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by Chen-Tung Chen[1,2] and Frank J. Millero[1]

ABSTRACT

The PVT properties of seawater were calculated from the sound speed data of Chen and Millero (1977d) over the range of 0 to 40‰ salinity, 0 to 40°C, and 0 to 1000 bars. The results were presented in the form of a secant bulk modulus (K) equation of state

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

where V^0 and V^P are the specific volumes of seawater at applied pressures zero and P, respectively; $K^0 = 1/\beta^0$, the reciprocal of the isothermal compressibility at 1-atm ($P = 0$), A and B are all salinity and temperature dependent parameters. The precision of the equation of state is $\pm 0.008 \times 10^{-6} \mathrm{bar}^{-1}$ in isothermal compressibility, the maximum error is $\pm 0.03 \times 10^{-6} \mathrm{bar}^{-1}$ at the temperature and pressure extremes. The precision of the specific volume is estimated to be better than $10 \times 10^{-6} \mathrm{cm}^3 \mathrm{g}^{-1}$ and the thermal expansibility is estimated to be reliable to within $\pm 2 \times 10^{-6} \mathrm{deg}^{-1}$. The equation of state agrees with the refitted direct measurements of Chen and Millero (1976a) to within $\pm 20 \times 10^{-6} \mathrm{cm}^3 \mathrm{g}^{-1}$ in specific volume, $\pm 2 \times 10^{-6} \mathrm{deg}^{-1}$ in thermal expansibility, and $\pm 0.04 \times 10^{-6} \mathrm{bar}^{-1}$ in isothermal compressibility over most of the oceanic ranges of salinity, temperature, and pressure; agrees with the direct measurements of Bradshaw and Schleicher (1970, 1976) to within $\pm 10 \times 10^{-6} \mathrm{cm}^3 \mathrm{g}^{-1}$ in specific volume, $\pm 2 \times 10^{-6} \mathrm{deg}^{-1}$ in thermal expansibility, and $\pm 0.05 \times 10^{-6} \mathrm{bar}^{-1}$ in isothermal compressibility over the range of their measurements. The equation of state also agrees with the sound derived work of Wang and Millero (1973), and Fine, Wang and Millero (1974) to within the combined precision of the various studies.

1. Introduction

In the last few years we have attempted to provide reliable PVT data that could be used to derive a new equation of state for seawater. In order to obtain a reliable equation of state we have examined two independent approaches: direct PVT measurements and sound-derived PVT properties. It is the purpose of the present paper to determine an equation of state from measurements on the relative speed of sound in seawater (Chen, 1977; Chen and Millero, 1977b). We will also compare these new results with the work of various investigators, especially the work of Chen and Millero (1976a) and Bradshaw and Schleicher (1970, 1976). Since much of the im-

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petus for our work on the equation of state is related to the historical controversy of earlier work, we have in the first section reviewed the past PVT studies on water and seawater.

2. Historical introduction

a. High pressure PVT properties of pure water. Seawater consists of 96.5% water. As a consequence, the studies on the PVT properties of seawater can be considered as the studies on the relatively small salt effect on the PVT properties of water. Since it is desirable to make the thermodynamic properties of seawater, an aqueous multicomponent electrolyte solution, consistent with an infinite dilution standard state, many PVT properties for seawater have been measured relative to pure water. For this reason, a reliable pure water equation of state is needed.

The recent work on the PVT properties of pure water are summarized in Table 1. Until recently the most reliable high pressure PVT properties of water were thought to be the results of Kell and Whalley (1965). They measured the specific volumes of pure water using elaborate precautions to obtain the highest possible accuracy and achieved a 4 to 7 ppm reproducibility in specific volume. Their standard deviation was $\pm$ 0.04 $\times$ 10^{-6}bar^{-1} in compressibility over the range of 0 to 150°C and 0 to 1000 bars. The data of Kell and Whalley were generally accepted as being the most reliable, and were used by Millero *et al.* (1972) to calibrate a high pressure densimeter. However, the sound derived 1-atm isothermal compressibilities of Kell (1970) differ from those determined by Kell and Whalley by as much as 0.11 $\times$ 10^{-6}bar^{-1}. These deviations are approximately 3 times the quoted precision of Kell and Whalley's results. Millero, Curry and Drost-Hansen (1969) measured the isothermal compressibilities of pure water over the range of 2 to 55°C and 0 to 18 bars and reported a standard deviation of $\pm$ 0.09 $\times$ 10^{-6}bar^{-1} in compressibility. Their results agree with the data of Kell and Whalley to $\pm$ 0.1 $\times$ 10^{-6}bar^{-1} over the temperature range of 0 to 55°C.

Using an iterative computer method, Wang and Millero in 1973 calculated the isothermal compressibilities of water from the sound speed measurements of Wilson (1959). The isothermal compressibilities were fit to an equation over the range of 0 to 90°C and 0 to 1000 bars. Their standard deviation was $\pm$ 0.02 $\times$ 10^{-6}bar^{-1} in compressibility. Later in 1973, using the method of Wang and Millero, Fine and Millero also obtained a pure water equation of state from a modified sound speed equation of Wilson. They fit the high pressure sound speeds of Wilson and forced them to come into the more reliable 1-atm sound speeds of Kell (1970). The equation of state given by Fine and Millero is precise to within $\pm$ 0.016 $\times$ 10^{-6}bar^{-1} in compressibility over the range of 0 to 95°C and 0 to 1000 bars. The sound derived specific volumes of Fine and Millero agree with the results of Wang and Millero to within 10 ppm over the range of 0 to 95°C and 0 to 1000 bars, but are consistently higher than the values of Kell and Whalley (by an average deviation of 115 ppm and

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Table 1. Studies on the P-V-T properties of pure water.

