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# The equation of state of seawater<sup>1</sup>

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## ABSTRACT

The  $P$ - $V$ - $T$  properties of seawater calculated from the sound derived equation of state of Wang and Millero (1973)

$$\frac{PV_W^O}{V^O - V^P} = B + A_1P + A_2P^2$$

(where  $V^O$  and  $V^P$  are the specific volumes at one atmosphere and pressure  $P$ ,  $V_W^O$  is the specific volume of pure water at one atmosphere;  $B$ ,  $A_1$  and  $A_2$  are empirical constants) are compared with the data of various workers. The equation of state was derived from the velocity of sound data of Wilson (1960b). Using the velocity of sound data of Del Grosso and Mader (1972), another equation of state was derived in the same form. The maximum absolute difference over the oceanographic range between the velocities of sound for the two sets of workers is 1.77 m/sec at 37‰, 5°C and 1000 bars pressure. Below 5°C the deviations remain large, especially at the higher pressures. At temperatures above 5°C the agreement is within the 0.3 m/sec standard deviation of Wilson's equation (after the two sets of data were shifted to agree at one atmosphere). The sound-derived  $P$ - $V$ - $T$  properties are in excellent agreement over the oceanographic range except at low temperatures. The sound-derived specific volumes agree to within  $\pm 35 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ , the compressibilities agree to within  $\pm 0.064 \times 10^{-6} \text{ bar}^{-1}$ , and the expansibilities agree to within  $\pm 1.8 \times 10^{-6} \text{ deg}^{-1}$ . Since the sound velocities of Del Grosso and Mader are not consistent with the direct experimental  $P$ - $V$ - $T$  measurements of Emmet and Millero (1974), Bradshaw and Schleicher (1973) and Chen and Millero (1974), we favor the equation of state derived from the sound velocity data of Wilson.  $P$ - $V$ - $T$  data calculated from this equation of state are compared to the results of Ekman (1908), Crease (1962), Newton and Kennedy (1965), Li (1967), Wilson and Bradley (1968), Bradshaw and Schleicher (1970), Lepple and Millero (1971), Bradshaw and Schleicher (1973), Duedall and Paulowich (1973), Emmet and Millero (1974), and Chen and Millero (1974). Our equation of state is precise in compressibility to within  $\pm 0.01 \times 10^{-6} \text{ bar}^{-1}$ , in specific volume to within  $\pm 10 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ , in expansibility to within  $\pm 2 \times 10^{-6} \text{ deg}^{-1}$ , and should therefore be used to obtain the most reliable  $P$ - $V$ - $T$  properties of seawater.

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## 1. Historical introduction

In recent years a great deal of controversy has centered on the P-V-T properties of seawater. The presently used equation of state for seawater (which is an analytical expression of the P-V-T properties) was based on the one atmosphere densities of Knudsen (1901) and the high pressure compressibilities of Ekman (1908). Recent work (Cox *et al.*, 1970; Kremling, 1972; Millero and Lepple, 1973) showed that the one atmosphere densities are accurate to within  $10 \times 10^{-6}$  g/cm<sup>3</sup>. The major controversy involved the effect of pressure on the P-V-T properties of seawater and the subsequent representation of this pressure effect by various equations of state. In this section, we briefly review work done on the high pressure P-V-T properties of seawater and the resulting equations of state of liquids (including seawater).

Many of the currently used equations of state are based on the Tait (1888) equation. This equation was derived to represent the P-V-T properties of pure water

$$k = \frac{V^0 - V^P}{V^0 P} = \frac{A}{\pi + P} \quad (1)$$

or rearranged

$$V^P = V^0 - V^0 P \frac{A}{\pi + P} \quad (1a)$$

$V^0$  and  $V^P$  are, respectively, the specific volumes at zero (one atmosphere) and  $P$  applied pressure,  $A$  is a constant, and  $\pi$  is a function of temperature. The term  $k$  is the secant compressibility. This was referred to by Tait and others (Ekman, 1908) as the average or mean compressibility. Using seawater samples from the HMS CHALLENGER expedition, Tait measured the secant compression (average compressibility) of seawater.

Hayward (1967) revealed that most authors in the last sixty years used the Tait equation in, what we shall refer to as, the misquoted form

$$-\frac{1}{V^0} \left( \frac{\partial V^P}{\partial P} \right)_T = \frac{C}{B + P} \quad (2)$$

or integrated

$$V^P = V^0 - CV^0 \ln \left( \frac{B + P}{B} \right) \quad (2a)$$

In equations (2) and (2a),  $C$  is a constant,  $B$  is a function of temperature and  $(V^0 - V^P)/P$  of the original Tait equation was replaced by  $-(\partial V^P/\partial P)$ .

As researched by Hayward (1967), the earliest occurrence of the use of the misquoted Tait equation was found in a book published by Tamman in 1907. We understand the history of misuse, since in the low pressure range (below 500 bars) that concerns the majority of workers, a plot of  $(V^0 - V^P)/V^0$  vs



pressure will give nearly a straight line. Therefore,  $(V^0 - V^P)/P$  will be almost equal to the negative of the slope  $(\partial V^P/\partial P)$ .

Shortly after Tait, Ekman (1908) measured the secant compression (or mean compressibility) of seawater at 31.13 and 38.53‰ salinity. He made his measurements relative to the 0°C compression data for pure water ( $k_W$ ) of Amagat (1893). His measurements covered the range of 0 to 20°C and 0 to 600 bars pressure. Ekman fitted his results to an equation of the form

$$(k - k_W) = a + bt + ct^2 + dt^3 - P(e + ft + ht^2) + lP^2t \quad (3)$$

in which  $t$  is the temperature in degrees centigrade,  $P$  is the pressure, and  $a$  through  $l$  are constants. Much of the present controversy surrounding the equation of state involves the work of Ekman. Many modern oceanographers examined his data and their results will be discussed throughout the paper.

At the same time as Ekman measured the compression of seawater, the Tumlriz (1909) equation was derived

$$(V^P - B)(P + D) = \lambda \quad (4)$$

in which  $B$ ,  $D$ , and  $\lambda$  are temperature dependent constants. Equation (4) was used by Eckart (1958) to fit the data of several workers (Amagat, 1893; Ekman 1908; Bridgman, 1913; Gibson and Loeffler, 1941; and Kennedy, 1957). He obtained results that were accurate to only  $\pm 200 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  in specific volume.

The Tumlriz equation (4) is actually a rearrangement of the Tait equation (1). This becomes apparent by realizing in equation (4), that at  $P = 0$  bars (one atmosphere absolute pressure)  $B = V^0 - \lambda/D$ . Then solving equation (4) for  $V^P$  and substituting the value for  $B$  at  $P = 0$ , we have

$$V^P = \left( V^0 - \frac{\lambda}{D} \right) + \frac{\lambda}{P + D} \quad (4a)$$

Finding a common denominator and adding the two terms in equation (4a) that are involved with  $\lambda$  results in

$$V^P = V^0 - \frac{\lambda}{D} \frac{P}{P + D} \quad (4b)$$

By comparing this equation with (1a), it is clear that if  $D$  is equated to  $\pi$  and  $\lambda/D = \lambda/\pi$  equated to  $AV^0$ , the Tumlriz equation becomes equivalent to the original Tait equation.

Using the Tumlriz equation, Wilson and Bradley (1968) fitted their measurements of the specific volume of seawater with a standard deviation of  $130 \times 10^{-6} \text{cm}^3 \text{gm}^{-1}$ . Employing a modified form of the Tumlriz equation,



Fisher and Dial (1968) fitted the same data of Wilson and Bradley to within  $70 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ . Wilson and Bradley estimated their experimental data to be six times more precise than the data represented by their equation. Although the P-V-T data of Wilson and Bradley are in fair agreement with the work of Newton and Kennedy (1965), their results are in poor agreement with all of the recent studies (Lepple and Millero, 1971; Emmet and Millero, 1974; Bradshaw and Schleicher, 1970; and Wang and Millero, 1973—as will be shown later in the paper).

