^6 \beta_T^0 (\text{bar}^{-1})$					
<u>s(°/∞)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	50.885 ₀	49.169 ₂	47.808 ₆	46.733 ₁	45.891 ₈
5	50.179	48.538	47.236	46.203	45.395
10	49.497	47.928	46.680	45.691	44.915
15	48.837	47.334	46.138	45.189	44.444
20	48.190	46.752	45.605	44.696	43.980
25	47.559	46.182	45.084	44.210	43.525
30	46.941	45.623	44.570	43.732	43.074
35	46.335	45.073	44.064	43.260	42.629
40	45.742	44.534	43.565	42.793	42.188

<u>s(°/∞)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	45.247 ₂	44.770 ₇	44.440 ₄	44.239 ₁
5	44.777	44.320	44.005	43.815
10	44.320	43.882	43.580	43.399
15	43.873	43.452	43.163	42.990
20	43.434	43.030	42.753	42.591
25	43.000	42.614	42.352	42.200
30	42.572	42.203	41.956	41.818
35	42.149	41.799	41.567	41.445
40	41.729	41.398	41.185	41.082

TABLE 14
VALUES OF K^0 FOR SEAWATER SOLUTIONS

<u>AT ONE ATMOSPHERE (bar)</u>					
<u>s(°/oo)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	19652.16	20337.94	20916.74	21398.11	21790.39
5	19928.66	20602.41	21170.29	21643.62	22028.86
10	20203.24	20864.63	21422.45	21886.15	22264.28
15	20476.28	21126.46	21674.11	22129.28	22500.23
20	20751.19	21389.46	21927.42	22373.37	22737.61
25	21026.51	21653.46	22180.82	22619.32	22975.30
30	21303.34	21918.77	22436.62	22866.55	23215.86
35	21581.96	22186.23	22694.26	23116.04	23458.21
40	21861.75	22454.75	22954.21	23368.31	23703.42
<u>s(°/oo)</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	
0	22100.82	22336.04	22502.05	22604.44	
5	22332.89	22563.18	22724.69	22823.23	
10	22563.18	22788.39	22946.31	23042.01	
15	22793.06	23013.90	23167.99	23261.22	
20	23023.44	23239.60	23390.17	23479.14	
25	23255.81	23466.47	23611.64	23696.68	
30	23489.62	23695.00	23834.49	23913.15	
35	23725.36	23924.02	24057.55	24128.36	
40	23964.15	24155.76	24280.68	24341.56	

TABLE 15

SUMMARY OF BULK MODULUS FIT OF SEAWATER AT 1 ATM

$$K^0 = K_W^0 + a S + b S^{3/2} + c S^2$$

<u>Parameters</u>	<u>$\Sigma \Delta^2 (K)$</u>	<u>$\sigma (K)$</u>	<u>$10^6 \sigma (B)^a$</u>
10(4A, 4B, 2C)	48.01	0.88	0.0018
9(4A, 4B, C)	80.44	1.13	0.0023
9(4A, 3B, 2C)	58.04	0.96	0.0019
8(4A, 3B, C)	90.63	1.19	0.0024
8(4A, 2B, 2C)	233.48	1.91	0.0038
8(3A, 3B, 2C)	491.07	2.77	0.0055
7(3A, 3B, C)	524.26	2.84	0.0057
7(3A, 2B, 2C)	665.60	3.20	0.0064
7(4A, 2B, C)	267.85	2.03	0.0041
6(3A, B, 2C)	688.57	3.23	0.0065
9(3A, 3B, 3C)	455.94	2.69	0.0054

$$K^0 = K_W^0 + a S + b S^{3/2}$$

8(4A, 4B)	228.61	1.89	0.0038
7(4A, 3B)	239.62	1.92	0.0038
6(4A, 2B)	415.80	2.51	0.0050
6(3A, 3B)	671.62	3.19	0.0064
5(3A, 2B)	849.13	3.56	0.0071
5(4A, B)	525.28	2.80	0.0056

a) $\sigma (B) = 0.002 \times \sigma (K)$

where K_W^0 is given by equation (16).

$$a = 54.6746 - 0.603459t + 1.09987 \times 10^{-2}t^2 - 6.1670 \times 10^{-5}t^3 \quad (23a)$$

$$b = 7.944 \times 10^{-2} + 1.6483 \times 10^{-2}t - 5.3009 \times 10^{-4}t^2 \quad (23b)$$

A comparison of the differences between the measured and calculated values of K^0 and β_T calculated from equation (23) are given in Tables 16 and 17. The standard errors are 1.92 bar in K^0 and 0.0040 bar^{-1} in $\beta_T 10^6$.

High Pressure Data Treatment

In this section we will outline the data treatment of the high pressure PVT data for water and seawater. To make the various data sets self-consistent, it was necessary to make some adjustments to the published results, which are outlined below.

Bradshaw and Schleicher have made compression measurements at 10°C on pure water and seawater solutions ($S = 15, 30, 35$ and $40^\circ/\text{oo}$). Their compression results are given in Table 18. The observed volumes were used to calculate the compression relative to $P_A = 7.390$ bars (absolute). Third degree polynomial fits to the volume data and the 1 atm density equation of Chen and Millero (1976) were used to calculate the density at $P_A = 7.390$ bars. The specific volume compression relative to $P_A = 7.390$ were calculated from

$$v_{7.390} - v_{P_A} = (v_{7.390} - v_{P_A})/v_{7.390} \times \rho_{7.390} \quad (24)$$

The salinity dependence of the compressions ($v_{7.390} - v_{P_A}$) was assumed to be of the form

$$v_{7.390} - v_{P_A} = (P_A - 7.39)[a(P_A - 7.39)S + b(P - 7.39)S^{3/2} + c(P - 7.39)S^2] \quad (25)$$

where $a(P_A - 7.39)$, $b(P_A - 7.39)$ and $c(P_A - 7.39)$ are polynomials in $(P_A - 7.39)$. This form of salinity dependence has been found (Millero, Gonzalez and Ward, 1976) to represent the 1 atm density of seawater accurately and it represents the specific volumes as good, if not better, than it does the densities.

TABLE 16

DEVIATIONS IN K^0 FOR SEAWATER AT 1 ATM DETERMINED FROM EQUATION (23)

<u>S(°/∞)</u>	$\Delta K^0 = K^0(\text{meas}) - K^0(\text{calc})$								
	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
5	2.19	3.32	2.97	3.63	3.73	2.88	2.07	0.53	-0.88
10	1.77	2.88	2.83	2.47	2.56	2.41	1.28	0.09	-0.80
15	-0.66	1.16	1.03	0.66	0.74	0.55	0.20	-0.33	0.37
20	-1.62	-0.13	-0.05	-1.19	-0.62	-1.58	-1.16	-0.28	0.78
25	-2.49	-1.03	-1.84	-2.07	-2.49	-2.40	-1.75	-0.97	1.28
30	-2.16	-1.19	-1.95	-2.44	-2.24	-2.39	-1.05	-0.31	1.11
35	-0.31	0.30	-0.87	-1.26	-0.87	-0.99	-0.20	0.54	0.06
40	<u>2.46</u>	<u>2.37</u>	<u>1.90</u>	<u>2.04</u>	<u>2.74</u>	<u>2.95</u>	<u>3.07</u>	<u>1.43</u>	<u>-2.65</u>
$\sum \Delta^2 =$	28.00	28.86	29.45	37.12	40.88	38.06	20.94	3.85	12.06

TABLE 17
DEVIATIONS IN β_T^0 FOR SEAWATER AT 1 ATM DETERMINED FROM EQUATION (23)

<u>S(°/∞)</u>	<u>$\Delta\beta_T 10^6$ ^a</u>								
	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
5	-0.006	-0.008	-0.007	-0.008	-0.008	-0.006	-0.004	-0.001	0.002
10	-0.004	-0.007	-0.006	-0.005	-0.005	-0.005	-0.002	0.000	0.002
15	0.002	-0.003	-0.002	-0.001	-0.001	-0.001	0.000	0.001	-0.001
20	0.004	0.000	0.000	0.005	0.001	0.003	0.002	0.001	-0.001
25	0.006	0.002	0.004	0.004	0.005	0.004	0.003	0.002	-0.002
30	0.005	0.002	0.004	0.005	0.004	0.004	0.002	0.001	-0.002
35	0.001	-0.001	0.002	0.002	0.002	0.002	0.000	-0.001	0.000
40	<u>-0.005</u>	<u>-0.005</u>	<u>-0.004</u>	<u>-0.004</u>	<u>-0.005</u>	<u>-0.005</u>	<u>-0.005</u>	<u>-0.002</u>	<u>0.004</u>
$10^3 \sum \Delta^2 =$	159	156	141	176	161	132	62	13	34

a) $\Delta\beta_T = \beta_T(\text{meas}) - \beta_T(\text{calc})$

TABLE 18
OBSERVED VALUES OF THE VOLUME OF DISTILLED WATER AND SEAWATER AS A
FUNCTION OF PRESSURE AT 10°C (IPOTS 48)

<u>S = 0^a</u>		<u>S = 14.987^o/oo</u>		<u>S = 30.707^o/oo</u>	
<u>Pressure</u> <u>(bars, absolute)</u>	<u>Volume^b</u> <u>(cm³)</u>	<u>Pressure</u> <u>(bars, absolute)</u>	<u>Volume</u> <u>(cm³)</u>	<u>Pressure</u> <u>(bars, absolute)</u>	<u>Volume</u> <u>(cm³)</u>
7.39	43.20807 ^c	7.39	45.90810	7.39	46.66906
10.83	43.20095	10.84	45.90079	10.84	46.66187
17.72	43.18677	17.73	45.88623	17.73	46.64765
201.30	42.81979	201.30	45.50948	201.30	46.27816
401.05	42.44327	401.06	45.12261	401.05	45.89821
600.79	42.08825	600.80	44.75749	600.78	45.53897
800.52	41.75363	800.52	44.41250	800.48	45.19918
1000.19	41.43709	1000.21	44.08607	1000.16	44.87704
<u>S = 34.891^o/oo</u>		<u>S = 38.878^o/oo</u>			
7.39	46.98518	7.39	47.56691		
10.84	46.97806	10.84	47.55975		
17.73	46.96389	17.73	47.54543		
201.31	46.59543	201.30	47.17563		
401.06	46.21646	401.05	46.79512		
600.79	45.85797	600.79	46.43508		
800.50	45.51869	800.51	46.09438		
1000.18	45.19684	1000.18	45.77105		

a) Salinities are weight dilution values, obtained from JPOTS values by making use of equation (8), in Millero, Gonzalez and Ward (1976).

b) The volumes given here differ very slightly (by at most 0.00002 cm³) from those at 0, 30.7, 34.9, and 38.9 ‰ presented in Bradshaw and Schleicher (1976); the pressures also differ (by at most 0.5 bars, at 1000 bars); both differences were the consequence of 1) a revision of calibration results and fluid head calculations, and 2) calibration of the pressure gage.

c) The volumes at the lowest pressure were adjusted to exactly 7.390 bars.

From polynomial fits at each salinity the highest power of P_A required is not greater than 4. Letting $X = S^{1/2}$, fits of successively higher order were tried according to the scheme outlined in Table 19. The estimated values of $v_{1.01} - v_{P_A}$ are given by

$$v_{1.01} - v_{P_A} = f(X, P_A - 7.39) - f(X, - 6.38) \quad (26)$$

where

$$\begin{aligned} f(X, P - 7.39) = & (a_{01} + a_{11}X^2 + a_{21}X^3 + a_{31}X^4)(P_A - 7.39) \\ & + (a_{02} + a_{12}X^2)(P - 7.39)^2 + (a_{03} + a_{13}X^2)(P - 7.39)^3 \\ & + a_{04}(P - 7.39)^4 \end{aligned} \quad (27)$$

The coefficients for equation (27) are given in Table 20. The residuals of the observations for this fit are given in Table 21. Equation (27) can be converted to applied pressure P and S by substituting $(P - 6.377) = P_A - 7.398$ and $S^{1/2} = X$.

$$\begin{aligned} f(S, P) = & [47.75297 - 0.1492812 S + 4.6343 \times 10^{-4} S^{3/2} \\ & + 1.880611 \times 10^{-4} S^2] (P - 6.377) + [-7.51105 \times \\ & 10^{-3} + 3.01752 \times 10^{-5} S] (P - 6.377)^2 \\ & + [1.13507 \times 10^{-6} - 3.4178 \times 10^{-9} S] (P - 6.377)^3 \\ & - 1.3383 \times 10^{-10} (P - 6.377)^4 \end{aligned} \quad (28)$$

The specific volumes at 10°C can be calculated from this function by using the equation

$$v^P(10^\circ\text{C}) = v^0(10^\circ\text{C}) + [f(S, 0) - f(S, P)]10^{-6} \quad (29)$$

TABLE 19

SUMMARY OF COMPRESSION ($v_{7.39} - v_{PA}$) FITS OF BRADSHAW AND SCHLEICHER'S RESULTS

<u>Parameters</u>	<u>Residuals</u>	<u>σ</u>
1	---	---
(P-7.39)	41,852,931	1049
X^2 , (P-7.39) ²	14,417,646	633
X^3 , (P-7.39) X^2 , (P-7.39) ³	54,294	40.6
X^4 , (P-7.39) X^3 , (P-7.39) ² X^2 , (P-7.39) ⁴ b	255.4	2.97
X^5 , (P-7.39) X^4 , (P-7.39) ² X^3 a, (P-7.39) ³ X^2	88.4	1.88
(P-7.39) ² X^4 , (P-7.39) ³ X^3 , (P-7.39) ⁴ X^2	71.6	1.80
(P-7.39) ³ X^4 , (P-7.39) ⁴ X^3	65.19	1.81
(P-7.39) ⁴ X^4	64.99	1.85

a) SS due to this term is 14.6 (F-test = 4.1, F 5% = 4.2). Term was judged to be not significant. Standard deviation of final equation = 1.99

b) The 4th power pressure term is by itself barely significant.

Note: The highest power allowed in X^n term was 5 since there are only 5 salinities.

TABLE 20

COEFFICIENTS FOR EQUATION (27)

$$\begin{aligned} a_{01} &= 47.75297 \\ a_{11} &= -0.1492812 \\ a_{21} &= 4.6343 \times 10^{-4} \\ a_{31} &= 1.880611 \times 10^{-4} \\ a_{02} &= -7.51105 \times 10^{-3} \\ a_{12} &= 3.01751 \times 10^{-5} \\ a_{03} &= 1.13507 \times 10^{-6} \\ a_{13} &= -3.4178 \times 10^{-9} \\ a_{04} &= -1.3383 \times 10^{-10} \end{aligned}$$

The residuals of the observations for this fit are given in Table 21.