Year	Investigator	Range	Properties Investigated	Remarks
1965	Kell & Whalley	0 to 150°C, 0 to 1000 bars	V^*	4 to 7 ppm reproducibility in specific volumes, $\pm$ 0.04 × 10⁻⁶bar⁻¹ standard deviation in compressibility
1969	Millero, *et al.*	2 to 55°C, 0 to 18 bars	β^{**}	$\pm$ 0.09 × 10⁻⁶bar⁻¹ precision
1973	Wang & Millero	0 to 90°C, 0 to 1000 bars	β	Derived from Wilson's sound speed measurements, maximum error $\pm$ 0.02 × 10⁻⁶bar⁻¹
1973	Fine & Millero	0 to 95°C, 0 to 1000 bars	β	Derived from Wilson's sound speed measurements, maximum deviation of the fit $\pm$ 0.016 × 10⁻⁶bar⁻¹
1975	Kell & Whalley	0 to 150°C, 0 to 1000 bars	V	Reanalysis of the 1965 work, 20 ppm claimed accuracy
1975	Kell & Whalley	0 to 100°C, 0 to 1000 bars	V	Derived from Wilson's as well as Barlow and Yazgan's sound speed measurements, reproducibility 20 × 10⁻⁶cm³g⁻¹
1976	Yayanos	5 and 15°C, 0 to 1045 bars	V	40 × 10⁻⁶cm³g⁻¹ accuracy
1976	Bradshaw & Schleicher	10°C, 8 to 1000 bars	β	Better than 10 × 10⁻⁶cm³g⁻¹ in specific volume
1977	Bradshaw & Schleicher	0 to 30°C, 0 to 1000 bars	$\alpha^\dagger$	Better than 2 × 10⁻⁶deg⁻¹ in thermal expansion
1977	Chen, *et al.*	0 to 100°C, 0 to 1000 bars	β	Derived from reanalyzed sound speed data of Wilson, maximum error $\pm$ 0.01 × 10⁻⁶bar⁻¹
1978	Caldwell	0 to 400 bars	$t_{MD}^\ddagger$	0.044°C standard deviation

* The specific volume of pure water.
** The isothermal compressibility of pure water.
† The thermal expansibility of pure water.
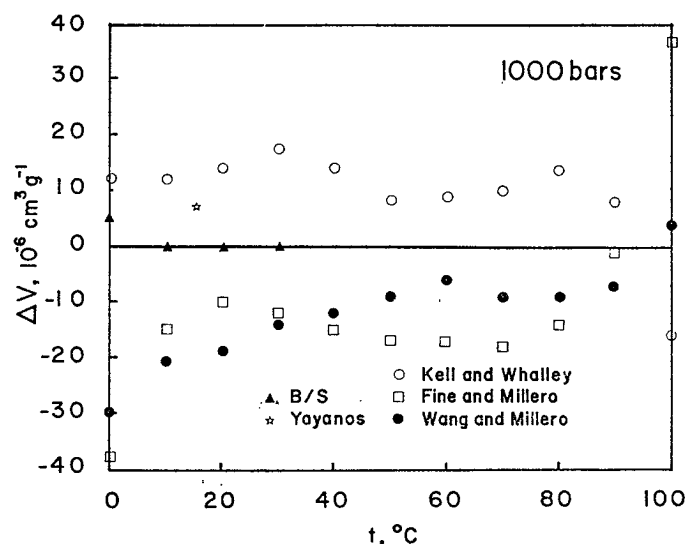‡ Temperature of maximum density.

Figure 1. Comparisons of the specific volumes of pure water at 1000 bars calculated from the sound derived equation of state of Chen, Fine and Millero (1977) and the data of various workers.

a maximum deviation of 169 ppm). In 1975, Kell and Whalley reanalyzed their direct measurements. They made comparisons with two sets of specific volume data obtained from Wilson's (1959) and Barlow and Yazgan's (1967) sound speed measurements, and concluded that the compressibility of the stainless steel container used in their 1965 studies was in error. By correcting for this effect, they redetermined the specific volumes of water from 0 to 150°C and 0 to 1000 bars with a claimed accuracy of 20 ppm at 1000 bars. Their new results agree to within ± 30 ppm with the sound derived data of Wang and Millero and Fine and Millero over the range of 5 to 95°C and 0 to 1000 bars.

In 1976, Yayanos made direct specific volume measurements on pure water at 5 and 15°C for pressures up to 1045 bars with an estimated accuracy of $40 \times 10^{-6} cm^3 g^{-1}$. In the same year, Bradshaw and Schleicher measured the compression of pure water at 10°C for pressures up to 1000 bars. Their data were represented by a polynomial equation with a standard deviation of $2 \times 10^{-6} cm^3 g^{-1}$ in specific volume. Bradshaw and Schleicher have recently completed measurements of the thermal expansions for water over the range of 0 to 30°C and 0 to 1000 bars (Bradshaw, personal communication, 1977). Caldwell (1978) recently presented an equation for the temperature of maximum density, t_{MD}, for pure water and saline water with a standard deviation of 0.044°C. This data can be used to test the validity of the temperature derivatives of an equation of state.

In 1976, Chen and Millero reevaluated the pure water sound speed data of Wilson (1959) and found that the data treatments of Wang and Millero (1973), Fine and Millero (1973), and Kell and Whalley (1975) were unsatisfactory. The systematic
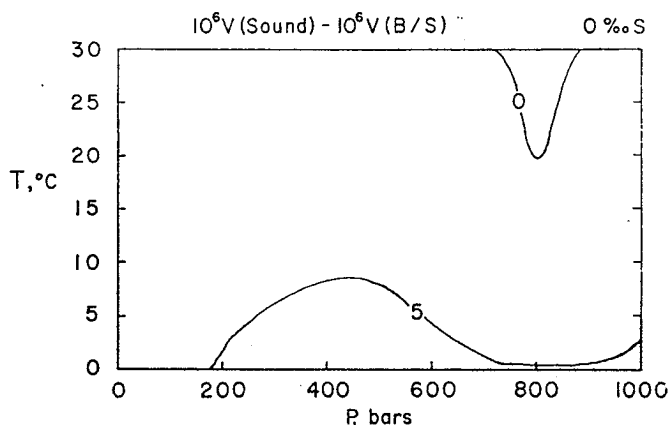
Figure 2. Comparisons of the specific volumes of water obtained by Chen, Fine and Millero (1977) and Bradshaw and Schleicher (personal communication 1977).