Newton and Kennedy (1965) measured the specific volume of seawater under pressure (0 to 1300 bars), from 0 to  $25^\circ\text{C}$  with a precision of  $70 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ . The comparisons of their specific volume data with other workers (Knudsen, 1901; Ekman, 1908; Crease, 1962) indicated (to them) that a systematic difference of up to  $500 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  occurred at the highest pressures.

In 1935, Gibson extended the misquoted Tait equation to solutions. He derived what is referred to as the Tait-Gibson equation

$$-\left(\frac{\partial VP}{\partial P}\right)_T = \frac{C' X_1}{B^* + P} \quad (5)$$

or integrated

$$VP = V^0 - X_1 C' \ln[(B^* + P)/B^*] \quad (5a)$$

$X_1$  is the weight fraction of solvent,  $C'$  is a constant, and  $B^*$  is a function of temperature and concentration.

Rearrangement of the Tait-Gibson equation gives

$$1/(\partial VP/\partial P) = a + bP \quad (6)$$

in which  $a = -B^*/C' X_1$  and  $b = -1/C' X_1$  in equation (5). Differentiation of the Tait equation (1a) with respect to pressure gives

$$1/(\partial VP/\partial P) = a' + b'P + c'P^2 \quad (7)$$

where  $a' = -\pi/V^0 A$ ,  $b' = -2/V^0 A$ , and  $c' = -1/V^0 A \pi$  in equation (1). Better results were obtained from fitting the sound-derived seawater data of Wilson (1960b) to equation (7) than to equation (6). For example, (Figure 1) at  $35^\circ/00$  and  $0^\circ\text{C}$ , the maximum deviation of the fitted sound data is  $1.068 \times 10^2 \text{ bar} - \text{g}/\text{cm}^3$  for the linear equation (6), and  $1.1 \text{ bar} - \text{g}/\text{cm}^3$  for the quadratic equation (7). These differences are equivalent to deviations of approximately  $0.2 \times 10^{-6} \text{ bar}^{-1}$  and  $0.002 \times 10^{-6} \text{ bar}^{-1}$ , respectively, in compressibility. Compressibility is the negative reciprocal of the specific volume times the partial derivative of the specific volume with respect to pressure  $[(\beta = -1/VP)(\partial VP/\partial P)_T]$ .

Li (1967) derived equations in the Tait-Gibson form from both compressibility and sound velocity data

$$VP = V^0 - (1 - S \times 10^{-3}) \times C' \log [(B + P)/B] \quad (8)$$

in which  $S$  is the salinity in parts per thousand (‰),  $C'$  is a constant, and  $B$  is a temperature and salinity dependent function. Although the  $B$  parameter should be independent of pressure, it actually does vary with pressure. This is evident, since neither the P-V-T pure water data of Kell and Whalley (1965), the pure water sound data (Fine and Millero, 1973), or the seawater sound data (see above), can be fitted to the Tait-Gibson equation (6) within experimental error. However, the specific volume data can be fitted to the true Tait equation (7) (Fine and Millero—in press) to within  $\pm 20 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ .

Li examined the one atmosphere sound data for seawater of Wilson (1960a) and the directly measured values of Ekman (1908) using eq. (8). He directed attention to a difference at one atmosphere between the compressibility data of Ekman and the sound-derived data of Wilson (1960a). Li concluded that in spite of this baseline shift, the work of Ekman was internally consistent. These conclusions were also arrived at by Crease (1962), Bradshaw and Schleicher (1970) and Lepple and Millero (1971).

Using the seawater velocity of sound equation of Wilson (1960b), Crease (1962) derived an equation of the form

$$VP = \sum_{ijk} A_{ijk} P^i t^j (S - 35)^k \quad (9)$$

in which there are twenty-two coefficients  $A_{ijk}$  for the ranges: 0 to 6°C, 0 to 1000 bars, 33 to 37‰; 0 to 30°C, 33 to 37‰, and 0 to 500 bars. The claimed accuracy of his equation was  $3 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  for the specific volume. However, this accuracy is in doubt due to the method of derivation of the equation (Wang and Millero, 1973). Crease concluded that over most of the oceans basins the error in the work of Ekman was less than  $30 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ .

Bradshaw and Schleicher (1970) measured the expansibility ( $\alpha$ )

$$\alpha = 1/VP (\partial VP / \partial T)_P \quad (10)$$

of seawater over the range  $-2^\circ$  to  $30^\circ \text{C}$ ; 30.50, 35.00, and 39.50‰; and 7 to 1000 bars. They reported a maximum uncertainty in their measurements of  $\pm 3 \times 10^{-6} \text{deg}^{-1}$ . After comparing their data to the temperature dependence of the equation of Ekman, they concluded that their results were in very good agreement.

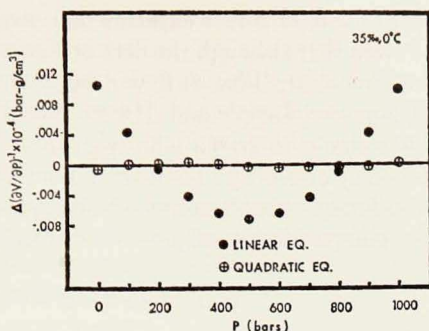


Figure 1. Deviations of the sound-derived  $1/(\partial VP/\partial P)$  from a linear [Equation (6)] and quadratic [Equation (7)] equation for 35‰ seawater at  $0^\circ \text{C}$  from 0 to 1000 bars.



From their direct experimental measurements, Lepple and Millero (1971) showed that although the data of Ekman is internally consistent, there is a large baseline shift. This shift will be discussed further in a later section. Using a piezometer, Lepple and Millero measured the compressibility of seawater over the range 0 to 40‰ salinity, 0 to 40°C, and up to 34 bars pressure with an accuracy of  $\pm 0.05 \times 10^{-6} \text{bar}^{-1}$ . They derived a theoretical compressibility equation for seawater in terms of the apparent equivalent compressibility ( $\varphi_K$ ) and the compressibility of pure water ( $\beta_W$ )

$$\beta = \beta_W + A_K Cl(‰) + B_K Cl(‰)^{3/2} \quad (11)$$

$A_K$  and  $B_K$  are temperature dependent constants related to the infinite dilution apparent molal compressibility ( $\varphi_K^0$ ) and a concentration dependent term;  $Cl(‰)$  is the chlorinity. They also showed that the constants,  $A_K$  and  $B_K$ , could be estimated for seawater from binary solution data. The resulting compressibilities agreed with the measured values to within  $\pm 0.07 \times 10^{-6} \text{bar}^{-1}$  over the entire salinity and temperature range (Millero, 1973).

Hayward (1967) investigated a more useful form of the Tait equation (1) known as the linear secant bulk modulus (K) equation

$$\frac{1}{k} = \frac{V^0 P}{V^0 - V^P} = K = K^0 + BP \quad (12)$$

This equation is a reciprocal form of the original Tait equation. This can be seen by letting  $K^0 = \pi/A$  and  $B = 1/A$  in equation (1). In equation (12),  $K^0$  is the bulk modulus at sea level pressure (equal to the reciprocal of the compressibility,  $1/\beta$ ) and  $B$  is a function of temperature and salinity.

Macdonald (1969) analyzed several experimental and analytical equations of state. He chose the Murnaghan equation.

$$\frac{V^P}{V^0} = (1 + \eta \beta^0 P)^{-1/\eta} \quad (13)$$

in which  $\eta = [\partial(1/\beta)/\partial P]_T$  at  $P = 0$  and  $\beta^0$  is the compressibility at  $P = 0$ , as generally superior to the misquoted Tait equation for pure water. But, he concluded that if the misquoted Tait equation and the Murnaghan equation were both expanded to second order in pressure, then the results obtained from both would agree.