TABLE 21

RESIDUALS OF ISOTHERMAL COMPRESSION OF SEAWATER REFERRED TO

$P_A = 7.39$ BARS AT 10°C

<u>Salinity</u>	<u>Pressure</u>	<u>Residual</u>	<u>Stand. Residual</u>
0.000	7.39	-0.6	-0.3
0.000	10.83	-0.0	-0.0
0.000	17.72	-0.1	-0.1
0.000	201.30	0.2	0.1
0.000	401.05	-0.8	-0.4
0.000	600.79	3.8	1.9
0.000	800.52	-2.3	-1.1
0.000	1000.19	-0.1	-0.1
14.955	7.39	0.0	0.0
14.955	10.84	0.2	0.1
14.955	17.73	0.3	0.2
14.955	201.30	1.2	0.6
14.955	401.06	-1.7	-0.9
14.955	600.80	-0.6	-0.3
14.955	800.52	0.2	0.1
14.955	1000.21	0.4	0.2
30.705	7.39	-0.5	-0.3
30.705	10.84	0.2	0.1
30.705	17.73	-0.8	-0.4
30.705	201.30	-0.3	-0.2
30.705	401.05	-2.6	-1.3
30.705	600.78	1.1	0.5

TABLE 21 (continued)

<u>Salinity</u>	<u>Pressure</u>	<u>Residual</u>	<u>Stand. Residual</u>
30.705	800.48	0.8	0.4
30.705	1000.16	2.3	1.1
34.891	7.39	2.5	1.3
34.891	10.84	2.2	1.1
34.891	17.73	1.1	0.5
34.891	201.31	0.9	0.4
34.891	401.06	-3.2	-1.6
34.891	600.79	-1.0	-0.5
34.891	800.50	-2.1	-1.1
34.891	1000.18	-0.4	-0.2
38.884	7.39	-2.1	-1.1
38.884	10.84	-2.1	-1.0
38.884	17.73	-1.0	-0.5
38.884	201.30	2.0	1.0
38.884	401.05	0.9	0.4
38.884	600.79	4.1	2.1
38.884	800.51	-0.3	-0.1
38.884	1000.18	-1.4	-0.7

where $f(S,0)$ is the function evaluated at applied pressure $P=0$ and $v^0(10^\circ\text{C})$ is the specific volume ($= 1/\rho$) evaluated from equation (7). The values of v^P at 10°C determined in this manner were used to convert the relative expansibilities measured by Bradshaw and Schleicher [$v^P(t^\circ\text{C}) - v^P(0^\circ\text{C})$] to specific volumes at a given pressure and temperature. The values of v_W^P for water at various temperatures and pressures calculated in this manner are given in Table 22.

The values of v_W^P for water from the sound derived equation of Chen, Fine and Millero are given in Table 23. These values have been adjusted to the 1 atm values of v_W^0 determined from equation (2). The values of v_W^P from the work of Bradshaw and Schleicher, and Chen, Fine and Millero have been used to calculate the secant bulk modulus

$$K_W^P = \frac{v_W^0 P}{v_W^0 - v_W^P} \quad (30)$$

These values of K_W^P have been fit to an equation of the form

$$K_W^P - K_W^0 = A_W P + B_W P^2 \quad (31)$$

where K_W^0 is given by equation (16). The Chen, Fine and Millero equation has 10 parameters ($5A_W, 5B_W$) and is valid from 0 to 100°C . We have, thus, started with the 10 parameter equation to fit the combined data. The results of the various fits are given in Table 24. The 7 parameter equation (4A, 3B) gives the best fit with the fewest number of parameters. An evaluation of the 6 and 7 parameter equations using the F-test indicates that at the 95% confidence level the 7 parameters are needed. The values of A_W and B_W are given by

$$A_W = 3.239908 + 1.43713 \times 10^{-3} t + 1.16092 \times 10^{-4} t^2 - 5.77905 \times 10^{-7} t^3 \quad (31a)$$

$$B_W = 8.50935 \times 10^{-5} - 6.12293 \times 10^{-6} t + 5.2787 \times 10^{-8} t^2 \quad (31b)$$

TABLE 22

γ_w^p FOR WATER FROM BRADSHAW AND SCHLEICHER

Temp	0 bar ^a	7.316 bar	100.304 bar	200.207 bar	300.104 bar
30	1.0043689	1.0040387	0.9999205	0.9956282	0.9914540
29	1.0040689	----	----	----	----
28	1.0037781	1.0034469	0.9993159	0.9950085	0.9908209
26	1.0032244	1.0028926	0.9987457	0.9944221	0.9902186
24	1.0027089	1.0023756	0.9982099	0.9938681	0.9896469
22	1.0022329	1.0018969	0.9977110	0.9933477	0.9891065
20	1.0017979	1.0014601	0.9972509	0.9928623	0.9885980
18	1.0014054	1.0010658	0.9968305	0.9924128	0.9881235
16	1.0010571	1.0007156	0.9964506	0.9920024	0.9876847
14	1.0007552	1.0004107	0.9961136	0.9916308	0.9872812
12	1.0005016	1.0001543	0.9958203	0.9913005	0.9869154
10	1.0002990	0.9999493	0.9955742	0.9910123	0.9865881
8	1.0001501	0.9997962	0.9953762	0.9907685	0.9863019
6	1.0000580	0.9997000	0.9952303	0.9905719	0.9860577
4	1.0000260	0.9996633	0.9951386	0.9904250	0.9858588
2	1.0000581	0.9996899	0.9951052	0.9903301	0.9857065
0	1.0001584	0.9997843	0.9951323	0.9902897	0.9856041
-1	1.0002356	----	----	0.9902919	0.9855726
-2	1.0003316	----	----	----	----
-4	1.0005827	----	----	----	----

a) From equation (2) where $(v = 1/\rho)$

TABLE 22 (continued)

<u>Temp</u>	<u>399.996</u>	<u>499.883</u>	<u>599.755</u>	<u>699.601</u>	<u>799.483</u>
30	0.9873978	0.9834570	0.9796191	0.9758835	0.9722482
29	----	----	----	----	----
28	0.9867528	0.9827992	0.9789494	0.9752040	0.9715578
26	0.9861346	0.9821679	0.9783047	0.9745464	0.9708878
24	0.9855459	0.9815621	0.9776845	0.9739119	0.9702401
22	0.9849869	0.9809838	0.9770889	0.9733005	0.9696135
20	0.9844582	0.9804334	0.9765196	0.9727134	0.9690082
18	0.9839589	0.9799120	0.9759768	0.9721500	0.9684260
16	0.9834913	0.9794193	0.9754610	0.9716115	0.9678667
14	0.9830580	0.9789570	0.9749731	0.9710988	0.9673318
12	0.9826590	0.9785264	0.9745124	0.9706121	0.9668199
10	0.9822954	0.9781286	0.9740827	0.9701530	0.9663323
8	0.9819690	0.9777646	0.9736840	0.9697223	0.9658717
6	0.9816810	0.9774362	0.9733169	0.9693202	0.9654371
4	0.9814333	0.9771439	0.9729826	0.9689474	0.9650286
2	0.9812281	0.9768895	0.9726830	0.9686047	0.9646479
0	0.9810670	0.9766748	0.9724182	0.9682951	0.9642950
-1	----	----	----	----	----
-2	0.9809534	0.9765022	0.9721915	0.9680184	0.9639729
-4	----	----	0.9720037	0.9677767	0.9636810

TABLE 22 (continued)

<u>Temp</u>	<u>913.132</u>	<u>978.533</u>	<u>978.553</u>
30	0.9682166	----	0.9659522
29	----	0.9655963	----
28	0.9675158	0.9652456	0.9652448
26	0.9668340	0.9645569	0.9645569
24	0.9661770	0.9638872	0.9638864
22	0.9655294	0.9632353	0.9632356
20	0.9649077	0.9626048	0.9626044
18	0.9643058	0.9619919	0.9619924
16	0.9637253	0.9614006	0.9614001
14	0.9631658	0.9608289	0.9608281
12	0.9626285	0.9602768	0.9602760
10	0.9621138	0.9597461	0.9597454
8	0.9616209	0.9592364	0.9592362
6	0.9611520	0.9587497	0.9587489
4	0.9607069	0.9582846	0.9582838
2	0.9602861	0.9578425	0.9578422
0	0.9598912	0.9574239	0.9574231
-1	----	----	----
-2	0.9595215	0.9570292	0.9570281
-4	0.9591780	0.9566584	0.9566577

TABLE 23

v_w^P FOR WATER FROM CHEN, FINE AND MILLERO

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
0	1.000158	1.000034	1.000299	1.000900	1.001798
100	0.995151	0.995195	0.995591	0.996294	0.997270
200	0.990307	0.990507	0.991026	0.991825	0.992875
300	0.985618	0.985963	0.986598	0.987488	0.988608
400	0.981078	0.981559	0.982301	0.983276	0.984463
500	0.976681	0.977287	0.978131	0.979185	0.980434
600	0.972420	0.973144	0.974081	0.975210	0.976517
700	0.968291	0.969123	0.970146	0.971345	0.972706
800	0.964289	0.965219	0.966323	0.967586	0.968998
900	0.960409	0.961429	0.962607	0.963929	0.965388
1000	0.956645	0.957748	0.958992	0.960369	0.961872

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
0	1.002962	1.004369	1.006001	1.007842
100	0.998491	0.999939	1.001597	1.003450
200	0.994152	0.995639	0.997322	0.999188
300	0.989937	0.991462	0.993169	0.995048
400	0.985842	0.987402	0.989133	0.991024
500	0.981860	0.983455	0.985208	0.987112
600	0.977988	0.979614	0.981389	0.983305
700	0.974219	0.975876	0.977672	0.979599
800	0.970550	0.972235	0.974050	0.975989
900	0.966976	0.968688	0.970521	0.972470
1000	0.963493	0.965231	0.967081	0.969039

TABLE 24

SUMMARY OF THE BULK MODULUS FIT OF PURE WATER DATA OF
BRADSHAW AND SCHLEICHER AND CHEN, FINE AND MILLERO ^a

$$K_W^P = K_W^0 + A_W P + B_W P^2$$

<u>Parameters</u>	<u>σ(K)</u>	<u>$10^6 \sigma$(V)</u>
10(5A, 5B)	5.93	4.33
9(5A, 4B)	5.91	4.32
8(5A, 3B)	5.91	4.32
7(5A, 2B)	5.95	4.45
6(5A, B)	9.00	8.45
8(4A, 4B)	5.91	4.34
7(4A, 3B)	5.91	4.33
6(4A, 2B)	5.94	4.46
5(4A, B)	9.06	8.46

a) The data were weighted by $P/200 + 1$. The results of Bradshaw and Schleicher at $P = 7.3$ bars were not used due to the large uncertainty in K_W .

The deviations between the measured values of v_W^P and those calculated from equation (31) are shown in Figures 1 and 2. The overall standard error is $4.33 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v_W^P .

The specific volume data for seawater of various workers (Chen and Millero, 1976 and Bradshaw and Schleicher, 1970) must be normalized to the same specific volumes of seawater at 1 atm (equation 7) and the same values of v_W at each pressure and temperature. The need for this normalization can be demonstrated by comparing the differences in v^P for seawater at 10°C calculated from Bradshaw and Schleicher's results (equations 28 and 29) and the sound derived equation of state of Chen and Millero (1978). The differences are shown in Table 25. The maximum deviation is $20 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. By normalizing the values to the same V^P for water, the deviations are reduced to a maximum of $8 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ (Table 26). These comparisons clearly demonstrate that the relative values of the specific volume for seawater ($v_{SW}^P - v_W^P$) are in excellent agreement. To take advantage of this internal precision of the various studies we have normalized the relative measurements of Chen and Millero and Bradshaw and Schleicher to the same pure water equation of state. Since the measurements of Chen and Millero were all made relative to pure water, the easiest way to normalize the data sets was to use an equation of state determined from the pure water from Bradshaw and Schleicher. The values of v_W^P from Bradshaw and Schleicher (Table 22) have been used to determine K_W^P which have been fit to equation (31). The results of the various fits are given in Table 27. The 7 parameter (4A, 3B) equations gives the best statistical fit of the data. The values of A_W and B_W are given by

$$K_W^P = K_W^0 + A_W P + B_W P^2 \quad (32)$$

$10^6 (V^P \text{ UNESCO} - V^P \text{ Bradshaw and Schleicher})$
For Water

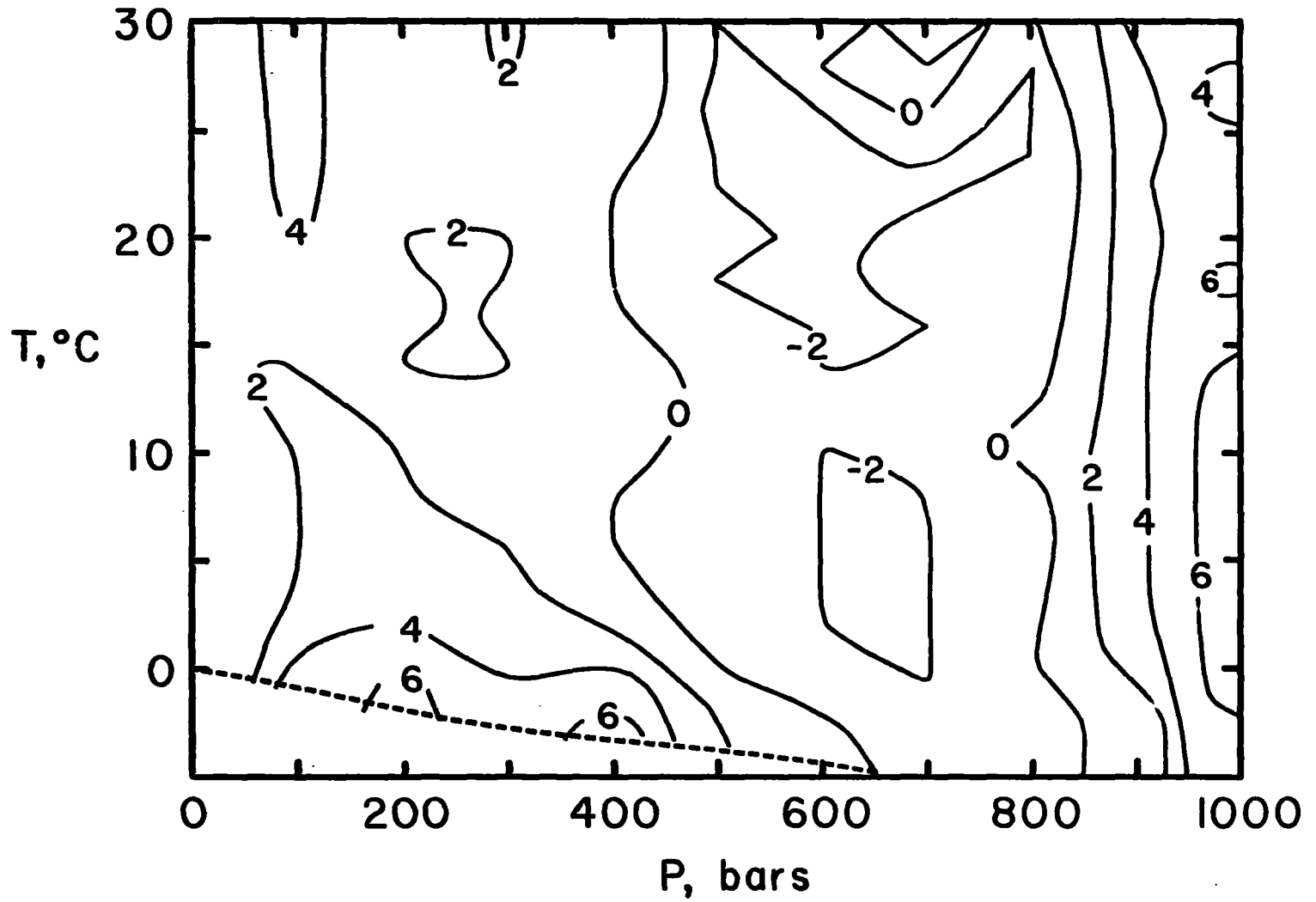


Figure 1

$10^6 (V^P \text{ UNESCO} - V^P \text{ Chen, Fine and Millero}), \text{ for Water}$