temperature bias in the sound speed data of Wilson was consequently corrected and a new sound speed equation presented (Chen and Millero, 1976b). This new equation has fewer terms but is more precise by at least a factor of two than any of the previous equations given by various workers. A new pure water equation of state (Chen *et al.*, 1977) was determined using the 1-atm sound speed equation of Del Grosso and Mader (1972a) and the new high pressure sound speed equation of Chen and Millero. This equation has a maximum error of $\pm$ 0.01 $\times$ 10^{-6}bar^{-1} in isothermal compressibility. In Figure 1 we compared the specific volumes from Chen *et al.* with the results of other workers at 1000 bars pressure. The differences at 1000 bars are larger than at lower pressures. The specific volumes calculated from the equation of state of Chen *et al.* are higher than those of Kell and Whalley (1975) by 10 $\times$ 10^{-6}cm^{3}g^{-1}; they are lower than those of Fine and Millero (1973) and Wang and Millero (1973) by 15 $\times$ 10^{-6}cm^{3}g^{-1} over most of the temperature range, 0 to 100°C. The equation of Chen *et al.* agrees with the data of Yayanos (1976) to within 40 $\times$ 10^{-6}cm^{3}g^{-1} in specific volume, which is within the claimed accuracy of Yayanos. The work of Bradshaw and Schleicher (1976) at 10°C agrees with Chen *et al.* to within 4 $\times$ 10^{-6}cm^{3}g^{-1} in specific volume (which is well within the combined precision of the two studies).

As mentioned earlier, Bradshaw and Schleicher have recently completed[3] a study of the thermal expansion of water from -2 to 30°C and 0 to 1000 bars. By combining these results with their compressibility measurements at 10°C, it is possible to generate specific volume for water from 0 to 30°C and 0 to 1000 bars. A comparison of these results with the sound derived specific volumes is given in Figure 2. The maximum deviation is 7 $\times$ 10^{-6}cm^{3}g^{-1} in specific volume over the entire tem-

3. Recently, B/S have recalibrated their dead weight tester and found a negative correction of as much as 0.35 bars at 1000 bars. This is equivalent to an increase of $\sim$ 15 $\times$ 10^{-6}cm^{3}g^{-1} in the specific volume of water and seawater at 1000 bars. The comparisons made in this paper do not include this pressure correction since the correction has not yet been made on the expansibility results.

Table 2. Studies on the high pressure PVT properties of seawater.

Year	Investigator	Range	Properties Investigated	Remarks
1881	Tait	0 to 15°C, 0 to 500 bars	β^*	The compressibility decreases with increasing temperature and pressure
1908	Ekman	31.13 and 38.53‰, 0 to 20°C, 0 to 600 bars	β	Results consistently high
1962	Crease	5 to 37‰, 0 to 30°C, 0 to 1000 bars	V^{**}	Derived from Wilson's sound speed measurements, standard deviation $\pm 3 \times 10^{-6} \text{cm}^3\text{g}^{-1}$ in volume
1965	Newton & Kennedy	0, 30, 35 and 40‰, 0 to 25°C, 0 to 1300 bars	V	Precision $70 \times 10^{-6} \text{cm}^3\text{g}^{-1}$
1966, 1968	Wilson & Bradley	0 to 40‰, 0 to 40°C, 0 to 1000 bars	V	$130 \times 10^{-6} \text{cm}^3\text{g}^{-1}$ standard deviation
1970	Bradshaw & Schleicher	0 to 40‰, −2 to 30°C, 0 to 1000 bars	$\alpha\dagger$	Estimated accuracy $\pm 3 \times 10^{-6}\text{deg}^{-1}$ standard deviation $\pm 1 \times 10^{-6}\text{deg}^{-1}$
1970	Caldwell & Tucker	34.7‰, 0.6 to 17.4°C, up to 1180 bars	α	Accuracy $4 \times 10^{-6}\text{deg}^{-1}$
1971	Lepple & Millero	0 to 40‰, 0 to 40°C, 0 to 34 bars	β	Experimental error $\pm 0.05 \times 10^{-6}\text{bar}^{-1}$
1973	Duedall & Paulowich	35‰, 10 and 15°C, 0 to 900 bars	β	± 0.03 to $\pm 0.07 \times 10^{-6}\text{bar}^{-1}$ precision
1973	Wang & Millero	30 to 40‰, 0 to 30°C, up to 1000 bars	β	Derived from Wilson's sound speed data, standard deviation $\pm 0.01 \times 10^{-6}\text{bar}^{-1}$

Year	Author	Range	Property	Remarks
1973	Duedall & Paulowich	35‰, 10 and 15°C, 0 to 900 bars	β	± 0.03 to ± 0.07 × 10⁻⁶ bar⁻¹ precision
1973	Wang & Millero	30 to 40‰, 0 to 30°C, up to 1000 bars	β	Derived from Wilson's sound speed data, standard deviation ± 0.01 × 10⁻⁶ bar⁻¹
1974	Fine, Wang & Millero	30 to 40‰, 0 to 30°C, up to 1000 bars	β	Derived from Del Grosso and Mader's sound speed data, precision ± 0.01 × 10⁻⁶ bar⁻¹ in compressibility, ± 10 × 10⁻⁶ cm³ gm⁻¹ in specific volume, ± 2 × 10⁻⁶ deg⁻¹ in expansibility
1974	Emmet & Millero	35‰, −0 to 40°C, 0 to 1000 bars	V	Standard deviation 11 × 10⁻⁶ cm³ g⁻¹
1975	Millero & Kubinski	5 to 40‰, 0 to 40°C, at 0 bars	β	Derived from sound speed measurements. The values of β have a precision of ± 0.003 × 10⁻⁶ bar⁻¹ in compressibility
1976	Bradshaw & Schleicher	30 to 40‰, 10°C, up to 1000 bars	β	Better than 10 × 10⁻⁶ cm³ g⁻¹ precision in volume
1976	Chen & Millero	5 to 40‰, 0 to 40°C, 0 to 1000 bars	V	Standard deviation 7 × 10⁻⁶ cm³ g⁻¹
1977	Bradshaw & Schleicher (personal communication)	15‰ and 35‰, −2 to 30°C, 0 to 1000 bars	α	Estimated accuracy ± 3 × 10⁻⁶ deg⁻¹. Standard deviation ± 1 × 10⁻⁶ deg⁻¹

* The isothermal compressibility of seawater.
** The specific volume of seawater.
† The thermal expansibility of seawater.

perature and pressure range. These comparisons confirm the validity of sound derived equation of state for water (Chen, Fine, and Millero, 1977) over the oceanic ranges of pressure and temperature.