Recently, several workers made high pressure compressibility or density measurements for seawater. Duedall and Paulowich (1973) employed a bellows-type differential compressimeter to determine the difference between the compressibility of pure water and 35‰ S seawater at 15°C and up to 900 bars. They reported a precision of from  $\pm 0.03 \times 10^{-6}$  to  $\pm 0.07 \times 10^{-6} \text{bar}^{-1}$  in their compressibility measurements. Emmet and Millero (1974) meas-



ured the density of 35‰ seawater using a high pressure magnetic float densimeter (Millero, *et. al.*, 1972). Their measurements covered the range of 0 to 40°C and 0 to 1000 bars pressure. They reported an accuracy of  $20 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$  in  $V^P$ . Bradshaw and Schleicher (personal communication, 1973) determined the compression of seawater at 10°C. Combination of these compression results with their earlier expansibility work (1970), enabled them to derive specific volumes for seawater over the entire oceanographic range. Chen and Millero (1974) measured the specific volume of 30, 35, and 40‰ salinity seawater using a high pressure magnetic float densimeter (Millero, *et. al.*, 1972). Their measurements covered the range of 0 to 40°C and 0 to 1000 bars pressure. They reported an accuracy of  $10 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ . These results (Duedall and Paulowich, Emmet and Millero, Bradshaw and Schleicher, and Chen and Millero) will be discussed in a later section.

In an attempt to resolve some of the above mentioned discrepancies and check the internal precision of the direct experimental measurements, Wang and Millero (1973) used the seawater velocity of sound data of Wilson (1960b) to determine a new equation of state in the form of the non-linear secant bulk modulus.

The purpose of this paper is to compare the sound derived P-V-T properties of seawater with direct experimental measurements. Employing the methods of Wang and Millero (1973), the sound speed data of Wilson (1960b) and that of Del Grosso and Mader (1972) were used to derive equations of state for seawater. We present a comparison of these two sets of velocity of sound data. In addition, we compare the P-V-T properties from the equation of state (derived from Wilson's sound speeds) to the P-V-T data of other workers.

## 2. The equation of state from sound speeds

To achieve an accuracy of  $0.01 \times 10^{-6} \text{ bar}^{-1}$  in compressibility we found it necessary to use a second degree bulk modulus equation for our equation of state

$$K = \frac{V_w^0 P}{V^0 - V^P} = B + A_1 P + A_2 P^2 \quad (14)$$

where  $K$  is the secant bulk modulus;  $V^0$  and  $V^P$  are the specific volumes ( $\text{cm}^3 \text{ g}^{-1}$ ) at sea level and applied pressure  $P$ ;  $V_w^0$  is the specific volume of pure water at sea level pressure;  $B$ ,  $A_1$ , and  $A_2$  are functions of temperature ( $t$  in °C) and salinity ( $S$  in ‰) defined in the appendix. Sea level absolute pressure of one atmosphere is equivalent to 0 bars of gauge pressure. Gauge or applied pressure is used in the equation of state.

In a compressible medium, the velocity of sound ( $c$ ) is related to the adiabatic compressibility ( $\beta_s$ ) by the Laplace equation

$$c^2 = \frac{VP}{\beta_S} \quad (15)$$

where  $\beta_S = -(1/VP)(\partial VP/\partial P)_S$  and  $S$  is the entropy. Although this equation is difficult to verify by direct experimental measurements (Hayward, 1969), it was indirectly verified at 1 atm by a number of workers (Lepple and Millero, 1971 and Bradshaw and Schleicher—personal communication).

The adiabatic compressibility ( $\beta_S$ ) is related to the isothermal compressibility via the ratio of the specific heats ( $C_P$  constant pressure and  $C_V$  constant volume)

$$\beta_S = \frac{C_V}{C_P} \beta \quad (16)$$

Therefore, by substituting the equation

$$C_P = C_V - \frac{T\alpha^2 P}{\beta} \quad (17)$$

( $T$  is the absolute temperature), which was derived from the first law of thermodynamics, and equation (16) into equation (15) we obtain

$$\beta = \frac{VP}{c^2} + \frac{T\alpha^2 VP}{C_P} \quad (18)$$

or

$$-\left(\frac{\partial VP}{\partial P}\right)_T = \frac{(VP)^2}{c^2} + \frac{T\alpha^2 (VP)^2}{C_P} \quad (19)$$

Thus, the compressibility ( $\beta$ ) or compression ( $\partial VP/\partial P$ ) can be determined from sound speeds, providing heat capacity, expansibility and specific volume data is available at  $P = 0$ . Since the second terms of eqs. (18) and (19) are small compared to the first terms, it is possible to determine  $\beta$  or ( $\partial VP/\partial P$ ) from sound data by treating the correction term as a perturbation to the general equation. That is

$$-(\partial VP/\partial P)_T = (VP)^2/c^2 + \Delta_S \quad (20)$$

where  $\Delta_S$  is the adiabatic correction.

Differentiation of our equation of state with respect to pressure gives

$$-\left(\frac{\partial VP}{\partial P}\right)_T = \frac{V_W^0 (B - A_2 P^2)}{(B + A_1 P + A_2 P^2)^2} \quad (21)$$

By combining this equation with eq. (19), it is possible to determine the constants  $B$ ,  $A_1$ , and  $A_2$  (given in the appendix) from sound speeds using the iterative computer technique developed by Wang and Millero (1973). To effect



this interactive technique, we used the pure water specific volume and compressibility data of Kell (1967, 1970); the one atmosphere seawater specific volumes from the Knudsen sigma- $t$ 's (1901), as formulated in an equation by Fofonoff (1962)—Sweers (1971); the specific heats of Cox and Smith (1959) or Millero, *et. al.* (1973); and then the velocity of sound data from Wilson (1960b). The heat capacities at higher pressures, which were needed in this interactive method, were calculated from the thermodynamic relationship

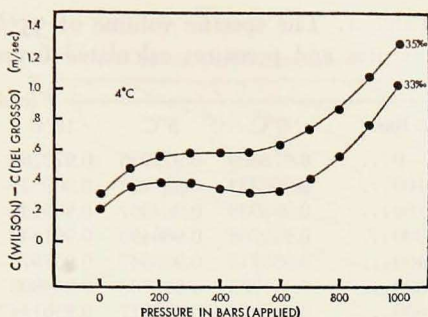


Figure 2. A comparison of the velocities of sound measurements of Wilson with those of Del Grosso and Mader for 33 and 35‰  $S$  seawater at 4°C from 0 to 1000 bars.

$$C_P(P) = C_P(0) - T \int_0^P (\partial^2 V^P / \partial T^2) dP \quad (22)$$

The accuracy or convergence in compressibility was achieved with a maximum deviation of less than  $\pm 0.01 \times 10^{-6} \text{bar}^{-1}$  over the real oceanographic range. (For a detailed description of the derivation, see Wang and Millero).