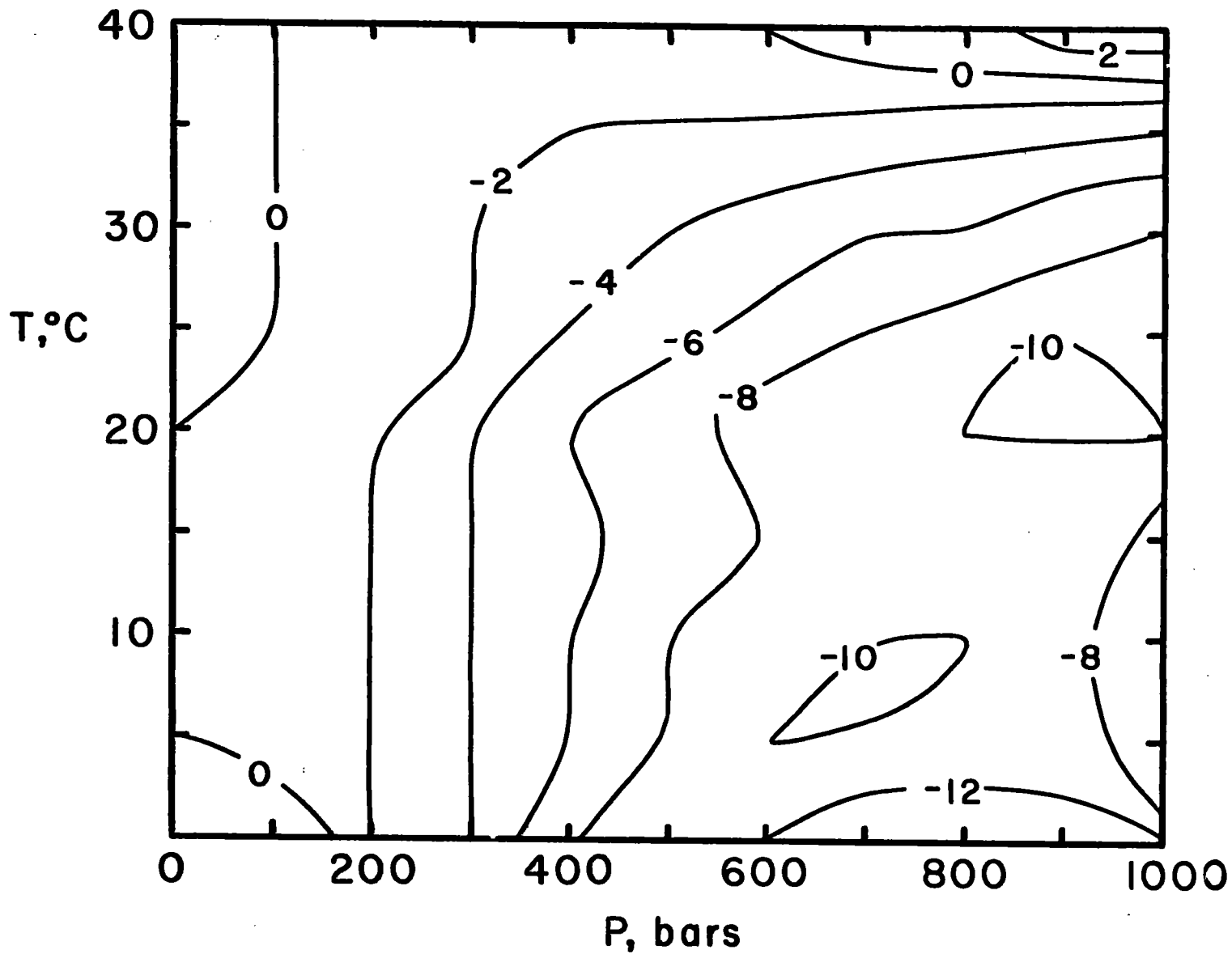


Figure 2

TABLE 25

COMPARISONS OF v^P OF BRADSHAW AND SCHLEICHER WITH

CHEN AND MILLERO AT 10°C

$\Delta v 10^6$ ^a

<u>P</u>	<u>S=0</u>	<u>S=15</u>	<u>S=30</u>	<u>S=35</u>	<u>S=40</u>
0	0	0	0	0	0
100	3	5	4	2	2
200	4	8	7	4	2
300	5	11	9	6	2
400	6	13	10	6	2
500	7	14	11	7	2
600	8	16	12	7	3
700	9	17	13	9	4
800	10	18	15	10	7
900	13	19	16	12	8
1000	14	20	17	14	11

a) $\Delta v 10^6 = v^P$ (Chen and Millero) - v^P (Bradshaw and Schleicher).

TABLE 26

COMPARISONS OF $v_{SW} - v_{H_2O}$ AT 10°C OBTAINED BY
BRADSHAW AND SCHLEICHER AND CHEN AND MILLERO

<u>P</u>	<u>$\frac{\Delta(v_{SW} - v_W)10^6}{}$</u>			
	<u>S=15</u>	<u>S=30</u>	<u>S=35</u>	<u>S=40</u>
0	0	0	0	0
100	2	1	-1	-1
200	4	3	0	-2
300	6	4	1	-3
400	7	4	0	-4
500	7	4	0	-5
600	8	4	1	-5
700	8	4	0	-5
800	8	5	0	-3
900	6	3	1	5
1000	6	3	0	3

TABLE 27

SUMMARY OF THE BULK MODULUS FIT OF PURE WATER OF

BRADSHAW AND SCHLEICHER^a

$$K_W^F = K_W^0 + A_W P + B_W P^2$$

<u>Parameters</u>	<u>$\sigma(K)$</u>	<u>$10^6 \sigma(v)$</u>
8(5A, 3B)	5.84	2.29
7(5A, 2B)	5.88	2.39
6(5A, B)	8.69	7.47
5(5A)	9.72	8.49
8(4A, 4B)	5.84	2.28
7(4A, 3B)	5.82	2.28
6(4A, 2B)	5.86	2.38
5(4A, B)	8.86	7.45

a) The data were weighted by $P/200 + 1$. The results at $P = 7.3$ bars were not used due to the large uncertainty in K_W^P .

$$A_W = 3.228404_5 + 1.659597 \times 10^{-3}t + 1.203186 \times 10^{-4}t^2 - 8.061151 \times 10^{-7}t^3 \quad (32a)$$

$$B_W = 9.533650_7 \times 10^{-5} - 6.485090 \times 10^{-6}t + 5.855590 \times 10^{-8}t^2 \quad (32b)$$

The overall standard deviation is 5.33 bar^{-1} in K_W^P and $2.28 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v_W^P . The deviations in v_W^P at various temperatures and pressures are given in Figure 3.

The specific volumes of seawater solutions have been calculated from the expansibility measurements of Bradshaw and Schleicher by using equations (28) and (29). The values of v^0 at 10°C have been determined from equation (7). The resulting specific volumes are given in Table 28. The values of v^P for seawater (normalized to equation 32) of Chen and Millero are given in Tables 29 and 30.

In the analysis of the direct measurements and sound derived secant bulk modulus data for seawater, Chen and Millero (1976, 1978) have found equation (1) adequately represented the data. They used an equation with 12 parameters (3A, 2B, 3C,D,3E) for the direct and 13 parameters (4A,2B,3C,D,3E) for the sound data which are given in Tables 31 and 32. The standard error of equation (1) for the direct measurements of Chen and Millero (1976) was $7.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The errors in v^P for the sound derived equation cannot be directly determined, since the values of K^P were obtained directly from the sound speeds. A comparison of the values of v^P for 35°‰ salinity seawater is shown in Figure 4. Over most of the oceanic ranges of T and P the two studies agree to within $\pm 20 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P .

By normalizing the values of K^P from the sound and direct measurements

$10^6 V^P_{\text{measured}} - 10^6 V^P_{\text{calculated}} \text{ (B/S), WATER}$

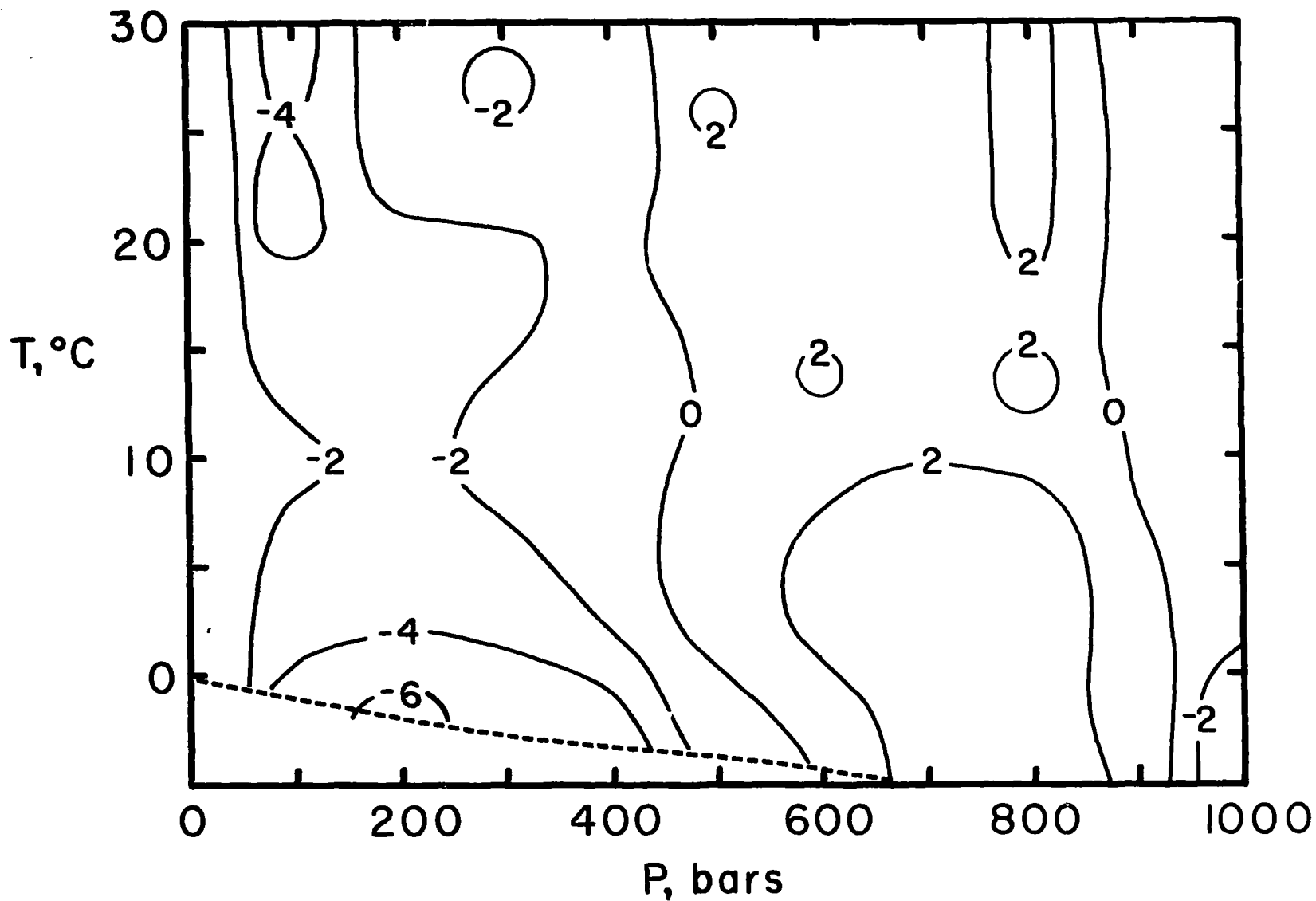


Figure 3.

TABLE 28

v^P FOR SEAWATER FROM BRADSHAW AND SCHLEICHER

S = 14.975

<u>Temp</u>	<u>200.207 bar</u>	<u>599.775 bar</u>	<u>1019.868 bar</u>
30°C	0.9848506	0.9694505	0.9549233
28	0.9842135	0.9687710	0.9542094
26	0.9836053	0.9681134	0.9535111
24	0.9830268	0.9674782	0.9528291
22	0.9824789	0.9668645	0.9521642
20	0.9819623	0.9662754	0.9515168
18	0.9814782	0.9657095	0.9508854
16	0.9810277	0.9651684	0.9502720
14	0.9806120	0.9646511	0.9496754
12	0.9802335	0.9641596	0.9490962
10	0.9798918	0.9636952	0.9485358
8	0.9795886	0.9632571	0.9479935
6	0.9793269	0.9628475	0.9474697
4	0.9791075	0.9624670	0.9469652
2	0.9789332	0.9621158	0.9464790
0	0.9788056	0.9617949	0.9460123
-1	0.9787606	-----	-----
-2	-----	0.9615058	0.9455657

TABLE 28 (continued)

S = 30.504

<u>Temp</u>	<u>200.2176 bar</u>	<u>599.7356 bar</u>	<u>999.161 bar</u>
30°C	0.9739092	0.9591056	0.9457589
28	0.9732545	0.9584163	0.9450424
26	0.9726259	0.9577468	0.9443416
24	0.9720251	0.9570977	0.9436556
22	0.9714509	0.9564694	0.9429846
20	0.9709058	0.9558620	0.9423292
18	0.9703898	0.9552753	0.9416889
16	0.9699029	0.9547107	0.9410649
14	0.9694467	0.9541679	0.9404563
12	0.9690225	0.9536482	0.9398635
10	0.9686315	0.9531514	0.9391885
8	0.9682743	0.9526795	0.9387281
6	0.9679534	0.9522317	0.9381856
4	0.9676687	0.9518085	0.9376599
2	0.9674232	0.9514115	0.9371513
0	0.9672182	0.9510416	0.9366597
-1	0.9671316	-----	-----
-2	-----	0.9506986	0.9361876

TABLE 28 (continued)

<u>Temp</u>	<u>S = 35.025</u>		<u>S = 35.032</u>	<u>S = 35.005</u>
	<u>100.324 bar</u>	<u>200.247 bar</u>	<u>293.226 bar</u>	<u>399.986 bar</u>
30°C	0.9746671	0.9707636	0.9671962	0.9632519
28	0.9740175	0.9701051	0.9665300	0.9625761
26	0.9733948	0.9694722	0.9658874	0.9619229
24	0.9728015	0.9688653	0.9652684	0.9612911
22	0.9722360	0.9682844	0.9646751	0.9606824
20	0.9716994	0.9677313	0.9641068	0.9600981
18	0.9711924	0.9672069	0.9635645	0.9595383
16	0.9707180	0.9667107	0.9630492	0.9590021
14	0.9702749	0.9662438	0.9625613	0.9584918
12	0.9696569	0.9658081	0.9621021	0.9580071
10	0.9694914	0.9654039	0.9616723	0.9575495
8	0.9691526	0.9650329	0.9612723	0.9571185
6	0.9688505	0.9646962	0.9609043	0.9567173
4	0.9685878	0.9643945	0.9605678	0.9563443
2	0.9683664	0.9641299	0.9602650	0.9560020
0	0.9681874	0.9639046	0.9599976	0.9556911
-1	-----	0.9638068	-----	-----
-2	-----	-----	0.9597676	0.9554130

TABLE 28 (continued)

<u>Temp</u>	S = 35.031	S = 35.004	S = 35.007	S = 35.002
	<u>499.883 bar</u>	<u>599.755 bar</u>	<u>699.621 bar</u>	<u>799.4836 bar</u>
30°C	0.9596269	0.9591316	0.9527045	0.9493674
28	0.9589436	0.9554393	0.9520060	0.9486638
26	0.9582810	0.9547673	0.9513264	0.9479752
24	0.9576390	0.9541160	0.9506635	0.9473036
22	0.9570188	0.9534817	0.9500203	0.9466487
20	0.9564189	0.9528696	0.9493950	0.9460122
18	0.9558419	0.9522781	0.9487891	0.9453928
16	0.9552880	0.9517075	0.9482026	0.9447909
14	0.9547579	0.9511590	0.9476356	0.9442078
12	0.9542501	0.9506310	0.9470876	0.9436429
10	0.9537675	0.9501252	0.9465611	0.9430967
8	0.9533095	0.9496462	0.9460568	0.9425704
6	0.9528788	0.9491839	0.9455729	0.9420629
4	0.9524744	0.9487500	0.9451109	0.9415748
2	0.9520967	0.9483405	0.9446716	0.9411074
0	0.9517472	0.9479563	0.9442545	0.9406615
-1	-----	-----	-----	-----
-2	0.9514274	0.9475597	0.9438617	0.9402358

TABLE 28 (continued)

<u>Temp</u>	<u>S = 35.012</u>	<u>S = 35.991</u>	<u>S = 35.006</u>
	<u>799.503 bar</u>	<u>906.245 bar</u>	<u>999.241 bar</u>
30°C	0.9490061	0.9458937	0.9429272
28	0.9486557*	0.9451826	0.9422113
26	0.9479672	0.9444872	0.9415086
24	0.9472952	0.9438063	0.9408202
22	0.9466416	0.9431413	0.9401469
20	0.9460045	0.9424929	0.9394884
18	0.9453851	0.9418604	0.9388449
16	0.9447833	0.9412444	0.9382173
14	0.9442009	0.9406451	0.9376041
12	0.9436359	0.9400622	0.9370081
10	0.9430895	0.9394967	0.9364264
8	0.9425616	0.9389490	0.9358620
6	0.9420547	0.9384185	0.9353120
4	0.9415668	0.9379058	0.9347794
2	0.9410993	0.9374121	0.9342625
0	0.9406532	0.9369360	0.9337631
-1	-----	-----	-----
-2	0.9402278	0.9364790	0.9332813
-4	0.9360408	0.9360408	-----

*Temperature for this data point is 29°C.