The values of t_{MD} calculated from Chen *et al.* agree with the data of Caldwell (1978) to within 0.04°C (which is within the precision of Caldwell's study) up to the highest pressure of his measurements, 400 bars. This also confirms the good temperature dependency of the equation of Chen *et al.*

b. High pressure PVT properties of seawater. Much of the controversy concerning the equation of state of seawater was concerned with the pressure dependence of the PVT properties. A list of the studies made on the PVT properties of seawater is given in Table 2.

Tait (1888) is believed to be the first scientist to measure the compressibility of seawater under high pressure. In 1881, he made a series of measurements on seawater over the range of 0 to 15°C and 0 to 500 bars in which he found that the compressibility decreases with increasing temperature and pressure.

In 1908, Ekman measured the compressions of seawater at 31.13 and 38.53‰ salinity over the range of 0 to 20°C and 0 to 600 bars. Ekman's high pressure compression data, as well as the earlier 1-atm density data of Knudsen (1901), form the basis for the presently used equation of state of seawater. It was shown by Millero *et al.* (1976), and others, that the 1-atm densities of Knudsen at 35‰ salinity are accurate to within 10 ppm. However, there was a lot of controversy concerned with the effect of pressure on the PVT properties of seawater. This controversy was due, in part, to the fact that Ekman's measurements were only made on two seawater samples of different salinity and to pressures of 600 bars; while his formulae were frequently extrapolated to 1000 bars at various salinities. Although Ekman's measurements were internally consistent, his compression results are consistently high (Lepple and Millero, 1971). This was partly due to his not measuring pressure directly, but instead using Amagat's (1893) zero degree celcius pure water data for his pressure calibration. It was known (Crease, 1962; Del Grosso, 1959; 1973) that Amagat's pressure gauge read too low (by approximately 0.2%), therefore, causing Ekman's compressibility values calculated from Amagat's data to be too high.

For the next half century, no studies were made on the high pressure PVT properties of seawater until 1962, when Crease investigated the specific volume of seawater under pressure. Using Wilson's (1960b) sound speed measurements, Crease derived an equation of state for seawater. The equation fits the sound derived specific volumes to within $3 \times 10^{-6} \mathrm{cm^3 g^{-1}}$ over the total range of 5 to 37‰, 0 to 30°C, and 0 to 1000 bars. Comparison of his work with Ekman's data (1908) showed that the two sets of numbers were consistent in specific volume to within $\pm 30 \times 10^{-6} \mathrm{cm^3 g^{-1}}$ over most ocean basins. There was a maximum deviation of $100 \times 10^{-6} \mathrm{cm^3 g^{-1}}$.

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Newton and Kennedy, in 1965, determined the PVT properties of seawater from 0 to 1300 bars at 100 bar intervals and from 0 to 25°C at 5°C intervals. Their determinations were based on three samples of different salinities, (30.52, 34.99 and 41.03‰ salinity) as well as a pure water sample. The precision of their measurements was estimated to be $70 \times 10^{-6} \text{cm}^3\text{g}^{-1}$ in specific volume. Newton and Kennedy reported that comparison of their specific volume data with other workers (Crease, 1962; Knudsen, 1901; Ekman, 1908) indicated a systematic difference as much as $500 \times 10^{-6}\text{cm}^3\text{g}^{-1}$.

The specific volumes of seawater were measured by Wilson and Bradley (1966; 1968) for salinities from 0 to 40‰, for temperatures from 0 to 40°C, and for pressures from 0 to 1000 bars. They fit their specific volume measurements of seawater to an equation having a standard deviation of $130 \times 10^{-6}\text{cm}^3\text{g}^{-1}$. It was suggested (Lepple and Millero, 1971; Fine, *et al.*, 1974; Emmet and Millero, 1974) that the specific volumes of Wilson and Bradley are in error due, in part, to their choice of the form of the equation used to represent their data. This will be discussed in detail in the next section.

In 1970, Bradshaw and Schleicher determined the thermal expansion of 30.50, 35.00 and 39.50‰ salinity seawater over the temperature range of −2 to 30°C at 2°C intervals and pressures from 8 to 1000 bars. An interpolation formula was given which fit the thermal expansion values to $\pm 1 \times 10^{-6}\text{cm}^3\text{g}^{-1}\text{deg}^{-1}$ with an estimated accuracy of $\pm 3 \times 10^{-6}\text{cm}^3\text{g}^{-1}\text{deg}^{-1}$. They concluded that the temperature derivative of the specific volume of seawater from the equation of Ekman (1908) and Knudsen (1901) are not in serious error, and those of Crease (1962) appear to be valid to within 2%. Bradshaw and Schleicher's results differ from Wilson and Bradley's (1968) and Newton and Kennedy's (1965) values by 10%. The data of Bradshaw and Schleicher were later reanalyzed by Bryden (1973) and a best-fit polynomial equation was given.

The isothermal compressibilities of seawater were measured by Lepple and Millero (1971). They used a piezometric technique for their measurements which ranged from 0 to 40‰ salinity at 5‰ salinity intervals, from 0 to 40°C at 5°C intervals and up to 34 bars. Their measurements had an experimental error of $\pm 0.05 \times 10^{-6}\text{bar}^{-1}$. The isothermal compressibility results at 1-atm and 35‰ salinity are in good agreement with the values calculated from Wilson's (1960a) sound speed data ($\pm 0.03 \times 10^{-6}\text{bar}^{-1}$), however, they disagree with the PVT data of Ekman (1908; $\pm 0.3 \times 10^{-6}\text{bar}^{-1}$), Newton and Kennedy (1965; $\pm 0.3 \times 10^{-6}\text{bar}^{-1}$) and Wilson and Bradley (1968; $\pm 0.3 \times 10^{-6}\text{bar}^{-1}$). The agreement with Ekman's data would be excellent ($\pm 0.03 \times 10^{-6}\text{bar}^{-1}$) if the two sets of data were normalized at 1-atm by using the same pure water compressibilities.