Equation (14) can be used to calculate the P-V-T properties of seawater over the entire oceanographic range. The specific volume at any pressure,  $P$ , was calculated from

$$V^P = V^0 - V_W^0 P / (B + A_1 P + A_2 P^2) \quad (23)$$

Equation (23) was differentiated with respect to temperature to give the expansibility

$$\alpha = \frac{1}{V^P} \left( \frac{\partial V^P}{\partial T} \right)_P = \frac{1}{V^P} \left( \frac{\partial V^0}{\partial T} \right) - \frac{P (\partial V_W^0 / \partial T)}{V^P (B + A_1 P + A_2 P^2)} + \left. \begin{array}{l} \\ PV_W^0 \frac{(\partial B / \partial T) + P (\partial A_1 / \partial T) + P^2 (\partial A_2 / \partial T)}{V^P (B + A_1 P + A_2 P^2)^2} \end{array} \right\} \quad (24)$$

and differentiated with respect to pressure to give the compressibility

$$\beta = - \frac{1}{V^P} \left( \frac{\partial V^P}{\partial P} \right)_T = \frac{V_W^0 (B - A_2 P^2)}{V^P (B + A_1 P + A_2 P^2)^2} \quad (25)$$

The  $V^P$ ,  $\alpha$ , and  $\beta$  for 35‰ salinity seawater generated from equations (23), (24), and (25), respectively, are given in Tables I, II, and III. Some of the many uses of these parameters to oceanographers are in the calculation of the stabilization frequency, the dynamic depth parameter, the adiabatic lapse rate, the velocity of sound, etc.



Table I. The specific volume of 35‰ salinity seawater at various temperatures and pressures calculated from the sound-derived equation of state.

P, Bars	$V(\text{cm}^3 \text{g}^{-1})$						
	0°C	5°C	10°C	15°C	20°C	25°C	30°C
0...	0.972669	0.973076	0.973764	0.974695	0.975844	0.977198	0.978743
100...	0.968233	0.968758	0.969539	0.970543	0.971748	0.973139	0.974710
200...	0.963933	0.964567	0.965436	0.966508	0.967765	0.969193	0.970789
300...	0.959762	0.960498	0.961449	0.962586	0.963892	0.965356	0.966975
400...	0.955715	0.956547	0.957575	0.958773	0.960125	0.961623	0.963266
500...	0.951788	0.952708	0.953808	0.955063	0.956459	0.957991	0.959657
600...	0.947975	0.948977	0.950144	0.951453	0.952892	0.954455	0.956145
700...	0.944272	0.945351	0.946580	0.947939	0.949418	0.951013	0.952726
800...	0.940675	0.941824	0.943111	0.944518	0.946035	0.947660	0.949397
900...	0.937180	0.938393	0.939734	0.941186	0.942740	0.944394	0.946155
1000...	0.933782	0.935055	0.936446	0.937941	0.939529	0.941212	0.942997

Table II. The expansibility of 35‰ salinity seawater at various temperatures and pressures calculated from the sound-derived equation of state.

P, Bars	$10^6 \alpha, \text{deg}^{-1}$						
	0°C	5°C	10°C	15°C	20°C	25°C	30°C
0...	51.52	113.91	167.22	214.21	256.92	296.82	335.03
100...	78.79	136.13	185.03	228.19	267.54	304.56	340.37
200...	104.43	157.10	201.93	241.52	277.75	312.09	345.68
300...	128.50	176.87	217.95	254.23	287.58	319.45	350.99
400...	151.51	195.51	233.14	266.37	297.07	326.66	356.33
500...	172.17	213.05	247.52	277.97	306.23	333.74	361.71
600...	191.88	229.53	261.14	289.06	315.09	340.72	367.17
700...	210.25	245.00	274.03	299.66	323.69	347.63	372.72
800...	227.31	259.50	286.22	309.80	332.05	354.48	378.38
900...	243.13	273.05	307.75	319.51	340.17	361.29	384.17
1000...	257.73	285.71	308.63	328.80	348.10	368.07	390.10

Table III. The compressibility of 35‰ salinity seawater at various temperatures and pressures calculated from the sound-derived equation of state.

P, Bars	$10^6 \beta, \text{bar}^{-1}$						
	0°C	5°C	10°C	15°C	20°C	25°C	30°C
0...	46.326	45.055	44.029	43.216	45.590	42.124	41.796
100...	45.109	43.911	42.940	42.168	41.568	41.119	40.797
200...	43.935	42.808	41.889	41.154	40.580	40.146	39.829
300...	42.802	41.742	40.874	40.175	39.625	39.204	38.891
400...	41.709	40.713	39.894	39.229	38.701	38.291	37.981
500...	40.653	39.719	38.946	38.314	37.807	37.407	37.098
600...	39.632	38.759	38.030	37.429	36.941	36.551	36.241
700...	38.646	37.830	37.143	36.572	36.102	35.720	35.410
800...	37.692	36.932	36.286	35.743	35.290	34.915	34.602
900...	36.769	36.063	35.456	34.940	34.503	34.133	33.818
1000...	35.877	35.221	34.652	34.161	33.739	33.375	33.057

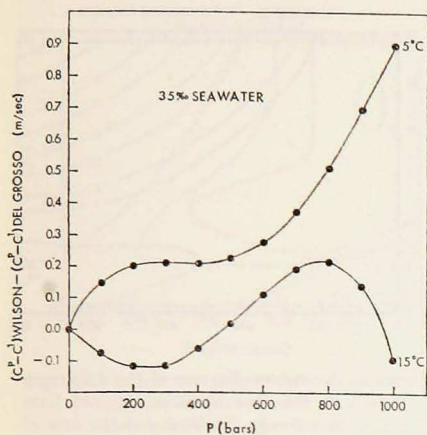


Figure 3. A comparison of the normalized (to 1 atm) velocities of sound measurements of Wilson with those of Del Grosso and Mader for 35‰ *S* seawater at 5 and 15°C from 0 to 1000 bars.

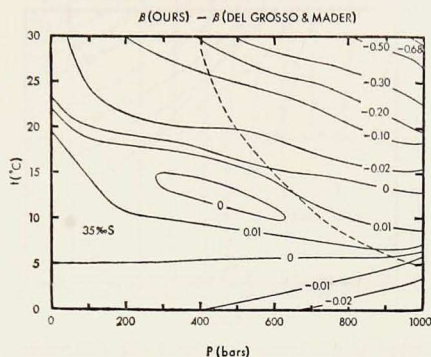


Figure 4. A contour diagram of the differences in the compressibilities obtained from our results (Wilson) and the data of Del Grosso and Mader for 35‰ *S* seawater from 0 to 30°C and 0 to 1000 bars (unit of contour is  $10^{-6}$  bar $^{-1}$ ). The broken line indicates the oceanographic range.

Recent high pressure velocity of sound measurements were published by Del Grosso and Mader (1972). Their measurements cover the range of 33 to 38‰ *S*, 0 to 15°C and 0 to 1000 bars. We also used their sound data (Table VI of their paper) to derive an equation of state of the same form as equation (14). The equation has an accuracy of  $\pm 0.02 \times 10^{-6}$  bar $^{-1}$  in compressibility. The constants  $B$ ,  $A_1$ , and  $A_2$  are given in the appendix.

Del Grosso and Mader claimed an accuracy in their sound measurements of  $\pm 0.05$  m/sec as compared to approximately  $\pm 0.20$  m/sec achieved by Wilson; their standard deviations were, respectively, 0.044 and 0.3 m/sec. Even if there was an error of 0.3 m/sec in sound velocity, this would result in an error of approximately  $0.01 \times 10^{-6}$  bar $^{-1}$  in compressibility. An error of this size is several times smaller than the accuracy achieved by the best direct experimental measurements in compressibility. In Figure 2 the velocity of sound measurements of Wilson (1960b) and those of Del Grosso and Mader (Table VI, 1972) are compared. This comparison is at 4°C, 33‰ and 35‰ salinity. The maximum deviation of 1.77 m/sec was found at 37‰ salinity, 5°C, and 1000 bars. This difference corresponds to an error in compressibility of approximately  $0.07 \times 10^{-6}$  bar $^{-1}$ . The effect of pressure on the sound velocities of Wilson and Del Grosso and Mader is shown in Figure 3. This comparison was made by subtracting the one atmosphere values from those obtained at higher pressures. The one atmosphere sound velocities of Wilson and Del Grosso (1970) were shown by a number of workers (Carnavale, *et. al.*, 1968; Del Grosso, 1970; Mackenzie, 1971) to disagree by as much as 0.6 m/sec. The comparisons in



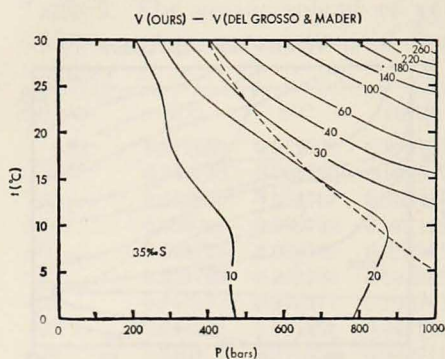


Figure 5. A contour diagram of the differences in the specific volumes obtained from our results (Wilson) and the data of Del Grosso and Mader for 35‰ seawater from 0 to 30°C and 0 to 1000 bars (unit of contour is  $10^{-6} \text{ cm}^3 \text{ g}^{-1}$ ). The broken line indicates the oceanographic range.