TABLE 28 (continued)

Temp	S = 39.502	S = 39.504	S = 39.507
	<u>200.227 bar</u>	<u>599.735 bar</u>	<u>999.221 bar</u>
30°C	0.9676361	0.9531664	0.9401004
28	0.9669731	0.9524720	0.9393815
26	0.9663356	0.9517964	0.9386783
24	0.9657225	0.9511410	0.9379881
22	0.9651356	0.9505049	0.9373128
20	0.9645747	0.9498881	0.9366523
18	0.9640413	0.9492909	0.9360069
16	0.9635358	0.9487146	0.9353752
14	0.9630584	0.9481589	0.9347586
12	0.9626109	0.9476234	0.9341581
10	0.9621942	0.9471099	0.9335718
8	0.9618095	0.9466189	0.9330013
6	0.9614575	0.9461506	0.9324466
4	0.9611384	0.9457059	0.9319068
2	0.9608561	0.9452845	0.9313846
0	0.9606110	0.9448884	0.9308780
-1	0.9605034	-----	-----
-2	-----	0.9445165	0.9303869

TABLE 29

v^P FOR SEAWATER FROM CHEN AND MILLERO (SOUND)

$S = 5^\circ/\text{oo}$

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.991182	0.991306	0.991766	0.992518	0.993532
200	0.986420	0.986693	0.987270	0.988115	0.989198
300	0.981808	0.982220	0.982908	0.983839	0.984990
400	0.977340	0.977883	0.978674	0.979686	0.980900
500	0.973012	0.973676	0.974563	0.975652	0.976925
600	0.968818	0.969593	0.970570	0.971730	0.973059
700	0.964752	0.965631	0.966691	0.967917	0.969297
800	0.960810	0.961784	0.962920	0.964208	0.965636
900	0.956988	0.958048	0.959255	0.960598	0.962071
1000	0.953281	0.954420	0.955690	0.957085	0.958599

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
100	0.994781	0.996247	0.997917	0.999777
200	0.990500	0.992004	0.993697	0.995568
300	0.986342	0.987881	0.989598	0.991480
400	0.982300	0.983873	0.985612	0.987506
500	0.978369	0.979975	0.981735	0.983641
600	0.974545	0.976182	0.977962	0.979879
700	0.970823	0.972490	0.974289	0.976216
800	0.967199	0.968892	0.970710	0.972648
900	0.963669	0.965387	0.967222	0.969170
1000	0.960228	0.961969	0.963820	0.965778

TABLE 29 (continued)

$s = 10^{\circ}/\infty$

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.987274	0.987471	0.987990	0.988790	0.989840
200	0.982593	0.982933	0.983564	0.984451	0.985568
300	0.978059	0.978531	0.979267	0.980238	0.981418
400	0.973666	0.974262	0.975096	0.976144	0.977385
500	0.969408	0.970119	0.971046	0.972166	0.973463
600	0.965281	0.966098	0.967111	0.968299	0.969648
700	0.961279	0.962195	0.963286	0.964537	0.965937
800	0.957397	0.958404	0.959569	0.960878	0.962323
900	0.953632	0.954722	0.955954	0.957317	0.958804
1000	0.949979	0.951144	0.952437	0.953849	0.955375

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
100	0.991117	0.992601	0.994281	0.996144
200	0.986894	0.988414	0.990117	0.991990
300	0.982792	0.984346	0.986069	0.987953
400	0.978803	0.980390	0.982134	0.984028
500	0.974924	0.976541	0.978305	0.980209
600	0.971150	0.972796	0.974579	0.976493
700	0.967476	0.969148	0.970950	0.972873
800	0.963897	0.965595	0.967413	0.969346
900	0.960410	0.962132	0.963966	0.965907
1000	0.957011	0.958755	0.960604	0.962553

TABLE 29 (continued)

$S = 15^{\circ}/\infty$

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.983406	0.983673	0.984249	0.985094	0.986178
200	0.978805	0.979207	0.979889	0.980818	0.981966
300	0.974347	0.974875	0.975657	0.976664	0.977873
400	0.970026	0.970672	0.971548	0.972629	0.973895
500	0.965837	0.966592	0.967556	0.968706	0.970026
600	0.961775	0.962632	0.963677	0.964892	0.966262
700	0.957835	0.958786	0.959907	0.961181	0.962598
800	0.954012	0.955050	0.956240	0.957570	0.959031
900	0.950303	0.951420	0.952674	0.954056	0.955556
1000	0.946702	0.947892	0.949205	0.950633	0.952171

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
100	0.987480	0.988983	0.990674	0.992540
200	0.983316	0.984852	0.986563	0.988438
300	0.979268	0.980836	0.982567	0.984451
400	0.975332	0.976930	0.978681	0.980574
500	0.971504	0.973131	0.974899	0.976802
600	0.967777	0.969432	0.971218	0.973129
700	0.964149	0.965829	0.967632	0.969552
800	0.960615	0.962319	0.964137	0.966065
900	0.957171	0.958897	0.960730	0.962665
1000	0.953814	0.955560	0.957406	0.959348

TABLE 29 (continued)

$s = 20^{\circ}/\infty$

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.979571	0.979905	0.980535	0.981422	0.982540
200	0.975047	0.975510	0.976241	0.977208	0.978386
300	0.970663	0.971245	0.972071	0.973113	0.974349
400	0.966412	0.967107	0.968022	0.969134	0.970424
500	0.962290	0.963089	0.964088	0.965266	0.966607
600	0.958292	0.959188	0.960264	0.961503	0.962892
700	0.954413	0.955398	0.956546	0.957843	0.959276
800	0.950647	0.951715	0.952930	0.954280	0.955754
900	0.946993	0.948136	0.949412	0.950811	0.952323
1000	0.943444	0.944657	0.945989	0.947432	0.948980

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
100	0.983867	0.985387	0.987088	0.988959
200	0.979758	0.981310	0.983030	0.984908
300	0.975764	0.977345	0.979084	0.980971
400	0.971880	0.973490	0.975246	0.977141
500	0.968100	0.969737	0.971511	0.973414
600	0.964421	0.966084	0.967874	0.969784
700	0.960839	0.962525	0.964330	0.966248
800	0.957348	0.959057	0.960876	0.962801
900	0.953946	0.955676	0.957508	0.959439
1000	0.950629	0.952377	0.954222	0.956158

TABLE 29 (continued)

$s = 25^{\circ}/\infty$

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.975764	0.976163	0.976844	0.977772	0.978921
200	0.971316	0.971837	0.972614	0.973618	0.974825
300	0.967004	0.967638	0.968507	0.969581	0.970843
400	0.962822	0.963563	0.964516	0.965658	0.966971
500	0.958765	0.959606	0.960638	0.961842	0.963203
600	0.954829	0.955762	0.956868	0.958131	0.959537
700	0.951009	0.952027	0.953202	0.954519	0.955967
800	0.947300	0.948397	0.949635	0.951002	0.952490
900	0.943698	0.944867	0.946164	0.947578	0.949102
1000	0.940199	0.941435	0.942785	0.944242	0.945799

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
100	0.980271	0.981808	0.983521	0.985398
200	0.976217	0.977784	0.979514	0.981398
300	0.972276	0.973871	0.975618	0.977509
400	0.968442	0.970064	0.971827	0.973726
500	0.964711	0.966358	0.968137	0.970042
600	0.961079	0.962749	0.964544	0.966455
700	0.957541	0.959234	0.961042	0.962959
800	0.954093	0.955807	0.957628	0.959551
900	0.950732	0.952465	0.954298	0.956226
1000	0.947454	0.949205	0.951049	0.952982

TABLE 29 (continued)

$s = 30^{\circ}/\infty$

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.971983	0.972444	0.973175	0.974142	0.975320
200	0.967608	0.968186	0.969008	0.970046	0.971279
300	0.963366	0.964052	0.964961	0.966066	0.967351
400	0.959251	0.960038	0.961028	0.962197	0.963531
500	0.955258	0.956140	0.957205	0.958433	0.959813
600	0.951383	0.952352	0.953487	0.954772	0.956194
700	0.947620	0.948671	0.949871	0.951207	0.952670
800	0.943966	0.945092	0.946352	0.947737	0.949236
900	0.940416	0.941611	0.942928	0.944356	0.945890
1000	0.936967	0.938225	0.939593	0.941062	0.942628
<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	
100	0.976692	0.978245	0.979970	0.981856	
200	0.972692	0.974273	0.976014	0.977906	
300	0.968802	0.970410	0.972166	0.974064	
400	0.965018	0.966650	0.968422	0.970326	
500	0.961334	0.962991	0.964777	0.966686	
600	0.957747	0.959426	0.961225	0.963140	
700	0.954253	0.955952	0.957764	0.959684	
800	0.950847	0.952566	0.954390	0.956314	
900	0.947526	0.949263	0.951097	0.953026	
1000	0.944287	0.946040	0.947884	0.949816	

TABLE 29 (continued)

S = 35°/∞

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.968224	0.968747	0.969526	0.970528	0.971734
200	0.963921	0.964555	0.965420	0.966491	0.967749
300	0.959748	0.960484	0.961432	0.962567	0.963873
400	0.955698	0.956531	0.957555	0.958750	0.960103
500	0.951767	0.952690	0.953786	0.955038	0.956434
600	0.947951	0.948957	0.950120	0.951424	0.952862
700	0.944245	0.945328	0.946553	0.947907	0.949382
800	0.940644	0.941799	0.943082	0.944481	0.945991
900	0.937145	0.938366	0.939702	0.941143	0.942686
1000	0.933744	0.935026	0.936410	0.937890	0.939463
<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>	
100	0.973127	0.974696	0.976434	0.978332	
200	0.969179	0.970775	0.972528	0.974430	
300	0.965340	0.966960	0.968727	0.970635	
400	0.961604	0.963248	0.965029	0.966941	
500	0.957967	0.959633	0.961427	0.963344	
600	0.954425	0.956112	0.957917	0.959839	
700	0.950974	0.952679	0.954497	0.956422	
800	0.947609	0.949333	0.951160	0.953089	
900	0.944328	0.946068	0.947905	0.949836	
1000	0.941127	0.942882	0.944727	0.946661	

TABLE 29 (continued)

S = 40°/∞

<u>P, bar</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>
100	0.964487	0.965071	0.965895	0.966932	0.968163
200	0.960254	0.960943	0.961850	0.962951	0.964231
300	0.956147	0.956934	0.957918	0.959081	0.960408
400	0.952161	0.953039	0.954097	0.955317	0.956687
500	0.948291	0.949255	0.950380	0.951654	0.953065
600	0.944533	0.945576	0.946765	0.948088	0.949539
700	0.940882	0.941998	0.943246	0.944617	0.946103
800	0.937333	0.938518	0.939821	0.941235	0.942754
900	0.933884	0.935131	0.936485	0.937939	0.939489
1000	0.930530	0.931835	0.933236	0.934726	0.936305

<u>P, bar</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
100	0.969575	0.971159	0.972911	0.974824
200	0.965679	0.967288	0.969054	0.970970
300	0.961890	0.963522	0.965300	0.967220
400	0.958201	0.959855	0.961646	0.963570
500	0.954610	0.956285	0.958087	0.960014
600	0.951111	0.952805	0.954619	0.956549
700	0.947702	0.949414	0.951237	0.953170
800	0.944378	0.946106	0.947939	0.949874
900	0.941135	0.942879	0.944720	0.946657
1000	0.937972	0.939729	0.941577	0.943515

TABLE 30

v^P FOR SEAWATER FROM CHEN AND MILLERO (DIRECT)

5.467^o/oo Salinity

<u>P(bars)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C</u>	<u>25°C</u>	<u>30°C</u>	<u>35°C</u>	<u>40°C</u>
199.66	0.986069	0.986355	0.986932	0.987793	0.988872	0.990178	0.991684	0.993374	0.995259
399.33	0.977023	0.977569	0.978365	0.979384	0.980594	0.981992	0.983572	0.985312	0.987224
599.00	0.968522	0.969301	0.970275	0.971443	0.972773	0.974259	0.975899	0.977680	0.979610
798.67	0.960534	0.961506	0.962642	0.963938	0.965362	0.966930	0.968627	0.970443	0.972390
998.34	0.953020	0.954162	0.955434	9.956831	0.958340	0.959969	0.961718	0.963573	0.965539

9.989^o/oo Salinity

199.66	0.982618	0.982956	0.983575	0.984474	0.985590	0.986913	0.988438	0.990130	0.992014
399.33	0.973685	0.974288	0.975115	0.976172	0.977413	0.978825	0.980416	0.982153	0.984076
599.00	0.965314	0.966134	0.967148	0.968336	0.969682	0.971181	0.972831	0.974605	----
798.67	0.957435	0.958446	0.959612	0.960924	0.962370	0.963936	0.965641	0.967458	0.969393
998.34	0.950018	0.951186	0.952482	0.953896	0.955425	0.957049	0.958804	0.960650	0.962604

TABLE 30 (continued)

14.949⁰/oo Salinity

<u>P(bars)</u>	<u>0°C</u>	<u>5°C</u>	<u>10°C</u>	<u>15°C</u>	<u>20°C^a</u>	<u>25°C^a</u>	<u>30°C^a</u>	<u>35°C^a</u>	<u>40°C^a</u>
199.66	0.978847	0.979257	0.979937	0.980871	0.981961	0.983301	0.984829	0.986537	0.988424
399.33	0.970071	0.970720	0.971596	0.972682	0.973888	0.975321	0.976911	0.978658	0.980558
599.00	0.961825	0.962696	0.963734	0.964948	0.966263	0.967771	0.969417	0.971199	0.973120
798.67	0.954065	0.955105	0.956299	0.957631	0.959040	0.960619	0.962319	0.964143	0.966078
998.34	0.946753	0.947947	0.949264	0.950697	0.952196	0.953825	0.955572	0.957416	0.959365