In 1973, using a bellows-type differential compressimeter, Duedall and Paulowich reported a precision of $\pm 0.07 \times 10^{-6}\text{bar}^{-1}$ in the relative isothermal compressibility $(\beta - \beta_W)$ measurements (where β_W is the compressibility of water). Their mea-

surements were for 35‰ salinity seawater at 10 and 15°C and to 900 bars. In the same year, Wang and Millero determined the isothermal compressibilities of seawater from the sound speed data of Wilson (1960b) by an iterative method. The standard deviation of the fit was $\pm 0.01 \times 10^{-6} \text{bar}^{-1}$. Fine, Wang and Millero in 1974, derived an equation of state of seawater from the sound speed data of Del Grosso and Mader (1972b), with a precision in isothermal compressibility of $\pm 0.01 \times 10^{-6} \text{bar}^{-1}$, in specific volume of $\pm 10 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$, and in thermal expansibility of $\pm 2 \times 10^{-6} \text{deg}^{-1}$. The sound derived data of Wang and Millero as well as Fine, Wang and Millero are in good agreement ($\pm 0.08 \times 10^{-6} \text{bar}^{-1}$ in compressibility), with the direct measurements of Lepple and Millero (1971) and Duedall and Paulowich (1973). However, there was still some controversy concerning the two sets of data that were derived from Wilson's and Del Grosso and Mader's sound speed measurements. The maximum absolute difference over the oceanic range between the speeds of sound of the two independent studies is 1.77 m sec^{-1}. This is four times the combined standard deviation of the two studies. At low temperatures (below 5°C), the deviations remain large, especially at the higher pressures. The large sound speed difference caused the derived specific volumes to differ by as much as 35 ppm at low temperatures and high pressures. The corresponding expansibility and compressibility data differ by $1.8 \times 10^{-6} \text{deg}^{-1}$ and $0.064 \times 10^{-6} \text{bar}^{-1}$, respectively.

Emmet and Millero (1974), using a high pressure magnetic float densimeter (Emmet, 1973) measured the specific volume of 35‰ salinity seawater from -2 to 40°C and from 0 to 1000 bars. The specific volumes were fit to an equation having a standard deviation of $11 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$. The results of their measurements were relatively good since they agree with Wang and Millero's results (1973) on the average to $\pm 7 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ with a maximum error of $30 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$, but were limited to 35‰ salinity.

In 1975 Millero and Kubinski measured the speed of sound in seawater relative to pure water from 0 to 40°C and 5 to 40‰ salinity at 1 atmosphere. The sound speeds were in good agreement (within 0.14 m sec^{-1}) with the measurements of Del Grosso (1974). The isothermal compressibilities of seawater solutions at 1-atm determined from the measurements have a precision of $\pm 0.003 \times 10^{-6} \text{bar}^{-1}$ (which is equivalent to a precision of ± 0.04 m sec^{-1} in the sound speeds). The sound derived β's agree with the direct measurements of Lepple and Millero (1971) on the average to $\pm 0.02 \times 10^{-6} \text{bar}^{-1}$ with a maximum error of $0.07 \times 10^{-6} \text{bar}^{-1}$.

In 1976 Bradshaw and Schleicher measured the compression of seawater of approximately 31, 35, and 39‰ salinity at 10°C for pressures from 8 to 1000 bars. The precision was estimated to be better than $10 \times 10^{-6} \text{cm}^3 \text{g}^{-1}$ in specific volume. In the same year, Chen and Millero made extensive direct measurements of the specific volume of seawater as a function of temperature (0 to 40°C, 5°C intervals), pressure (0 to 1000 bars at 100 or 200 bar intervals), and salinity (5 to 40‰, 5‰

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intervals). The results of the measurements were fit to a secant bulk modulus equation with a standard deviation of $7 \times 10^{-6} \text{cm}^3\text{g}^{-1}$ in specific volume. The specific volumes, thermal expansibilities, and isothermal compressibilities derived from the equation of state agree very well with the sound derived data of Wang and Millero (1973) and Fine, Wang and Millero (1974) ($\pm$ 20 ppm in volume, $\pm 2 \times 10^{-6}\text{deg}^{-1}$ in expansibility and $\pm 0.04 \times 10^{-6}\text{bar}^{-1}$ in compressibility over the oceanic ranges of salinity, temperature, and pressure). Chen and Millero's results show that the specific volumes calculated from the work of Ekman (1908) are too low by as much as $80 \times 10^{-6}\text{cm}^3\text{g}^{-1}$ in the low temperature and high pressure region.

Recently, Bradshaw and Schleicher (personal communication, 1977) have made further expansibility measurements on seawater at 15‰ and 35‰ salinity from −2 to 30° and 0 to 1000 bars. The precision and accuracy of these measurements are the same as their earlier results.

Caldwell (1978) has recently made measurements on the temperature of maximum density for saline water from 0 to 30‰ salinity and up to 400 bars. His results will be useful in testing the temperature derivatives of the equation of state of seawater.

c. Equations of state. Many attempts (Ben-Naim, 1972; Weres and Rice, 1972; Gibbs *et al.*, 1973) have been made to derive an equation of state from molecular theory, but none of them resulted in an adequate equation capable of expressing the results of direct measurements within the experimental error. To meet this need, it was necessary to employ some empirical equations; the major justification for each is that it fits the experimental data. It is also desirable to choose an equation that gives reliable concentration, temperature, and pressure derivatives.

Table 3 summarizes the most frequently used equations of state. Many of the equations are based on the Tait (1888) equation:

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

or rearranged

$$V^P = V^0 - V^0 A \frac{P}{\pi + P} \tag{2}$$

where k is the mean or secant compression, V^0 and V^P are the specific volumes at zero and P applied pressure, respectively. A is a constant and π is a temperature dependent parameter. Tait was able to fit his seawater data to this equation with a standard deviation of $\pm 0.3 \times 10^{-6}\text{bar}^{-1}$ in compressibility over the range of 0 to 15°C and 0 to 500 bars.

It was recently revealed by Hayward (1967) that two generations of workers were misled into using what they came to call "the Tait equation." They did not realize that this well known equation was not Tait's original equation. The Tait equation

Table 3. Studies on equations of state.