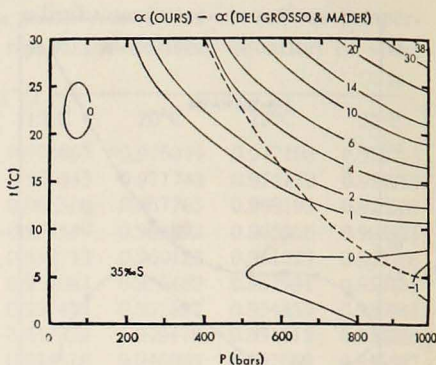


Figure 6. A contour diagram of the differences in the expansibilities obtained from our results (Wilson) and the data of Del Grosso and Mader for 35‰ seawater from 0 to 30°C and 0 to 1000 bars (unit of contour is  $10^{-6} \text{ deg}^{-1}$ ). The broken line indicates the oceanographic range.

Figure 3 show that above 5°C, at all the salinities in the range of both their measurements, the differences are less than 0.3 m/sec (which is the standard deviation of the equation of Wilson). At temperatures of 5°C and below, however, the discrepancies are larger than 0.3 m/sec (maximum is 1.26 m/sec or  $0.05 \times 10^{-6} \text{ bar}^{-1}$  in  $\beta$ ). We are presently making high pressure sound velocity measurements on seawater in an attempt to clear up this discrepancy.

Using a contour diagram, Figure 4 shows the differences in compressibilities at 35‰ salinity determined from the sound data. The data for this figure is from the two equations of state which we derived. The dotted line indicates the boundary for the oceanographic range. The differences displayed in this figure were normalized to agree at one atmosphere, and over most of the oceanographic range are within the accuracy of the equations of state ( $\pm 0.02 \times 10^{-6} \text{ bar}^{-1}$ ). It should be pointed out that the larger deviations occurring at the higher temperatures, even at low pressures, are due to the use of the equation of Del Grosso and Mader outside of the range of their measurements (their high pressure sound data is only valid to 15°C). For example, at 35‰, 30°C and 400 bars the difference between the velocities of sound of Del Grosso and Mader and Wilson is 5.08 m/sec. As shown in Figure 4, this gives a large compressibility difference ( $0.23 \times 10^{-6} \text{ bar}^{-1}$ ). When discussing our comparisons, we only consider the data within the range of Del Grosso and Mader's measurements (*i.e.*, below 15°C).

The difference between the specific volumes obtained from the two equations of state are examined in Figure 5. At zero bars pressure, both equations use the Knudsen densities causing  $\Delta V^0$  to be equal to zero. The maximum



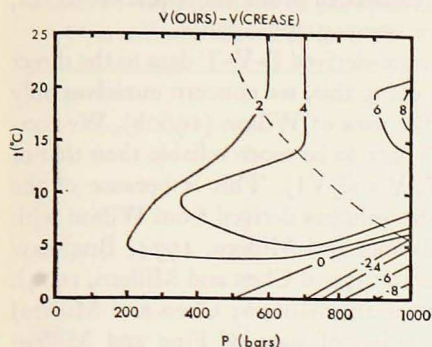


Figure 7. A contour diagram of the differences in the specific volumes obtained from our results and the data of Crease for 35‰ seawater from 0 to 25°C and 0 to 1000 bars (unit of contour is  $2 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ ). The broken line indicates the oceanographic range.

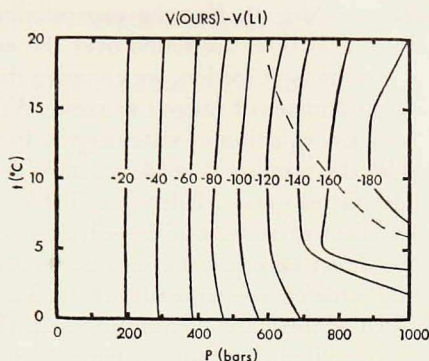


Figure 8. A contour diagram of the differences in the specific volumes obtained from our results and the data of Li for 35‰ seawater from 0 to 20°C and 0 to 1000 bars (unit of contour is  $20 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ ). The broken line indicates the oceanographic range.

deviation found in the range of both equations was  $35 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  occurring at 37‰, 0°C, and 1000 bars. In Figure 6 the expansibilities derived from the equations of state are compared. Over most of the oceanographic range, the agreement is excellent (within  $\pm 1 \times 10^{-6} \text{deg}^{-1}$ ). These results point out the insensitivity of high pressure expansibilities to compressibility errors.

Crease (1962) and Li (1967) also derived equations of state for seawater from Wilson's sound data. The specific volumes, compressibilities, and expansibilities calculated from these equations were compared to our sound-derived data (Wilson, 1960b). In Figures 7 and 8 the specific volumes for 35‰ salinity at various temperatures and pressures are compared. Over most of the oceanographic range our specific volume results agree with those of Crease to within  $\pm 4 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ . The results of Li show larger deviations (maximum to  $160 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ ). As discussed elsewhere (Wang and Millero, 1973), although Crease reported an error of  $3 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  in his derived specific volumes, this error is in doubt due to the method used by him to determine his equation. Wang and Millero also showed that except at one atmosphere, the compressibilities derived from the equation of Li were in poor agreement ( $0.2 \times 10^{-6} \text{bar}^{-1}$ ) with those derived from equation (25). These differences were caused by the use of only 1 atm. sound data, and the failure of Li's equation of state (*i.e.*, the Tait-Gibson equation). The compressibilities from the equation of Crease are in excellent agreement with ours in the low and middle pressure range. Differences of up to  $0.06 \times 10^{-6} \text{bar}^{-1}$  occur at 1000 bars, 0°C, and 35‰ salinity. At the low salinities (30‰) the deviations are much greater (up to  $0.13 \times 10^{-6} \text{bar}^{-1}$ ). The expansibilities of Crease are in good agreement with ours at 35‰ salinity. At low salinities the deviations are larger (up to

$10 \times 10^{-6} \text{deg}^{-1}$ ). For the expansibilities calculated from the equation of Li, large deviations are found over the entire oceanographic range.

In the next section, we compare the sound-derived P-V-T data to the direct measurements of various workers. When doing this, we concern ourselves only with the equation of state derived from the data of Wilson (1960b). We consider the pressure dependence of Wilson's data to be more reliable than that of Del Grosso and Mader (see Tables IV, V and VI). This is because of the excellent agreement of the seawater specific volumes derived from Wilson with the direct experimental measurements (Emmet and Millero, 1974; Bradshaw and Schleicher—personal communication, 1973; and Chen and Millero, 1974). Two of these sets of measurements (Emmet and Millero; Chen and Millero) were calibrated with the pure water equation of state of Fine and Millero (1973). That equation was derived from the sound data of Wilson (1959). The agreement of the sound-derived and direct experimental data shows the good internal consistency of the sound data of Wilson.