20.082⁰/oo Salinity

199.66	0.974991	0.975461	0.976195	0.977164	0.978340	0.979708	0.981254	0.982971	0.984852
399.33	0.966366	0.967066	0.967983	0.969096	0.970383	0.971834	0.973437	0.975190	0.977091
599.00	0.958257	0.959152	0.960231	0.961471	0.962856	0.964378	0.966034	0.967819	0.969739
798.67	0.950612	0.951682	0.952900	0.954252	0.955738	0.957318	0.959027	0.960846	0.962792
998.34	0.943404	0.944628	0.945967	0.947414	0.948965	0.950622	0.952368	0.954204	----

24.989⁰/oo Salinity

199.66	0.971327	0.971854	0.972632	0.973635	0.974840	0.976220	0.977789	0.979514	0.981419
399.33	0.962841	0.963593	0.964538	0.965675	0.966933	0.968462	0.970073	0.971834	0.973760
599.00	0.954851	0.955788	0.956901	0.958157	0.959574	0.961106	0.962763	0.964570	0.966512
798.67	0.947333	0.948425	0.949662	0.951041	0.952526	0.954128	0.955842	0.957684	0.959625
998.34	0.940222	0.941468	0.942828	0.944289	0.945849	0.947511	0.949266	0.951104	0.953081

TABLE 30 (continued)

30.003^o/∞ Salinity

<u>P(bars)</u>	<u>-0.051°C</u>	<u>4.948°C</u>	<u>9.946°C</u>	<u>14.940°C</u>	<u>19.935°C</u>	<u>24.929°C</u>	<u>29.926°C</u>	<u>34.924°C</u>	<u>39.919°C</u>
99.83	0.971983	0.972437	0.973169	0.974138	0.975304	0.976673	0.978215	0.979942	0.981821
199.66	0.967604	0.968190	0.969017	0.970046	0.971272	0.972680	0.974249	0.975984	0.977873
299.50	0.963356	0.964062	0.964966	0.966068	0.967347	0.968790	0.970386	0.972137	0.974023
399.33	0.959247	0.960041	0.961032	0.962201	0.963535	0.965004	0.966628	0.968403	0.970296
499.16	----	0.956148	0.957211	0.958438	0.959813	0.961329	0.962974	0.964750	0.966653
599.00	0.951373	0.952355	0.953494	0.954782	0.956209	0.957738	0.959410	0.961209	0.963122
698.83	0.947615	0.948679	0.949879	0.951226	0.952676	0.954254	0.955945	0.957765	0.959702
798.67	----	0.945104	0.946369	0.947751	0.949247	0.950850	0.952563	0.954403	0.956355
898.50	0.940413	0.941618	0.942951	0.944378	0.945920	0.947535	0.949276	0.951129	0.953097
998.34	----	0.938236	0.939605	0.941086	0.942666	0.944316	0.946078	0.947946	0.949916

TABLE 30 (continued)

35.003⁰/oo Salinity

<u>P(bars)</u>	<u>0°C</u>	<u>4.948°C</u>	<u>9.946°C</u>	<u>14.940°C</u>	<u>19.935°C</u>	<u>24.929°C</u>	<u>29.926°C</u>	<u>34.924°C</u>	<u>39.919°C</u>
99.83	0.968233	0.968759	0.969535	0.970531	0.971733	0.973124	0.974686	0.976417	0.978319
199.66	0.963944	0.964572	0.965435	0.966497	0.967759	0.969184	0.970773	0.972515	0.974420
299.50	0.959766	0.960505	0.961460	0.962585	0.963885	0.965351	0.966958	0.968733	0.970633
399.33	0.955723	0.956554	0.957579	0.958768	0.960122	0.961615	0.963259	0.965024	0.966950
499.16	0.951791	0.952712	0.953812	0.955061	0.956455	0.957981	0.959645	0.961434	0.963364
599.00	0.947974	0.948976	0.950155	0.951448	0.952883	0.954439	0.956127	----	0.959879
698.83	0.944275	0.945347	0.946589	0.947931	0.949402	0.950986	0.952704	0.954520	0.956469
798.67	0.940671	0.941820	0.943123	0.944508	0.946012	0.947627	0.949365	0.951203	0.953158
898.50	0.937170	0.938394	0.939739	0.941181	0.942713	0.944355	0.946112	0.947963	0.949920
998.34	0.933787	----	0.936447	0.937923	0.939499	0.941168	0.942932	0.944810	0.946769

TABLE 30 (continued)

39.864°/oo Salinity

<u>P(bars)</u>	<u>-0.051°C</u>	<u>4.948°C</u>	<u>9.946°C</u>	<u>14.940°C</u>	<u>19.935°C</u>	<u>24.929°C</u>	<u>29.926°C</u>	<u>35.000°C^b</u>	<u>40.000°C^b</u>
99.83	0.964590	0.965172	0.965987	0.967023	0.968246	0.969662	0.971232	0.973033	0.974952
199.66	0.960359	0.961047	0.961952	0.963053	0.964330	0.965766	0.967370	0.969178	0.971105
299.50	0.956252	0.957049	0.958025	0.959190	0.960511	0.961979	0.963607	0.965441	0.967363
399.33	0.952272	0.953147	0.954201	0.955429	0.956789	0.958289	0.959944	0.961795	0.963722
499.16	0.948399	0.949364	0.950487	0.951766	0.953172	0.954705	0.956386	0.958250	0.960175
599.00	0.944642	0.945683	0.946875	0.948211	0.949650	0.951208	0.952916	0.954789	0.956719
698.83	0.940988	0.942113	0.943359	0.944733	0.946212	0.947805	0.949529	0.951424	0.953351
798.67	0.937447	0.938632	0.939933	0.941350	0.942866	0.944488	0.946236	0.948128	0.950067
898.50	----	0.935244	0.936601	0.938056	0.939618	0.941252	0.943021	0.944922	0.946863
998.34	----	0.931950	0.933354	0.934845	0.936435	0.938104	0.939878	0.941781	0.943735

a) 15.034°/oo salinity.

b) 39.827°/oo salinity.

TABLE 31

COEFFICIENTS FOR EQUATION (12) FROM THE DIRECT MEASUREMENTS

OF CHEN AND MILLERO

$$a = 51.261 - 0.4506t + 2.643 \times 10^{-3}t^2$$

$$b = 0.6623 + 7.274 \times 10^{-3}t$$

$$c = 4.809 \times 10^{-3} - 1.675 \times 10^{-4}t + 3.598 \times 10^{-6}t^2$$

$$d = -2.929 \times 10^{-4}$$

$$e = -1.125 \times 10^{-6} + 1.363 \times 10^{-7}t - 2.134 \times 10^{-9}t^2$$

$$\sigma = 7.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ in } v^P$$

TABLE 32
COEFFICIENTS FOR EQUATION (12) FROM THE SOUND MEASUREMENTS
OF CHEN AND MILLERO

$$a = 53.751 - 0.4607t + 7.030 \times 10^{-3}t^2 - 5.107 \times 10^{-5}t^3$$

$$b = 0.2322 - 4.838 \times 10^{-3}t$$

$$c = 4.692 \times 10^{-3} - 8.387 \times 10^{-5}t + 4.68 \times 10^{-7}t^2$$

$$d = 1.332 \times 10^{-4}$$

$$e = -1.412 \times 10^{-6} + 9.006 \times 10^{-8}t - 1.551 \times 10^{-9}t^2$$

$10^6 (V^P \text{ Sound} - V^P \text{ Direct})$ Chen and Millero, SW (35‰)

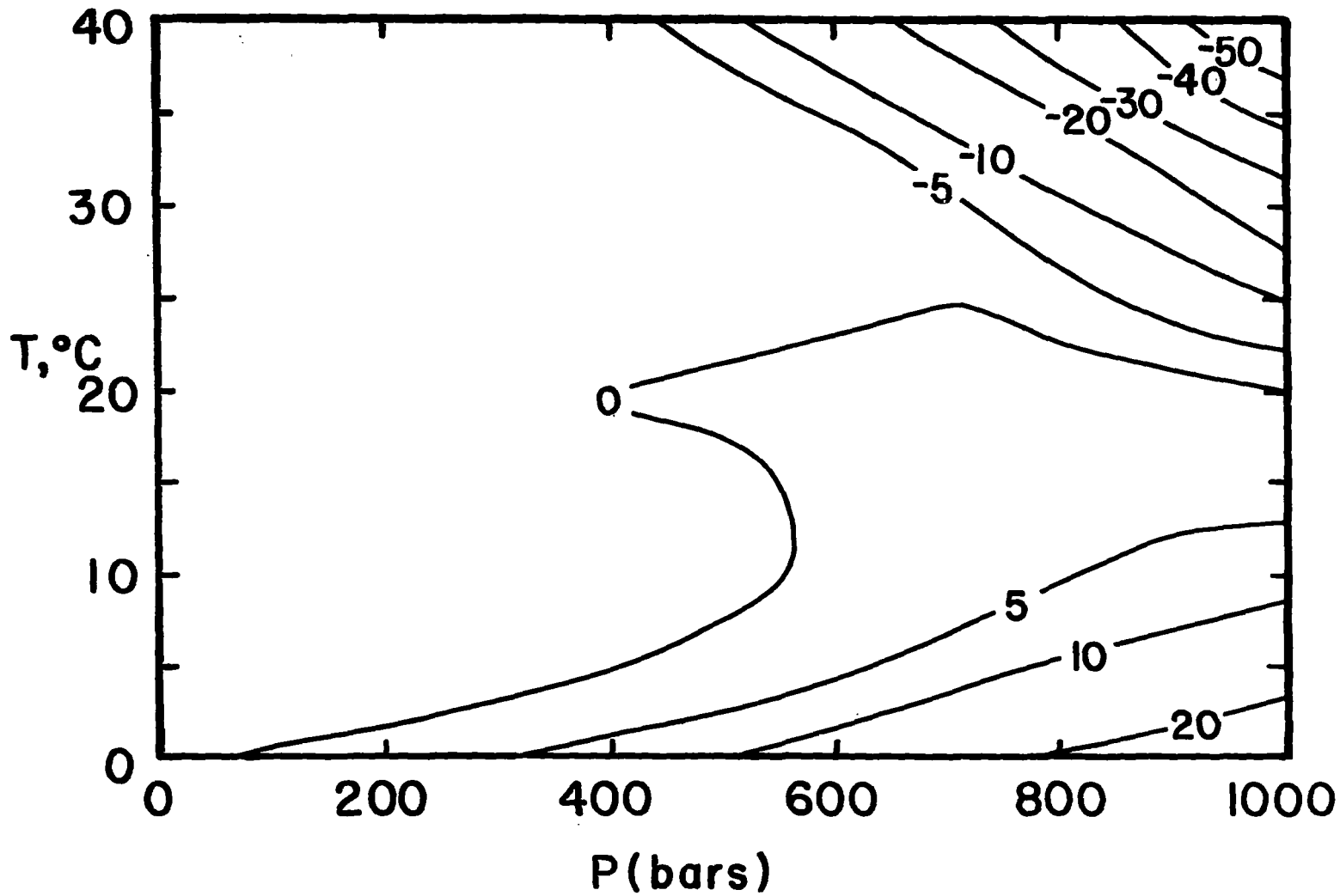


Figure 4.

of Chen and Millero to the same pure water (equation 32) and 1 atm values of the secant bulk modulus for seawater (equation 23), we have

$$K^P - K_W^P - (K^O - K_W^O) = [c S + d S^{3/2}]P + [e S]P^2 \quad (33)$$

The values of c, d, and e are given by

$$c = 2.5410 \times 10^{-3} - 1.5917 \times 10^{-5}t - 1.6231 \times 10^{-6}t^2 \quad (33a)$$

$$d = 1.6716 \times 10^{-4} \quad (33b)$$

$$e = -1.1722 \times 10^{-6} + 2.4204 \times 10^{-8}t + 9.9866 \times 10^{-10}t^2 \quad (33c)$$

The overall standard deviation in the fit is $9.8 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The standard deviation in v^P is $13.4 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the direct measurements, and $6.3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the sound derived data. Comparisons of the calculated and measured values of v^P for 35‰ salinity seawater are given in Figures 5 and 6. (The overall standard deviation of the fit from 0-30°C is $7.6 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$).

The values of K^P for seawater from Bradshaw and Schleicher's work have also been analyzed by using equation (33). A summary of the standard errors in K^P and v^P are given in Table 33. An analysis of the variance of the various forms using the F-test indicates that at the 5% confidence level the 7 parameter (3C, D, 3E) is the preferred form - which is the same form found by Chen and Millero for their experimental measurements. The values of c, d, and e are given by

$$c = 2.4289 \times 10^{-3} - 7.8668 \times 10^{-5}t + 1.5649 \times 10^{-6}t^2 \quad (34a)$$

$$d = 2.0285 \times 10^{-4} \quad (34b)$$

$$e = -1.1439 \times 10^{-6} + 8.0470_6 \times 10^{-8}t - 1.8638 \times 10^{-9}t^2 \quad (34c)$$

$10^6(V^P \text{ Combined} - V^P \text{ Chen and Millero, Direct}), \text{ SW}(35\text{‰})$

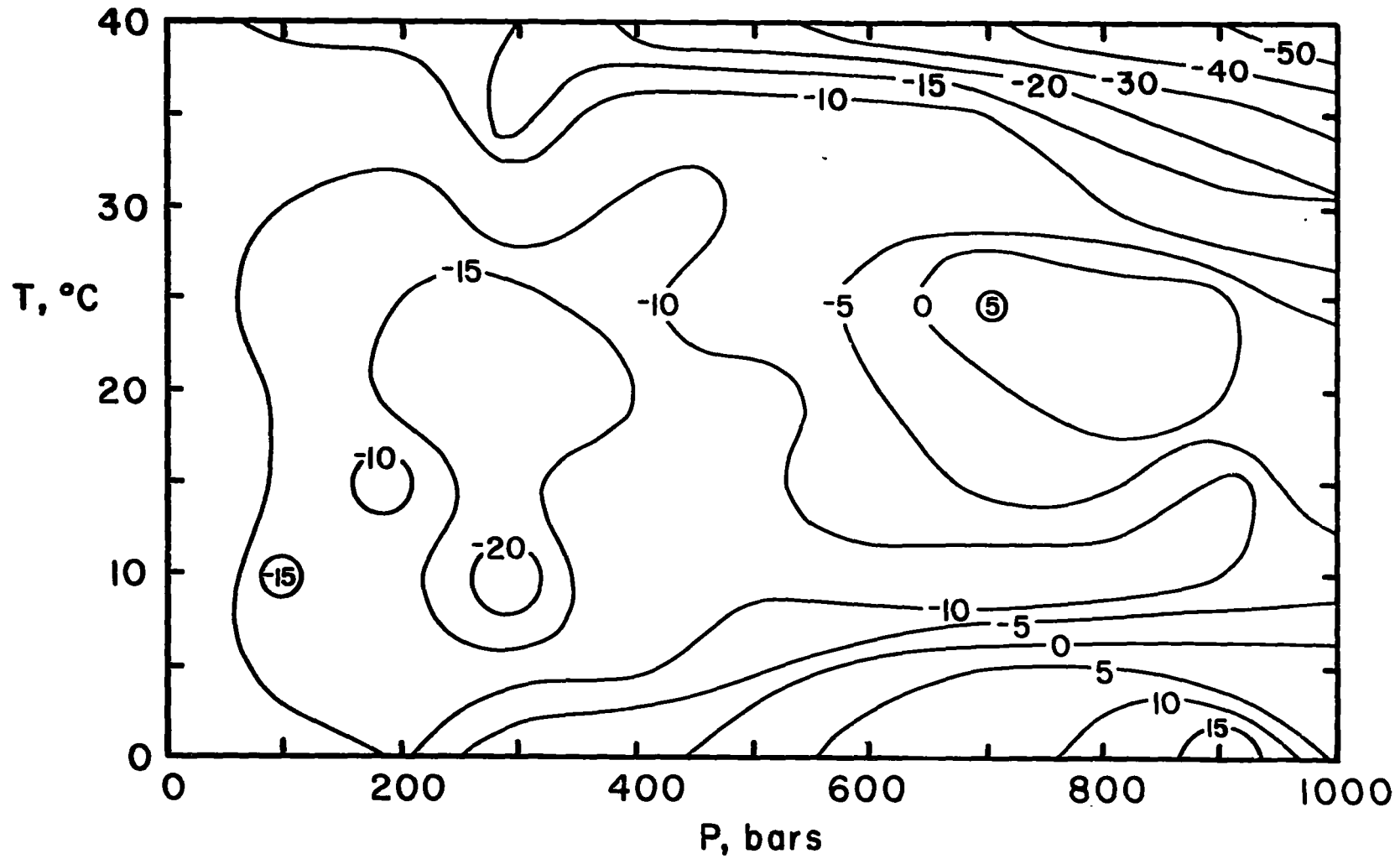


Figure 5.