Year	Investigator	Form
1888	Tait	$V^P = V^0 - V^0 AP/(\pi + P)$
1895	Tammann	$V^P = V^0 - CV^0 \, 1n[(B + P)/B]$
1908	Ekman	$V^P = V^0 + AP + BP^2 + CP^2$
1909	Tumlirz	$V^P = B + D/(C + P)$
1935	Gibson	$V^P = V^0 - CX_1 \, 1n[(B + P)/B]$
1944	Murnaghan	$V^P = V^0 \, (1 + \eta\beta^0 P)^{-1/\eta}$
1962	Crease	$V^P = \sum_{i,j,k} A_{ijk} P^i t^j (S - 35)^k$
1965	Kell and Whalley	$V^P = V^0(1 + \sum_k \sum_l A_{k,l} t^k P^l)$
1967	Li	$V^P = V^0 - V^0 P/(K^0 + BP)$
1967	Hayward	$V^P = V^0 - V_w^0 P/(K^0 + AP + BP^2)$
1973	Wang and Millero	$V^P = V^0 - V^0 P/(K^0 + AP + BP^2)$
1974	Emmet and Millero	$V^P = V^0 - (1 - 10^{-3}S) \times C \times 1n[(B + P)/B]$
1976	Bradshaw and Schleicher	$V^P = \left[1 - \sum_{i,j} A_{ij} P^i S^i \right] \left[V^0(0\,°C) + \int \dfrac{\partial V}{\partial T} \, dT \right]$
1977	Gebhart and Mollendorf	$d^P = d^0(1 - \alpha\|t - t_{MD}\|^a)$

was first misquoted by Tammann in 1895. The misquoted form of the Tait equation (which we shall refer to as the Tammann equation) is:

$$\frac{1}{V^0}\left(\frac{\partial V}{\partial P}\right)^P = -\frac{C}{B + P} \tag{3}$$

or integrated (B and C are independent of pressure)

$$V^P = V^0 - CV^0 \, 1n\frac{B + P}{B} \tag{4}$$

Comparisons with equation (2) reveal that Tammann replaced Tait's compression term, $(V^0 - V^P)/V^0 P$ by the corresponding differential coefficient $(\partial V/\partial P)^P/V^0$. In the low pressure range (below 500 bars) that concerns the majority of workers, $(V^0 - V^P)/V^0 P$ is almost equal to $(\partial V/\partial P)^P/V^0$, enabling one to understand the long history of misuse.

By rearranging the Tammann equation (3), we have,

$$(\partial P/\partial V)^P = (\partial P/\partial V)^0 + a\,P \tag{5}$$

where $(\partial P/\partial V)^0 = -B/CV^0$ and $a = -1/CV^0$. Differentiation of the Tait equation (1) with respect to pressure gives,

$$(\partial P/\partial V)^P = (\partial P/\partial V)^0 + a'P + b'P^2 \tag{6}$$

where $(\partial P/\partial V)^0 = -\pi/AV^0$, $a' = -2/AV^0$, and $b' = -1/A\pi V^0$. By comparing equations (5) and (6), it is clear that the Tammann equation contains one less pres-
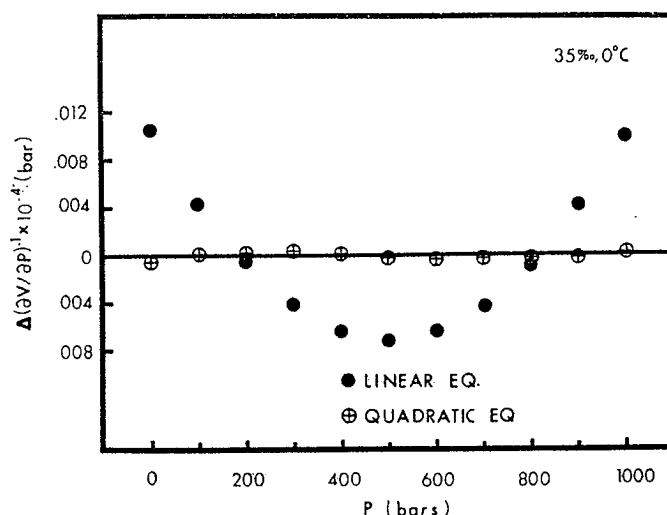
Figure 3. Fitting errors of the sound derived values of $(\partial V/\partial P)^{-1}$ from a linear (equation 5) and quadratic (equation 6) equation for 35‰ salinity seawater at 0°C from 0 to 1000 bars.

sure term than the Tait equation in bulk modulus form. (It should be pointed out that both equations have the same number of adjustable parameters, the terms $(\partial P/\partial V)^0$, a' and b' are interrelated to each other). The Tait equation (in bulk modulus form, equation 6) fits compression data about 100 times better than the Tammann equation (Fine, Wang and Millero, 1974). This is demonstrated in Figure 3 by examining $(\partial P/\partial V)^P$ determined from sound speed data (Wilson, 1960b). The maximum deviation of the fitted data is 1.068×10^2 bar g cm^{-3} for equation (5) and 1.1 bar g cm^{-3} for equation (6). These differences are equivalent to 0.2×10^{-6}bar^{-1} and 0.002×10^{-6}bar^{-1}, respectively, in compressibility and demonstrate that the Tait equation is superior to the Tammann equation.

The pressure dependence of $(\partial P/\partial V)^P$ can be tested by fitting $[(\partial P/\partial V)^P - (\partial P/\partial V)^0]/P$ vs. pressure. It is clearly shown in Figure 4 that the values of $[(\partial P/\partial V)^P$
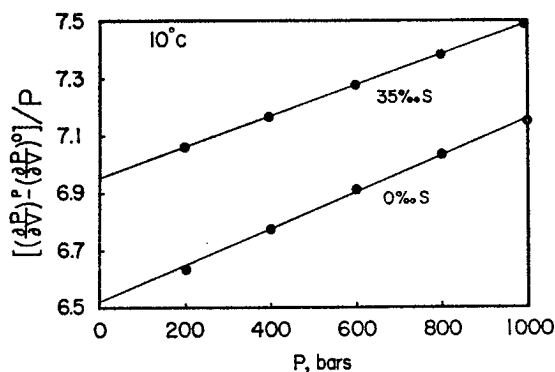
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Figure 4. Values of $[(\partial P/\partial V)^P - (\partial P/\partial V)^0]/P$ versus P at 10°C for pure water and 35‰ salinity seawater. The lines have been determined by a linear least squares fit of the data. The error bars are smaller than the thickness of the lines.

$- (\partial P/\partial V)^{\circ}]/P$ for pure water and 35‰ salinity seawater determined from sound speed data (Chen and Millero, 1976b; 1977d) increase almost linearly with pressure. This indicates that P^2 or even higher order terms are needed to represent $(\partial P/\partial V)$ over the pressure range of 0 to 1000 bars. In other words, the Tammann equation does not represent the PVT properties for pure or saline water as well as the original Tait equation.