### 3. Comparisons with direct measurements

In this section we compare the P-V-T results derived from our seawater equation of state [from the sound velocity data of Wilson (1960b)] to that of other workers. Since we used the one atmosphere density data of Knudsen (Sweers, 1971), in this paper we are only examining the pressure effect on the sound-derived P-V-T data. Therefore, the differences found at one atmosphere are due to comparisons between the data of Knudsen and that of the

Table IV. Comparisons of the specific volumes obtained by various workers for 30‰ salinity seawater at 0°C.

P, Bar	$10^6 \Delta V, \text{cm}^3 \text{g}^{-1}$					
	a	b	c	d	e	f
0.....	0	0	-6	53	0	0
100.....	0	17	133	77	1	2
200.....	2	25	66	92	-2	4
300.....	3	27	131	99	0	6
400.....	5	27	23	101	-1	8
500.....	7	25	238	97	-4	9
600.....	9	26	270	89	-6	8
700.....	11	28	214	78	-9	6
800.....	12	36	267	63	-11	2
900.....	12	50	324	47	-11	-7
1000.....	12	72	280	30	-9	-17

a)  $V$  (our results) -  $V$  (Del Grosso and Mader)

b)  $V$  (our results) -  $V$  (Ekman)

c)  $V$  (our results) -  $V$  (Newton and Kennedy)

d)  $V$  (our results) -  $V$  (Wilson and Bradley)

e)  $V$  (our results) -  $V$  (Bradshaw and Schleicher), at 10°C

f)  $V$  (our results) -  $V$  (Chen and Millero)



Table V. Comparisons of the specific volumes obtained by various workers for 35‰ salinity seawater at 0°C.

P, Bar	$10^6 \Delta V, \text{cm}^3 \text{g}^{-1}$						
	a	b	c	d	e	f	g
0.....	0	0	77	103	0	0	0
100.....	2	18	84	131	3	0	9
200.....	4	28	82	149	6	1	14
300.....	6	32	98	159	6	2	15
400.....	8	33	62	163	6	3	13
500.....	11	33	33	160	5	4	9
600.....	14	34	19	152	4	5	5
700.....	17	38	16	140	3	5	1
800.....	21	48	117	124	3	3	-2
900.....	24	64	121	106	6	1	-4
1000.....	28	89	122	85	9	3	-5

a)  $V$  (our results) -  $V$  (Del Grosso and Mader)b)  $V$  (our results) -  $V$  (Ekman)c)  $V$  (our results) -  $V$  (Newton and Kennedy)d)  $V$  (our results) -  $V$  (Wilson and Bradley)e)  $V$  (our results) -  $V$  (Bradshaw and Schleicher), at 10°Cf)  $V$  (our results) -  $V$  (Chen and Millero)g)  $V$  (our results) -  $V$  (Emmet and Millero)

Table VI. Comparisons of the specific volumes obtained by various workers for 40‰ salinity seawater at 0°C.

P, Bar	$10^6 \Delta V, \text{cm}^3 \text{g}^{-1}$					
	a	b	c	d	e	f
0.....	0	0	84	157	0	0
100.....	3	20	81	188	5	-1
200.....	6	31	65	207	9	-2
300.....	9	37	76	221	11	-1
400.....	13	39	107	225	12	0
500.....	16	41	53	223	14	1
600.....	21	43	111	214	15	2
700.....	26	49	76	201	16	2
800.....	32*	60	143	183	19	0
900.....	38*	79	109	162	24	-3
1000.....	46*	106	170	138	32	-8

a)  $V$  (our results) -  $V$  (Del Grosso and Mader),

\* out of range of measurements of Del Grosso and Mader

b)  $V$  (our results) -  $V$  (Ekman)c)  $V$  (our results) -  $V$  (Newton and Kennedy)d)  $V$  (our results) -  $V$  (Wilson and Bradley)e)  $V$  (our results) -  $V$  (Bradshaw and Schleicher), at 10°Cf)  $V$  (our results) -  $V$  (Chen and Millero)

workers in question. We estimate that the one atmosphere results of Knudsen are good to within  $10 \times 10^{-6} \text{g/cm}^3$ . At 1000 bars the internal precision of our equation of state in terms of specific volume is  $3 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ , the accuracy is  $10 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ .



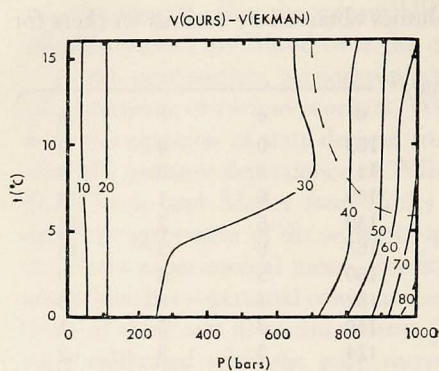


Figure 9. A contour diagram of the differences in the specific volumes obtained from our results and the data of Ekman for 35‰ *S* seawater from 0 to 16°C and 0 to 1000 bars (unit of contour is  $10 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ ). The broken line indicates the oceanographic range.

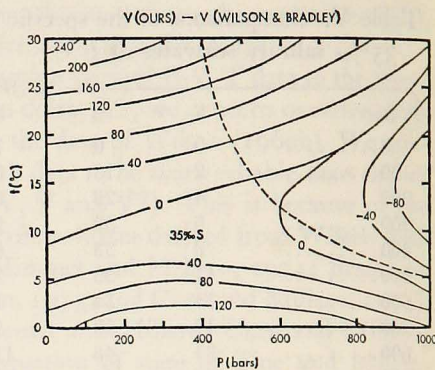


Figure 10. A contour diagram of the differences in the specific volumes obtained from our results and the data of Wilson and Bradley for 35‰ *S* seawater from 0 to 30°C and 0 to 1000 bars (unit of contour is  $40 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ ). The broken line indicates the oceanographic range.

### 3a. Specific volume.

In this section we compare the specific volumes determined from our sound-derived equation of state to the specific volumes measured directly by various workers. In Tables IV, V, and VI we have a comparison of the differences in the specific volumes between our work, and that obtained by others for 30‰, 35‰ and 40‰ salinity seawater at 0°C and various pressures from 0 to 1000 bars. The comparisons of our results, and those of Bradshaw and Schleicher, were made at 10°C (the temperature at which they made their compression measurements).

As is apparent from these comparisons, the directly measured specific volumes of Ekman (1908), Newton and Kennedy (1965), and Wilson and Bradley (1968) do not agree with our sound-derived data; while the recent work of Emmet and Millero (1974), Bradshaw and Schleicher (1973), and Chen and Millero (1974) agree with the sound data to within  $\pm 19 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  over the entire oceanographic range. The average deviations for the latter three workers, respectively, are 7.0, 7.9, and  $3.5 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  over the entire salinity range. Figures 9, 10, and 11 are a pictorial representation at 35‰ salinity of the deviations of the direct experimental data from our work. The contour diagrams show the poorer agreement of our results with the data of Ekman (Figure 9) and Wilson and Bradley (Figure 10). This is in comparison to the better agreement shown with the more recent data of Bradshaw and Schleicher (Figure 11).

The agreement of the specific volume sound data with the work of Newton and Kennedy, as well as with that of Wilson and Bradley at 35‰ *S* would

be better if the data were baseline shifted at one atmosphere. If this were done, the maximum deviations at 35‰ salinity and 0°C would then be 61 and  $60 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ , respectively. The poor agreement of the sound data with that of Wilson and Bradley at higher pressures is probably due, in part, to their choice of the Tumlirz equation (4) to represent the data. This equation employs a first order pressure dependence for the secant bulk modulus. From our results it is apparent that more than a first order pressure relationship is necessary to achieve greater accuracy in the representation of the specific volume data.