$10^6 (V^P \text{ Combined} - V^P \text{ Chen and Millero, Sound}), \text{ SW } (35\%)$

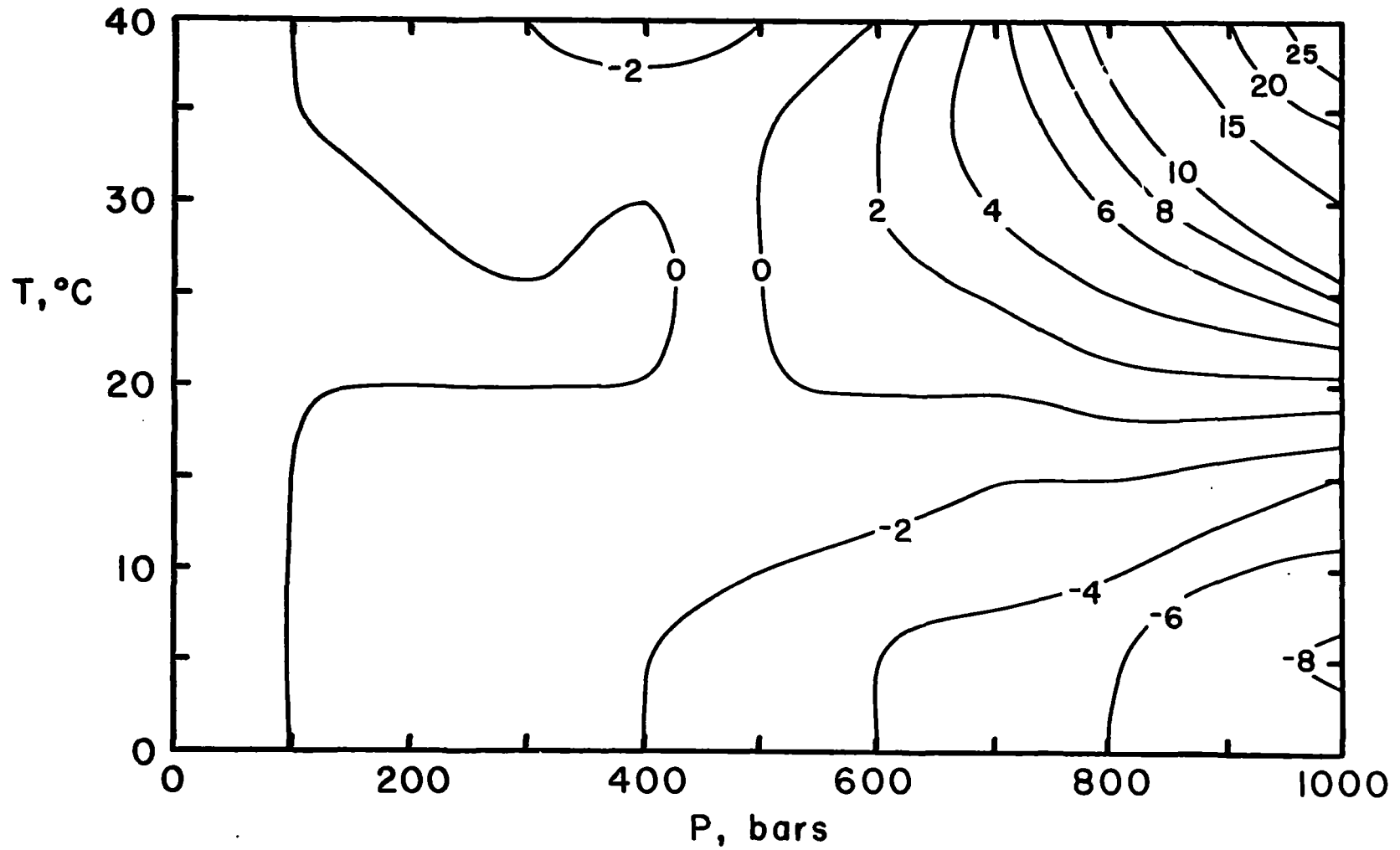


Figure 6.

TABLE 33

SUMMARY OF THE BULK MODULUS FIT OF SEAWATER FROM

BRADSHAW AND SCHLEICHER'S WORK^a

$$K^P - K_W^P - (K^0 - K_W^0) = (c S + d S^{3/2})P + e SP^2$$

<u>Parameters</u>	<u>$\sigma(K)$</u>	<u>$10^6 \sigma(v)$</u>
12(4C, 4D, 4E)	8.50	3.80
11(4C, 4D, 3E)	8.59	3.87
11(4C, 3D, 4E)	8.51	3.83
10(4C, 4D, 2E)	8.63	3.88
10(4C, 2D, 4E)	8.53	3.95
9(4C, 4D, E)	8.69	4.10
9(4C, D, 4E)	8.54	3.95
9(3C, 3D, 3E)	8.72	3.97
8(4C, 4D)	8.67	5.02
8(4C, 4E)	9.01	4.50
8(3C, 3D, 2E)	8.69	4.03
8(3C, 2D, 3E)	8.67	4.13
7(3C, 3D, E)	8.75	4.24
7(3C, D, 3E)	8.68	4.13
6(3C, 3D)	8.74	5.13
6(3C, 3E)	9.14	4.66

- a) The values of K^P at the lowest pressure ($P = 7.37$) were not used. The data were weighted by $P/125 + 1$ since the high pressure values of K^P are more reliable. The total number of data points used was 341.

The standard error of the fit is $4.13 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The differences in the measured and calculated values of v^P for Bradshaw and Schleicher's results at 35^o/oo salinity seawater are shown in Figure 7. As shown in Figures 8, 9 and 10, the values of v^P determined from the results of Bradshaw and Schleicher at 35^o/oo salinity seawater are in good agreement with the direct, sound derived and combined values of v^P determined by Chen and Millero.

We have also analyzed the sound derived values of K^P from Chen and Millero combined with the values of Bradshaw and Schleicher using equation (33). The 7 parameter equation (3C, D, 3E) gives a standard error of $3.97 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The values of c, d, and e are given by

$$c = 3.6709 \times 10^{-3} - 3.2062 \times 10^{-5}t - 7.2114 \times 10^{-7}t^2 \quad (35a)$$

$$d = -1.6279 \times 10^{-5} \quad (35b)$$

$$e = -1.1319 \times 10^{-6} + 5.9578 \times 10^{-8}t - 8.2546 \times 10^{-10}t^2 \quad (35c)$$

These results indicate that sound data of Chen and Millero are internally consistent with Bradshaw and Schleicher's work to $\sim 4 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ which is the σ we get for the Bradshaw and Schleicher data. The direct measurements of Chen and Millero appear to have a slightly higher spread when compared with the sound data (as well as the Bradshaw and Schleicher data), $\sim 8 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$. Since all the data sets have σ 's of a similar order of magnitude, we have not attempted to weight the data sets.

The combined values of K^P determined from the values of v^P of Bradshaw and Schleicher and Chen and Millero have been fitted to various forms of equation (33). A summary of the standard errors in K^P and v^P for the various forms is given in Table 34. It is not possible to make a selection of the "best" fit by using various statistics since the σ is greatly affected by

$10^6 (V^P \text{exp} - V^P \text{calc})$ Bradshaw and Schleicher, SW (35%)

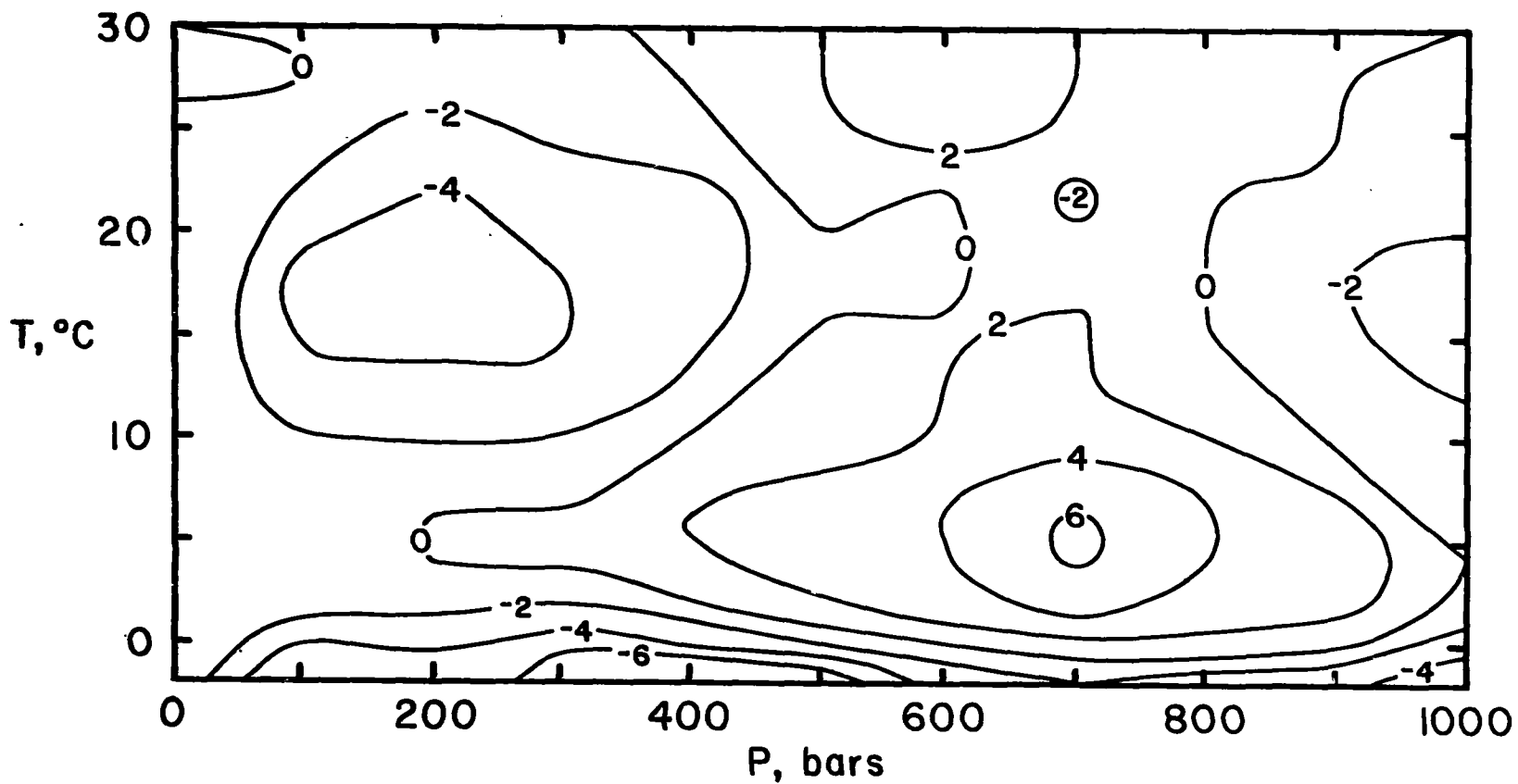


Figure 7.