It was mentioned that Ekman (1908) measured the compression of seawater relative to pure water (k_W) at 0°C. He fit his results to an equation of the form

$$k - k_W = A + BP + CP^2 \tag{7}$$

At the same time Ekman was making his compression measurements, Tumlirz (1909) presented an equation of state of the form

$$(V^P - B)(P + C) = D \tag{8}$$

where B, C, and D are temperature dependent parameters. Tumlirz's equation is just a rearrangement of the Tait equation. Replacing B, C, D in equation (8) by $V^0 - V^0 A$, π and $V^0 A \pi$, respectively, equation (8) becomes

$$(V^P - V^0 + V^0 A)(P + \pi) = V^0 A \pi \tag{9}$$

or

$$V^P = V^0 - \frac{V^0 A P}{\pi + P} \tag{10}$$

which is the original Tait equation (1).

In 1958 Eckart fitted the pure water data of several workers (Amagat, 1893; Ekman, 1908; Bridgman, 1913; Gibson and Loeffler, 1941; Kennedy, 1957) to the Tumlirz equation. These different sets of data could only be fitted with a standard deviation of ± 200 ppm in specific volume. Wilson and Bradley (1968) also fitted their specific volumes of seawater to the Tumlirz equation with a standard deviation of ± 130 ppm. The results from Wilson and Bradley's equation agree fairly well with Eckart's formulation of the data of Ekman (1908). But this agreement arises mainly from the use of the same equation of state to represent the data. In both cases, the agreement is not supported by Wilson and Bradley's data themselves. The fact that the reported standard deviation of all the data is 130 ppm in the specific volume, while that of the data at each salinity about "individual least-squares fit" is 20 ppm in the specific volume, indicates that the equation is a poor fit to the data. Fisher and Dial (1968) fit the data of Wilson and Bradley to a modified Tumlirz equation to within $70 \times 10^{-6} \text{cm}^3\text{g}^{-1}$.

In 1935, Gibson extended the Tammann equation to solutions and published what is referred to as the Tait-Gibson equation

$$\left(\frac{\partial V}{\partial P}\right)^P = \frac{-CX_1}{B + P} \tag{11}$$

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$$V^P = V^0 - CX_1 \ln \frac{B+P}{B} \qquad (12)$$

where X_1 is the weight fraction of water, C is a constant $(0.315/V^0)$ and B is a function of temperature and concentration. For most of the systems examined (Gibson, 1935, 1937; Gibson and Loeffler, 1939, 1941), C was found to be nearly independent of temperature and concentration.

In 1944, Murnaghan published an equation of the form (Murnaghan, 1944; 1949)

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

in which β^0 is the isothermal compressibility at sea level pressure, η is $\partial(1/\beta)/\partial P$.

In 1962, Crease published an equation of state of seawater of the form

$$V^P = \sum_{ijk} A_{i,j,k} \, P^i t^j \, (S-35)^k \qquad (14)$$

where S is the salinity in parts per thousand, $A_{i,j,k}$ is a constant at the corresponding pressure, temperature, and salinity, respectively. Crease was able to fit his sound derived specific volumes with a standard deviation of 3 ppm. However, the reliability of his equation is in doubt because he generated specific volumes from sound speeds directly. (It was pointed out by Wang and Millero, 1973, that the sound speeds should be used to generate compressibilities rather than specific volumes in order to ensure the best precision of the generated quantities).

In 1965, Kell and Whalley fit the results of their pure water specific volume measurements to the polynomial

$$V = V^0 \left(1 + \sum_k \sum_l A_{k,l} t^k P^l \right) \qquad (15)$$

The standard deviation was reported to be 3 ppm at the lower pressures and 10 ppm at the higher pressures.

In 1967, Li published a variation of the Tait-Gibson equation for seawater from both compressibility and sound speed data

$$V^P = V^0 - (1 - 10^{-3}S)C \ln \frac{B+P}{B} \qquad (16)$$

where S is the salinity in parts per thousand, C is a constant, and B is a temperature and salinity dependent parameter. Li examined the seawater results of Ekman (1908) and Wilson (1960a) using this equation and found that the results could be fitted to $\pm 10 \times 10^{-6} \text{cm}^3\text{g}^{-1}$ over the oceanic range of pressure, temperature, and salinity. He also noticed a difference at 1-atm between the compressibilities of Ekman and the sound derived data of Wilson. These differences were later shown by Lepple and Millero (1971) to be due to errors in Ekman's work.

Li's equation was used (Fine *et al.*, 1974) to represent Kell and Whalley's (1965) as well as Fine and Millero's (1973) pure water and seawater results, however, neither could be fit to within the experimental error.

Hayward, in 1967, extensively investigated different forms of equations of state and suggested the reciprocal form of the Tait equation

$$\frac{1}{k} = \frac{V^0 P}{V^0 - V^P} = K = K^0 + BP \tag{17}$$

where $K^0 = \pi/A$ and $B = 1/A$ in equation (1). In equation (17), K is the secant bulk modulus, K^0 is the secant bulk modulus at sea level pressure, and equals the reciprocal of the isothermal compressibility, $1/\beta$, B is a function of salinity and temperature. Hayward concluded that the linear secant bulk modulus equation best represented the compression properties of liquids over the pressure range from zero to several hundred bars. With the addition of one or two extra terms the equation can be extended to cover all liquids at pressures up to 12 Kb over a wide range of temperatures.

Macdonald (1969, 1971) analyzed[4] several equations of state which had a variety of mathematical forms including the Tammann equation and the secant bulk modulus equation chosen by Hayward. He disagreed with Hayward and selected the Murnaghan equation to be superior to either the Tammann equation or the linear secant bulk modulus equation chosen by Hayward. If, however, the Tammann equation and the Murnaghan equation were both expanded to second order in pressure, then Macdonald found that the results obtained from both equations would agree. As shown earlier, the expansion of the Tammann equation to second order is equivalent to the bulk modulus form of the original Tait equation.