### 3b. Expansibility.

The expansibilities from the direct experimental data are compared to those from the sound-derived equation of state. The comparisons in Table VII are at 35‰ salinity seawater, 0°C and 0 to 1000 bars pressure. Except for the data of Wilson and Bradley (1968) and Ekman (1908), the results at 0°C and 35‰ salinity are representative of the results at the other temperatures and salinities. Smaller one atmosphere shifts were found for the data of Wilson and Bradley at higher temperatures; however, the absolute deviations remained the same. Smaller deviations were also found from the data of Ekman at higher temperatures. These deviations sometimes amounted to half of those found at 0°C.

Bradshaw and Schleicher (1970) are the only workers who have directly measured the expansibility of seawater under pressure. They estimated their maximum uncertainty to be within  $\pm 3 \times 10^{-6} \text{deg}^{-1}$ . At one atmosphere the sound-derived expansibilities were obtained by differentiating (with respect to temperature) Foffonoff and Sweer's reformulation of Knudsen's  $\sigma_T$ 's. In Table VII, the one atmosphere expansibilities derived from Knudsen are compared to the one atmosphere expansibilities from the measurements of Bradshaw and Schleicher. As a result of this comparison, a baseline shift was revealed in the data of Bradshaw and Schleicher compared to Knudsen (a similar shift was found at 30 and 40‰ salinity at 0°C). After the experimental data is shifted to agree with Knudsen's values at one atmosphere (Table VII—column *d* in brackets), then over the whole range, the results of the comparison with the

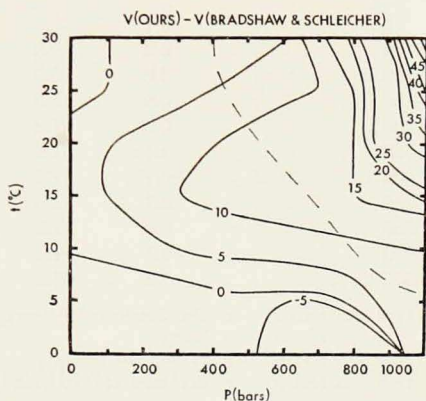


Figure 11. A contour diagram of the differences in the specific volumes obtained from our results and the data of Bradshaw and Schleicher for 35‰ *S* seawater from 0 to 30°C and 0 to 1000 bars (unit of contour is  $5 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ ). The broken line indicates the oceanographic range.



Table VII. Comparisons of the expansibilities obtained by various workers for 35‰ salinity seawater at 0°C.

P, Bar	$10^6 \Delta\alpha$ , deg <sup>-1</sup>					
	a	b	c		d	
0.....	-0.1	-0.1	-27.9	[ 0 ]	-2.3	[ 0 ]
100.....	0.0	-0.3	-28.1	[-0.2]	-2.2	[ 0.1]
200.....	0.0	-0.5	-28.4	[-0.5]	-2.3	[ 0.0]
300.....	0.0	-0.8	-28.7	[-0.9]	-2.5	[-0.2]
400.....	0.0	-1.2	-29.2	[-1.3]	-2.8	[-0.5]
500.....	0.1	-1.6	-29.9	[-2.0]	-3.2	[-0.9]
600.....	0.1	-2.1	-30.7	[-2.8]	-3.6	[-1.3]
700.....	0.1	-2.6	-31.7	[-3.8]	-4.1	[-1.8]
800.....	0.0	-3.3	-32.9	[-5.0]	-4.4	[-2.1]
900.....	-0.1	-4.1	-34.4	[-6.5]	-4.8	[-2.5]
1000.....	-0.3	-5.0	-36.0	[-8.1]	-5.1	[-2.8]

a)  $\alpha$  (our results) -  $\alpha$  (Del Grosso and Mader)

b)  $\alpha$  (our results) -  $\alpha$  (Ekman)

c)  $\alpha$  (our results) -  $\alpha$  (Wilson and Bradley)

d)  $\alpha$  (our results) -  $\alpha$  (Bradshaw and Schleicher)

sound are well within the maximum uncertainty of Bradshaw and Schleicher's measurements ( $\pm 3 \times 10^{-6} \text{deg}^{-1}$ ).

Table VII also shows the excellent agreement of our expansibilities with those derived from the sound data of Del Grosso and Mader (1972) and those from the data of Ekman (1908)—especially in the lower pressure (below 600 bars) range where he made his measurements. The expansibility data of Wilson and Bradley (1968) are also in reasonable agreement with our results, once it is baseline shifted to agree with the sound-derived data at one atmosphere.

### 3c. Compressibility.

The one atmosphere compressibilities for 30.5‰, 35‰, and 39.5‰ salinity seawater obtained from equation (25) are compared in Table VIII to the direct measurements of Lepple and Millero (1971) and Bradshaw and Schleicher (1973). From this comparison, we note that at one atmosphere our sound-derived compressibilities are in excellent agreement with the direct experimental measurements. The maximum deviation from the sound-derived data is  $0.06 \times 10^{-6} \text{bar}^{-1}$  for Lepple and Millero and  $0.05 \times 10^{-6} \text{bar}^{-1}$  for Bradshaw and Schleicher. The average deviations are  $0.02 \times 10^{-6} \text{bar}^{-1}$  for both workers.

As was done for the specific volumes and expansibilities, we compared the compressibilities (up to 1000 bars pressure) derived from the sound equation of state to the direct experimental measurements of several workers at 0°C and 35‰ salinity seawater. From the results of extensive comparisons, as typified by Table IX, we estimate that the compressibilities derived from the sound data of Del Grosso and Mader (1972) agree with our results to within  $\pm 0.07 \times 10^{-6} \text{bar}^{-1}$ , the experimental compressibilities of Ekman (1908) agree to

Table VIII. Comparisons of the one atmosphere compressibilities obtained by various workers for seawater.

Temp, °C	$10^6 \Delta\beta, \text{bar}^{-1}$					
	30.5‰ S		35‰ S		39.5‰ S	
	a	b	a	b	a	b
0.....	0.01	0.02	0.00	0.01	0.01	0.03
5.....	0.01	0.01	0.01	0.00	0.00	0.02
10.....	0.00	0.01	0.01	0.01	-0.03	0.04
15.....	0.02	0.01	0.01	0.02	0.00	0.02
20.....	-0.02	0.02	-0.04	-0.03	0.06	0.01
25.....	0.05	0.03	0.02	-0.04	0.04	0.00
30.....	-0.01	0.05	-0.02	0.02	-0.04	0.03
35.....	0.04	-	0.04	-	0.03	-
40.....	0.01	-	0.01	-	-0.03	-

a)  $\beta$  (our results) -  $\beta$  (Lepple and Millero)b)  $\beta$  (our results) -  $\beta$  (Bradshaw and Schleicher)

Table IX. Comparisons of the compressibilities obtained by various workers for 35‰ salinity seawater at 0°C.