$10^6 (V^P B/S - V^P \text{Direct}, C/M), SW (35\text{‰})$

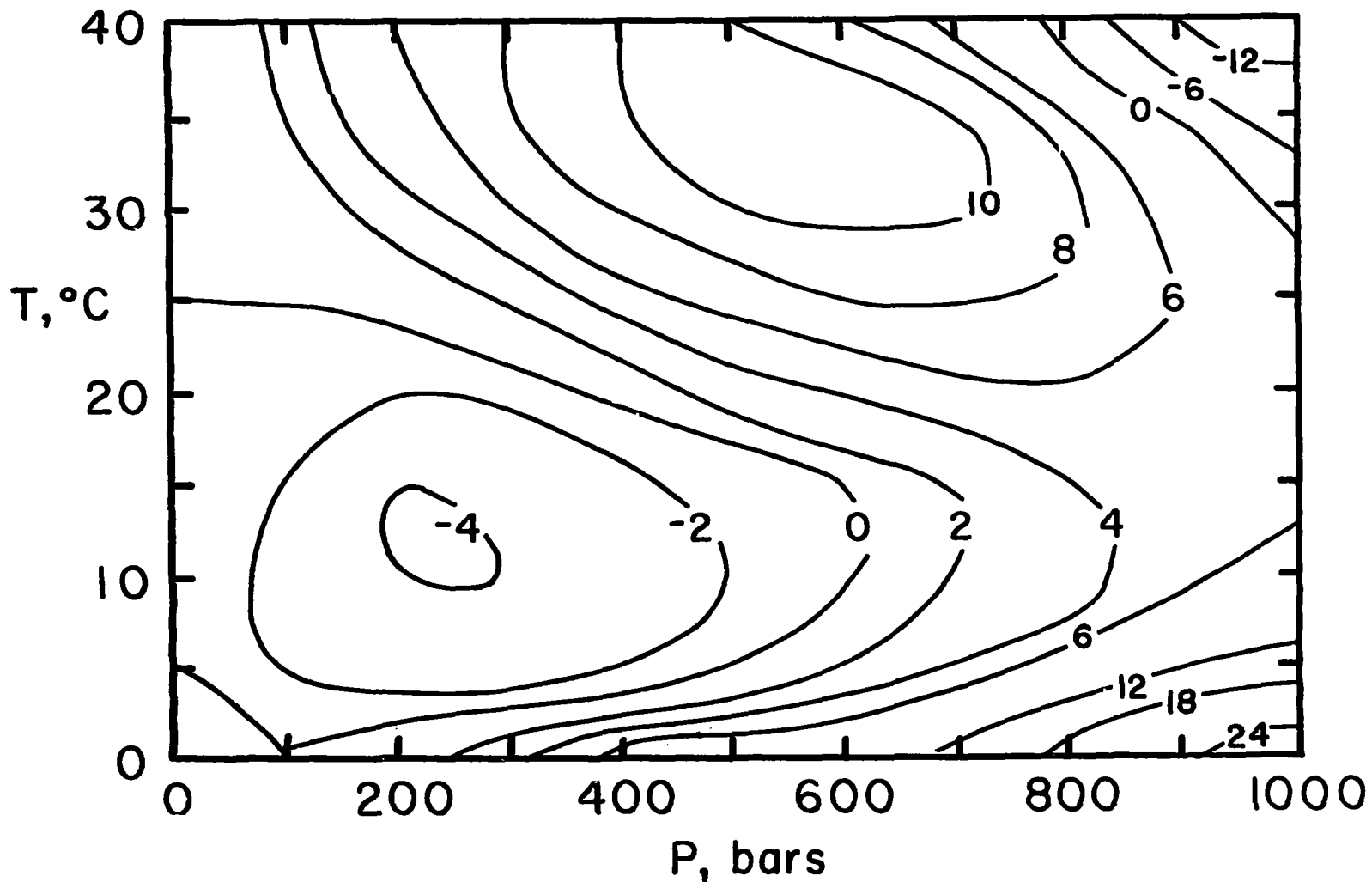


Figure 8

$10^6 (V^P B/S - V^P \text{ Sound, C/M}), \text{ SW (35\%)}$

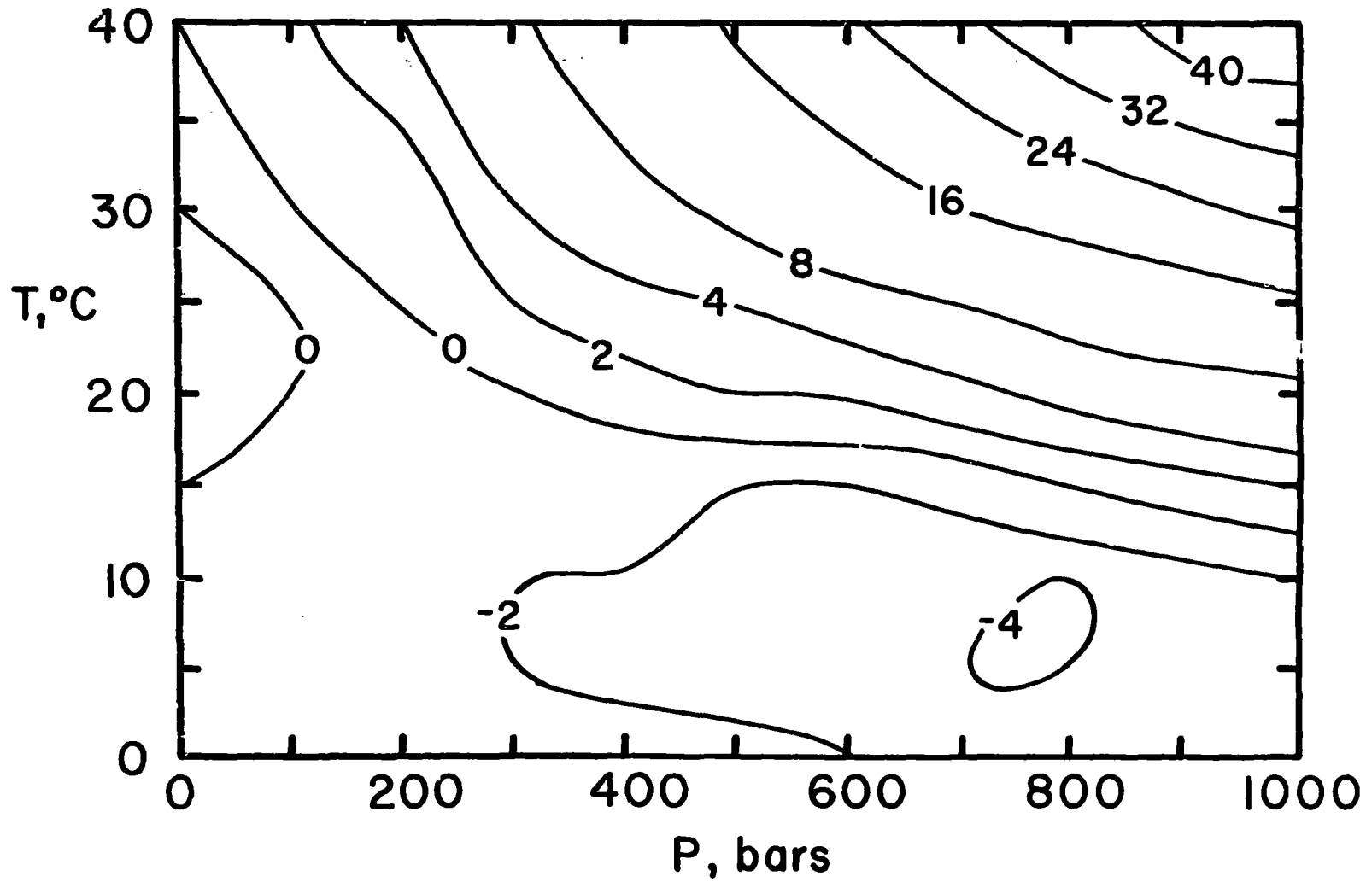
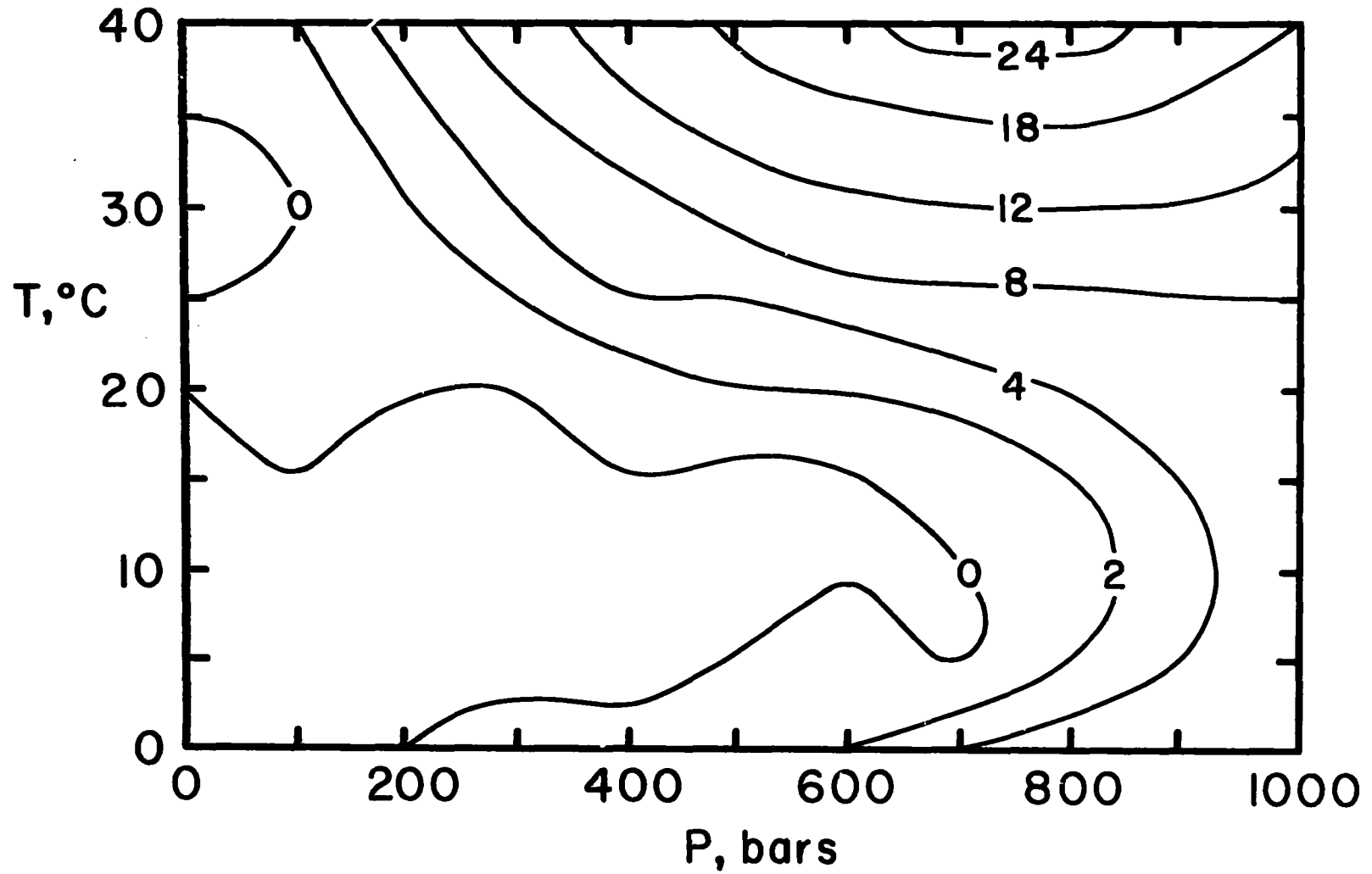


Figure 9

$10^6(V^P B/S - V^P \text{ Combined}, C/M), \text{ SW } (35\%)$



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Figure 10.

TABLE 34

SUMMARY OF BULK MODULUS FIT OF SEAWATER USING COMBINED DATA^a

$$K^P - K_W^P - (K^0 - K_W^0) = (c S + d S^{3/2})P + e SP^2$$

<u>Parameters</u>	<u>$\sigma(K)$</u>	<u>$10^6 \sigma(V)$</u>
12(4C, 4D, 4E)	9.96	8.78
11(4C, 3D, 4E)	9.97	8.79
11(4C, 4D, 3E)	9.99	8.80
10(4C, 2D, 4E)	10.04	8.96
10(4C, 4D, 2E)	10.00	8.80
9(4C, D, 4E)	10.08	8.99
9(4C, 4D, E)	10.30	9.06
9(3C, 3D, 3E)	10.01	8.84
8(4C, 4D)	10.31	9.10
8(4C, 4E)	10.46	9.34
8(3C, 3D, 2E)	10.02	8.84
8(3C, 2D, 3E)	10.07	9.00
7(3C, 3D, E)	10.32	9.10
7(3C, D, 3E)	10.12	9.02
6(3C, 3D)	10.33	9.14
6(3C, 3E)	10.50	9.37

a) The data were weighted by $P/699 + 1$.

the divergence of the data sets at high pressures and temperatures. Since the individual data sets all were found to fit the same equation from a statistical analysis, we feel that the 7 parameter (3C, D, 3E) gives the best representation of the data. The values of c, d, and e are given by

$$c = 2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}t - 1.6078 \times 10^{-6}t^2 \quad (36a)$$

$$d = 1.9107_5 \times 10^{-4} \quad (36b)$$

$$e = -9.9348 \times 10^{-7} + 2.0816 \times 10^{-8}t + 9.1697 \times 10^{-10}t^2 \quad (36c)$$

The overall standard error is $9.02 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P . The standard deviation is $4.03 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for Bradshaw and Schleicher's data, $9.62 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the direct measurements of Chen and Millero, and $5.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ for the sound measurements of Chen and Millerc. A comparison at $S = 35^\circ/00$ of the new equation with the equations generated from the individual data sets are shown in Figures 11, 12 and 13. Over the oceanic ranges of P, t and S the three independent data sets agree with the combined equation to $6 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in v^P (the overall $\sigma = 5 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$).

The specific volume, v, can be calculated from the secant bulk modulus (equation 1) using

$$v^P = v^0 \left(1 - \frac{P}{K}\right) \quad (37)$$

Values of v^P calculated from equation (37) are given in UNESCO Tables.* The thermal expansibility, α , can be calculated from the temperature derivative of equation (37)

$$\alpha^P = \frac{1}{v^P} \left[\frac{\partial v^0}{\partial T} \left(1 - \frac{P}{K}\right) + \frac{v^0 P}{K^2} \frac{\partial K}{\partial T} \right] \quad (38)$$

$10^6(V^P \text{ UNESCO} - V^P \text{ B/S}), \text{ SW } (35\text{‰})$

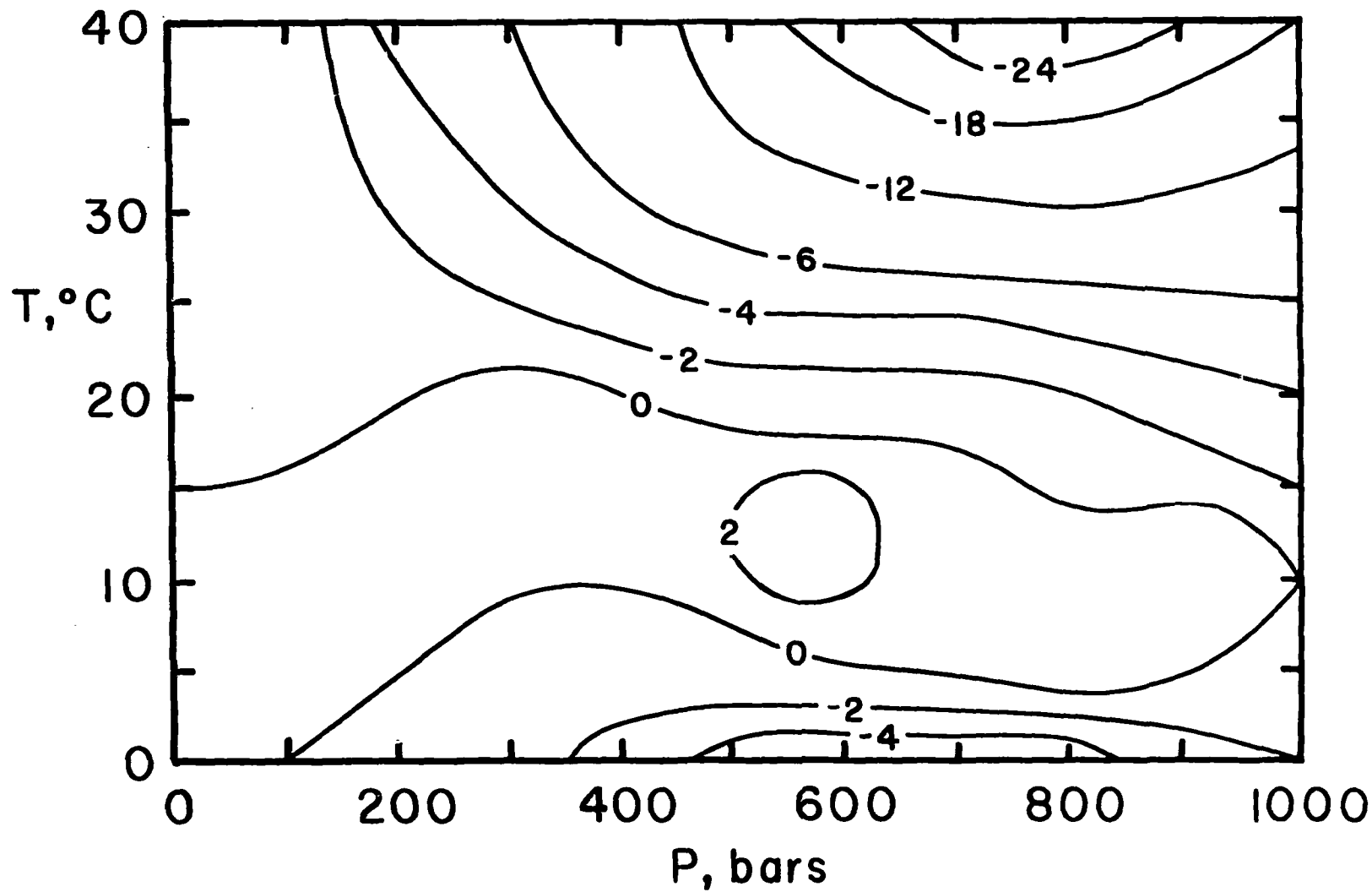
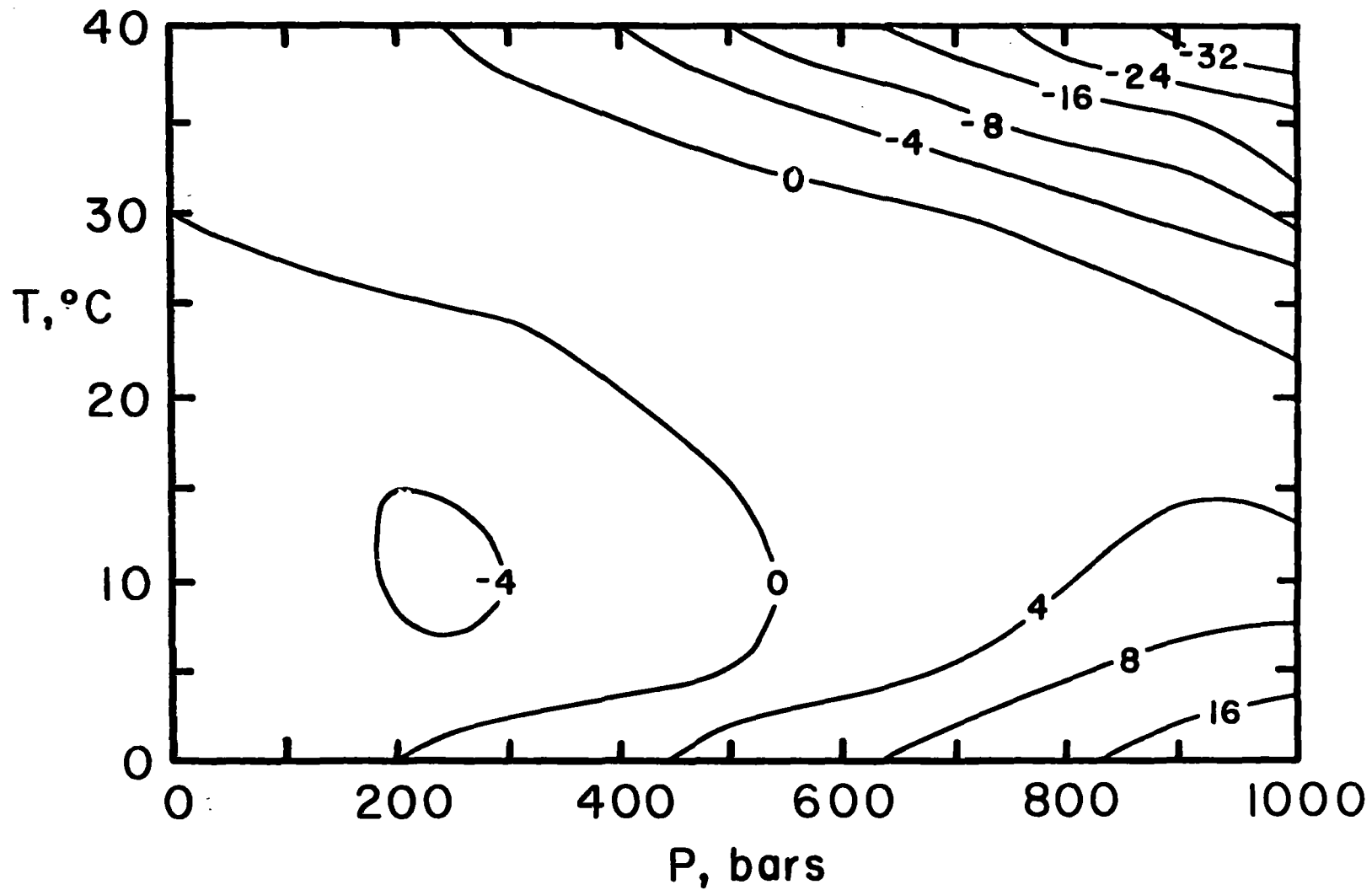