P, Bar	$10^6 \Delta\beta, \text{bar}^{-1}$				
	a	b	c	d	e
0.....	-0.02	-0.24	-0.33	0.03	-0.01
100.....	-0.02	-0.14	-0.23	0.01	0.00
200.....	-0.02	-0.06	-0.14	-0.01	0.01
300.....	-0.02	-0.02	-0.07	-0.01	0.02
400.....	-0.03	0.00 <sub>1</sub>	0.00	-0.01	0.03
500.....	-0.03	-0.00 <sub>2</sub>	0.06	-0.01	0.04
600.....	-0.03	-0.03	0.10	0.01	0.04
700.....	-0.04	-0.07	0.14	0.03	0.06
800.....	-0.04	-0.13	0.17	0.04	0.07
900.....	-0.04	-0.20	0.19	0.07	0.07
1000.....	-0.04	-0.29	0.21	0.09	0.07

a)  $\beta$  (our results) -  $\beta$  (Del Grosso and Mader)b)  $\beta$  (our results) -  $\beta$  (Ekman)c)  $\beta$  (our results) -  $\beta$  (Wilson and Bradley)d)  $\beta$  (our results) -  $\beta$  (Chen and Millero)e)  $\beta$  (our results) -  $\beta$  (Emmet and Millero)

within  $\pm 0.2 \times 10^{-6} \text{bar}^{-1}$ , those of Wilson and Bradley (1968) agree to within  $\pm 0.3 \times 10^{-6} \text{bar}^{-1}$ , and those of Chen and Millero (1974) agree to within  $\pm 0.09 \times 10^{-6} \text{bar}^{-1}$ . As was found for the expansibilities, with the exception of the data of Wilson and Bradley and Ekman, the compressibility differences at 35‰ salinity and 0°C (Table IX) are representative of the differences found elsewhere.

Table X compares the recent compressibility work of Duedall and Paulowich (1973) to the sound-derived compressibilities. The comparison is in the form of the measurements of Duedall and Paulowich. This is a difference between



Table X. Difference between the compressibility of 35‰ salinity seawater and pure water at 15°C.

P, Bar	$-10^6 \Delta\beta, \text{bar}^{-1}$	
	a	b
0 .....	3.52	3.54 ± 0.07
100.2 .....	3.37	3.42 ± 0.06
200.2 .....	3.24	3.30 ± 0.05
300.4 .....	3.10	3.18 ± 0.05
400.6 .....	2.99	3.06 ± 0.04
500.6 .....	2.88	2.93 ± 0.03
600.4 .....	2.78	2.81 ± 0.03
700.2 .....	2.69	2.67 ± 0.03
800.2 .....	2.60	2.54 ± 0.04
900.2 .....	2.52	2.41 ± 0.04

a) Our results:  $\beta$  (seawater) -  $\beta$  (water)

b) Duedall and Paulowich:  $\beta$  (seawater) -  $\beta$  (water)

the compressibility of seawater at 35‰ salinity and pure water. Their results are in good agreement with the sound data considering their estimated error at each point. The poorest agreement was found at their highest pressure, 900.2 bars. Since we used the sound data from our equation of state for pure water (Fine and Millero, 1973), this comparison shows the good internal consistency of the sound data of Wilson (1959, 1960b).

#### 4. Conclusions

Equations of state for seawater were derived from the sound velocity data of Wilson (1960b) and from that of Del Grosso and Mader (1972). The maximum difference between the two sets of sound data (1.77 m/sec) resulted in a difference of  $35 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$  in specific volume. Because of the excellent agreement with the direct experimental measurements, as demonstrated in this paper, we favor the equation of state derived from Wilson's sound data. In addition, we conclude that the excellent agreement of the sound data of Wilson with the direct measurements of Bradshaw and Schleicher (1970), Lepple and Millero (1971), Duedall and Paulowich (1973), Emmet and Millero (1974), Bradshaw and Schleicher (in preparation, 1973), and Chen and Millero (1974) strongly substantiate the validity of this equation, and the internal consistency of the sound data of Wilson (1959, 1960a, 1960b). The equation of state is reliable in specific volume to within  $\pm 10 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ , in expansibility to within  $\pm 2 \times 10^{-6} \text{deg}^{-1}$ , and in compressibility to within  $\pm 0.01 \times 10^{-6} \text{bar}^{-1}$ . Therefore, it should be used to calculate the most precise P-V-T properties of seawater.

### Appendix

The equation of state of seawater:

$$\frac{V_W^O P}{V^O - V^P} = B + A_1 P + A_2 P^2$$

in which  $V^O$  is the specific volume at sea level,  $V^P$  is the specific volume at pressure  $P$ ,  $V_W^O$  is the specific volume of pure water at sea level, and  $B$ ,  $A_1$  and  $A_2$  are functions of temperature ( $t$  in °C) and salinity ( $S$  in ‰).  $P$  is the applied pressure in bars.

$$\begin{aligned} V_W^O &= (1 + 18.159725 \times 10^{-3}t) (0.9998396 + 18.224944 \times 10^{-3}t - 7.922210 \times 10^{-6}t^2 - \\ &\quad 55.44846 \times 10^{-9}t^3 + 149.7562 \times 10^{-12}t^4 - 393.2952 \times 10^{-15}t^5)^{-1} \text{ [Kell, 1967] cm}^3/\text{g} \\ V^O &= 1.000027 / (1 + \sigma_t \times 10^{-3}) \text{ [Fofonoff-Sweers, 1971] cm}^3/\text{g} \\ \sigma_T &= A_T + B_T \sigma_0 + C_T \sigma_0^2 \\ \sigma_0 &= -9.344586324 \times 10^{-2} + 0.814876577 S - 4.8249614 \times 10^{-4} S^2 + 6.76786136 \times 10^{-6} S^3 \\ A_T &= (4.53168t - 0.545939t^2 - 1.98248 \times 10^{-3}t^3 - 1.438 \times 10^{-7}t^4) (t + 67.26)^{-1} \\ B_T &= 1 - 4.7867 \times 10^{-3}t + 9.8185 \times 10^{-5}t^2 - 1.0843 \times 10^{-6}t^3 \\ C_T &= 1.803 \times 10^{-5}t - 8.164 \times 10^{-7}t^2 + 1.667 \times 10^{-8}t^3 \\ B &= B_1 + B_2 \\ B_1 &= 10^{-6} / \beta_W^O = (1.0 + 2.165928 \times 10^{-2}t) (50.8863 + 0.7171582t + 0.7819867 \times 10^{-3}t^2 + \\ &\quad 31.62214 \times 10^{-6}t^3 - 0.1323594 \times 10^6 t^4 + 0.634575 \times 10^{-9}t^5)^{-1} \text{ [Kell, 1970] bar} \end{aligned}$$

For equation derived from the data of Wilson (1960b) the constants are:

$$\begin{aligned} B_2 &= S [7.270886 \times 10^1 - 4.77264 \times 10^{-1}t + 1.53360 \times 10^{-2}t^2 - 5.24748 \times 10^{-4}t^3 + \\ &\quad 6.59438 \times 10^{-6}t^4 + 0.109644 \times (S - 35.0)] \text{ bar} \\ A_1 &= 3.4823 - 4.937 \times 10^{-3}t + 1.763 \times 10^{-4}t^2 + 6.2 \times 10^{-3} \times (S - 35.0) \\ A_2 &= 4.028 \times 10^{-5} - 2.776 \times 10^{-6}t + 1.049 \times 10^{-7}t^2 - 7.3 \times 10^{-7} \times (S - 35.0) \end{aligned}$$

For equation derived from the data of Del Grosso and Mader (1972) the constants are:

$$\begin{aligned} B_2 &= S [7.25116 \times 10^1 - 4.6352 \times 10^{-1}t + 6.841 \times 10^{-3}t^2 - 6.6586 \times 10^{-5}t^3 + \\ &\quad 3.8731 \times 10^{-7}t^4 + 6.51 \times 10^{-2} (S - 35.0)] \text{ bar} \\ A_1 &= 3.4737 - 7.1486 \times 10^{-3}t + 1.0250 \times 10^{-3}t^2 - 3.9478 \times 10^{-5}t^3 + 2.9681 \times 10^{-7}t^4 + \\ &\quad 9.45 \times 10^{-3} (S - 35.0) \\ A_2 &= 3.796 \times 10^{-5} - 1.015 \times 10^{-6}t - 3.790 \times 10^{-7}t^2 + 2.044 \times 10^{-8}t^3 - 3.190 \times 10^{-10}t^4 - \\ &\quad 4.57 \times 10^{-6} (S - 35.0) \end{aligned}$$

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