Figure 11

$10^6 (V^P \text{ UNESCO} - V^P \text{ Direct, C/M}), \text{ SW } (35\text{‰})$



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Figure 12

$10^6 (V^P \text{ UNESCO} - V^P \text{ Sound, C/M}), \text{ SW } (35\text{‰})$

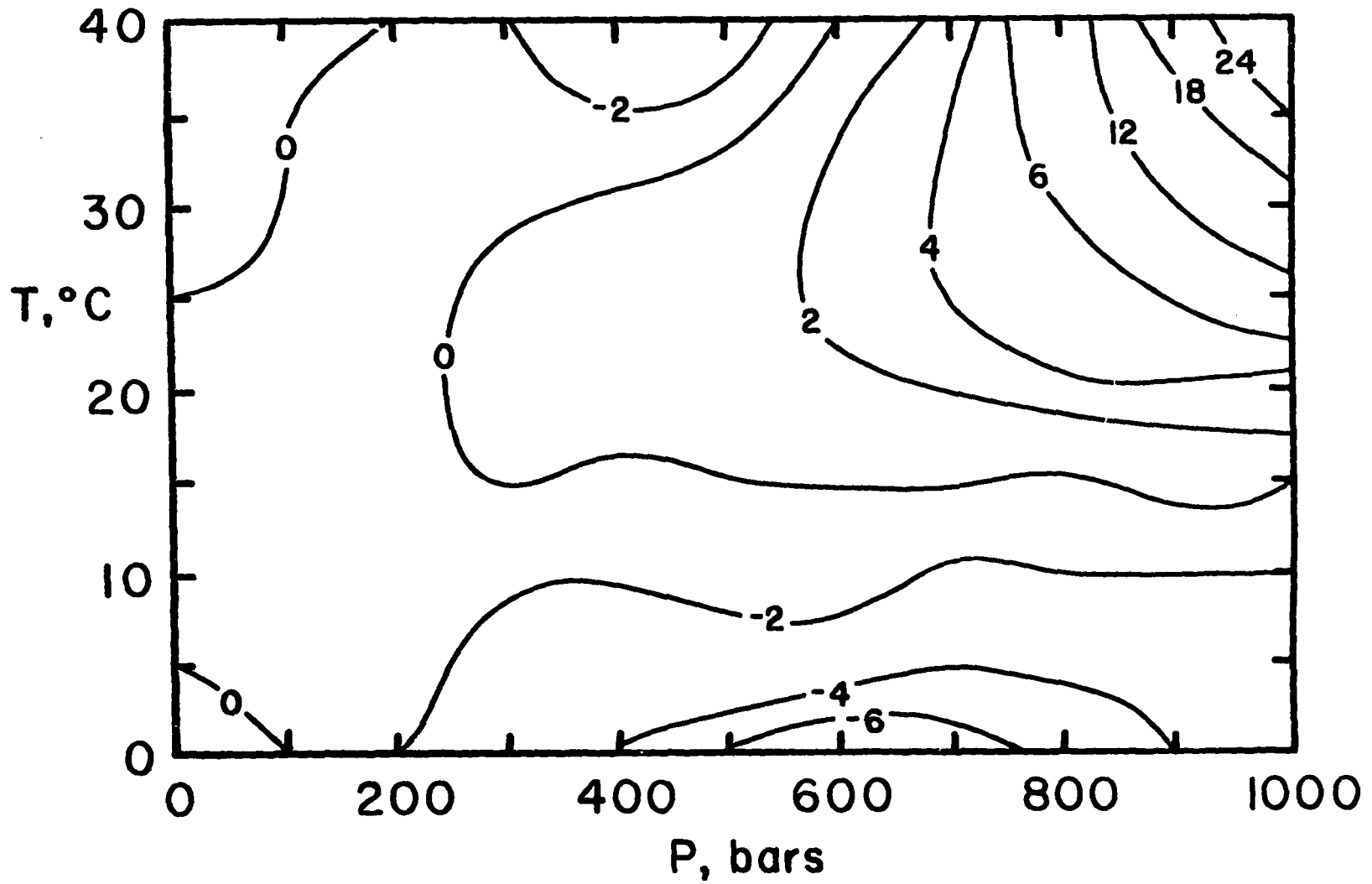


Figure 13

Values of α^P calculated from equation (38) are given in UNESCO Tables.* The isothermal compressibility, β^P , can be calculated from the pressure derivative of equation (37),

$$\beta^P = \frac{-1}{v^P} \left[\frac{v^0}{K} \frac{\partial K}{\partial P} \right] \quad (39)$$

Values of β^P calculated from equation (39) are given in UNESCO Tables.*

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* Tables giving v^P , α^P and β^P for seawater as a function of P, t and S will be published by UNESCO in the near future (UNESCO 1981).

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CONCLUSION

During its last meeting in September 1980, the Joint Panel on Oceanographic Tables and Standards drafted a document on the Practical Salinity Scale and the International Equation of State of Seawater. In conclusion, and set out hereunder, is a reproduction of the section of this document relative to the International Equation of State of Seawater, 1980. The following equations are to be used to compute density of seawater.

The International Equation of State of Seawater, 1980

A new equation of state of seawater diluted with pure water or concentrated by evaporation has been determined to be used with the practical salinity scale (Millero, Chen, Bradshaw and Schleicher, 1980; Millero and Poisson, 1981,a). This equation is more precise than the currently used equations (Knudsen, Forch and Sørensen, 1902; Ekman, 1908; Cox, McCartney and Culkin, 1970) and covers a wider range of temperature and pressure. Data reports describing the details of the fitting procedure are available (Millero, Chen, Bradshaw and Schleicher, 1981; Millero and Poisson, 1981,b in Unesco 1981,b).

The density (ρ , kg m^{-3}) of seawater as a function of practical salinity (S), temperature (t, $^{\circ}\text{C}$) and applied or gauge pressure (p, bars) is given by :

$$\rho(S,t,p) = \rho(S,t,0) / \{1 - p/K(S,t,p)\} \quad (7)$$

where $K(S,t,p)$ is the secant bulk modulus. The specific volume ($v = 1/\rho$, $\text{m}^3 \text{kg}^{-1}$) of seawater can be obtained from

$$v(S,t,p) = v(S,t,0) \{1 - p/K(S,t,p)\} \quad (8)$$

The density of seawater at one standard atmosphere ($p = 0$) can be determined from

$$\begin{aligned} \rho(S,t,0) = & \rho_w + (b_0 + b_1t + b_2t^2 + b_3t^3 + b_4t^4)S \\ & + (c_0 + c_1t + c_2t^2)S^{3/2} + d_0S^2 \end{aligned} \quad (9)$$

$$\begin{aligned}
b_0 &= 8.244\ 93 \times 10^{-1} & c_0 &= -5.724\ 66 \times 10^{-3} \\
b_1 &= -4.0899 \times 10^{-3} & c_1 &= 1.0227 \times 10^{-4} \\
b_2 &= 7.6438 \times 10^{-5} & c_2 &= -1.6546 \times 10^{-6} \\
b_3 &= -8.2467 \times 10^{-7} & & \\
b_4 &= 5.3875 \times 10^{-9} & d_0 &= 4.8314 \times 10^{-4}
\end{aligned}$$

The density of the reference pure water (SMOW) is given by (IUPAC, 1976)

$$\rho_w = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4 + a_5 t^5 \quad (10)$$

where

$$\begin{aligned}
a_0 &= 999.842\ 594 \\
a_1 &= 6.793\ 952 \times 10^{-2} \\
a_2 &= -9.095\ 290 \times 10^{-3} \\
a_3 &= 1.001\ 685 \times 10^{-4} \\
a_4 &= -1.120\ 083 \times 10^{-6} \\
a_5 &= 6.536\ 332 \times 10^{-9}
\end{aligned}$$

Should more reliable data for pure water become available in the future, equation 9 can be easily modified.

The secant bulk modulus (K) of seawater is given by

$$K(S, t, p) = K(S, t, 0) + Ap + Bp^2 \quad (11)$$

where

$$K(S, t, 0) = K_w + (f_0 + f_1 t + f_2 t^2 + f_3 t^3)S + (g_0 + g_1 t + g_2 t^2)S^{3/2} \quad (12)$$

$$\begin{aligned}
f_0 &= 54.6746 & g_0 &= 7.944 \times 10^{-2} \\
f_1 &= -0.603\ 459 & g_1 &= 1.6483 \times 10^{-2} \\
f_2 &= 1.099\ 87 \times 10^{-2} & g_2 &= -5.3009 \times 10^{-4} \\
f_3 &= -6.1670 \times 10^{-5} & &
\end{aligned}$$

$$A = A_w + (i_0 + i_1 t + i_2 t^2)S + j_0 S^{3/2} \quad (13)$$

$$\begin{aligned}
i_0 &= 2.2838 \times 10^{-3} & j_0 &= 1.910\ 75 \times 10^{-4} \\
i_1 &= -1.0981 \times 10^{-5} & & \\
i_2 &= -1.6078 \times 10^{-6} & &
\end{aligned}$$

$$B = B_w + (m_0 + m_1 t + m_2 t^2) S \quad (14)$$

$$m_0 = -9.9348 \times 10^{-7}$$

$$m_1 = 2.0816 \times 10^{-8}$$

$$m_2 = 9.1697 \times 10^{-10}$$

The pure water terms of the secant bulk modulus are given by

$$K_w = e_0 + e_1 t + e_2 t^2 + e_3 t^3 + e_4 t^4 \quad (15)$$

$$e_0 = 19\,652.21$$

$$e_1 = 148.4206$$

$$e_2 = -2.327\,105$$

$$e_3 = 1.360\,477 \times 10^{-2}$$

$$e_4 = -5.155\,288 \times 10^{-5}$$

$$A_w = h_0 + h_1 t + h_2 t^2 + h_3 t^3 \quad (16)$$

$$h_0 = 3.239\,908$$

$$h_1 = 1.437\,13 \times 10^{-3}$$

$$h_2 = 1.160\,92 \times 10^{-4}$$

$$h_3 = -5.779\,05 \times 10^{-7}$$

$$B_w = k_0 + k_1 t + k_2 t^2 \quad (17)$$

$$k_0 = 8.509\,35 \times 10^{-5}$$

$$k_1 = -6.122\,93 \times 10^{-6}$$

$$k_2 = 5.2787 \times 10^{-8}$$

The International equation of state is valid for $S = 0$ to 42;
 $t = -2$ to 40°C ; $p = 0$ to 1000 bars.

The following values are provided for checking the correct use of the
 above equation. (Units : ρ in kg m^{-3} and K in bars)

S	t($^\circ\text{C}$)	p(bars)	$\rho(S,t,p)$	$K(S,t,p)$
0	5	0	999.966 75	20 337.803 75
		1000	1044.128 02	23 643.525 99
	25	0	997.047 96	22 100.721 06
		1000	1037.902 04	25 405.097 17
35	5	0	1027.675 47	22 185.933 58
		1000	1069.489 14	25 577.498 19
	25	0	1023.343 06	23 726.349 49
		1000	1062.538 17	27 108.945 04

The International Equation of State is meant for use in all oceanic waters. However, these equations should be used with caution in waters that have a chemical composition different from standard seawater. In such waters, densities derived with the equations related in this report, i.e. based on practical salinity measurements and the International Equation of State, may deviate measurably from the true densities (Millero, Gonzales and Ward, 1976; Millero and Kremling, 1976; Millero, Gonzales, Brewer and Bradshaw, 1976; Millero, Forsht, Means, Gieskes and Kenyon, 1978; Poisson, Lebel and Brunet, 1980; Poisson, Lebel and Brunet, 1981). However, it is important to note that in water masses different in composition from standard seawater, the differences in densities derived by the new equations involve only very small errors (Lewis and Perkin, 1978). Corrections to the calculated densities can be made from direct density measurements or from calculations involving the use of partial molal volume data and conductivity data if the chemical composition is known (Brewer and Bradshaw, 1975; Poisson and Chanu, 1976 and 1980; Poisson, 1978; Millero, Forsht, Means, Gieskes and Kenyon, 1978; Poisson, Périé, Périé and Chemla, 1979).

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