Wang and Millero (1973) and Fine *et al.* (1974) used the second degree secant bulk modulus equation to represent the sound-derived isothermal compressibilities of pure water as well as seawater to a precision of better than $0.01 \times 10^{-6} \mathrm{bar}^{-1}$. The second degree secant bulk modulus equation was given by

$$K = PV_w^0/(V^0 - V^P) = K^0 + AP + BP^2 \tag{18}$$

where V_w^0 and V^0 are the 1-atm specific volumes of pure water and seawater, respectively. V^P is the specific volume of seawater at applied pressure P, K^0, A and B are salinity and temperature dependent parameters. Emmet and Millero (1974) used a similar equation to fit their specific volume measurements on standard seawater (35‰S) to a standard deviation of $11 \times 10^{-6} \mathrm{cm}^3 \mathrm{g}^{-1}$;

$$K = PV^0/(V^0 - V^P) = K^0 + AP + BP^2 \tag{19}$$

In 1976 Bradshaw and Schleicher presented an equation which can be used to calculate the specific volumes of seawater:

4. In his statistical analysis, Macdonald used the PVT data of Kell and Whalley (1965) which has been shown to be in error. Thus, the conclusions of Macdonald may be questionable.

$$V(T,P,S) = [1 - C(10,P,S)] \times [V(0,0,S) + E(10,0S)]$$
$$+ E(T,P,S) - E(10,P,S) \tag{20}$$

$$C(10,P,S) = \sum_{i,j} b_{i,j} P^i S^j \tag{20a}$$

$$E(T,P,S) = \int_0^T \frac{\partial V(T,P,S)}{\partial T} dT \tag{20b}$$

where $V(T,P,S)$, $C(T,P,S)$ and $E(T,P,S)$ are the specific volume, compression, and thermal expansion of seawater at temperature T, applied pressure P, and salinity, S, respectively.

In 1976 Chen and Millero (1976a) published an equation of state for seawater based on the sound derived pure water equation of state of Fine and Millero (1973). Later in that year, a new pure water equation of state was determined (Chen, Fine, and Millero, 1977) and the data of Chen and Millero (1976a) were consequently refitted based on the new pure water equation of state in the form of second degree secant bulk modulus equation with a standard deviation of $7 \times 10^{-6} \text{cm}^3\text{g}^{-1}$ in specific volume.

$$K = P V^0/(V^0 - V^P) = K^0 + AP + BP^2 \tag{21}$$

$$K^0 = K_W^0 + a S(\%_o) + b S(\%_o)^{3/2} \tag{21a}$$

$$A = A_W + c S(\%_o) + d S(\%_o)^{3/2} \tag{21b}$$

$$B = B_W + e S(\%_o) \tag{21c}$$

The 1-atm densities of pure water, ρ_W^0, taken from the work of Kell (1975), were refitted into the equation with a standard deviation of $\pm 0.04 \times 10^{-6} \text{ g cm}^{-3}$ over the range of 0 to 50°C. Equations for the calculations of ρ_W^0, K_W^0, A_W, and B_W are given below (Chen, Fine and Millero, 1977)

$$V_W^0 = 1/\rho_W^0 \tag{22}$$

$$\rho_W^0 = 0.9998395 + 6.7914 \times 10^{-5}t - 9.0894 \times 10^{-6}t^2$$
$$+ 1.0171 \times 10^{-7}t^3 - 1.2846 \times 10^{-9}t^4$$
$$+ 1.1592 \times 10^{-11}t^5 - 5.0125 \times 10^{-14}t^6 \tag{23}$$

$$K_W^0 = 19652.17 + 148.183t - 2.29995t^2 + 0.012810t^3$$
$$- 4.91564 \times 10^{-5}t^4 + 1.03553 \times 10^{-7}t^5 \tag{24}$$

$$A_W = 3.26138 + 5.223 \times 10^{-4}t + 1.324 \times 10^{-4}t^2$$
$$- 7.655 \times 10^{-7}t^3 + 8.584 \times 10^{-10}t^4 \tag{25}$$

$$B_W = 7.2061 \times 10^{-5} - 5.8948 \times 10^{-6}t + 8.699 \times 10^{-8}t^2$$

$$- 1.010 \times 10^{-9}t^3 + 4.322 \times 10^{-12}t^4 \tag{26}$$

The 1-atm density for seawater, ρ^0, was taken from the relative density equation of Millero, Gonzalez, and Ward (1976). The absolute density (ρ) is related to the relative density (d) by $\rho = d\,\rho_{MAX}$, where ρ_{MAX} is the maximum density of water. Multiplying the equation by $\rho_{MAX} = 0.999974$ g cm^{-3} (Millero and Emmet, 1976) for MIAMI water, we have

$$V^0 = 1/\rho^0 \tag{27}$$

$$\rho^0 - \rho_W{}^0 = (8.25917 \times 10^{-4} - 4.4490 \times 10^{-6}t$$

$$+ 1.0485 \times 10^{-7}t^2 - 1.2580 \times 10^{-9}t^3$$

$$+ 3.315 \times 10^{-12}t^4)\,S(\%_0) + (-6.33761 \times 10^{-6}$$

$$+ 2.8441 \times 10^{-7}t - 1.6871 \times 10^{-8}t^2$$

$$+ 2.83258 \times 10^{-10}t^3)\,S(\%_0)^{3/2} + (5.4705 \times 10^{-7}$$

$$- 1.97975 \times 10^{-8}t + 1.6641 \times 10^{-9}t^2$$

$$- 3.1203 \times 10^{-11}t^3)\,S(\%_0)^2 \tag{28}$$

The values of a, b, c, d, and e for equation (21) are given below:

$$a = 51.261 - 0.4506t + 2.643 \times 10^{-3}t^2 \tag{29}$$

$$b = 0.6623 + 7.274 \times 10^{-3}t \tag{30}$$

$$c = 4.809 \times 10^{-3} - 1.675 \times 10^{-4}t + 3.598 \times 10^{-6}t^2 \tag{31}$$

$$d = -2.929 \times 10^{-4} \tag{32}$$

$$e = -1.125 \times 10^{-6} + 1.363 \times 10^{-7}t - 2.134 \times 10^{-9}t^2 \tag{33}$$

The differences between the specific volumes determined from the refitted data (eqs. 29-33) and the original equation (Chen and Millero, 1976a) are equal to the differences in the two equations of state for pure water (Chen, Fine and Millero, 1977; Fine and Millero, 1973) and are shown in Figure 5.

In the next section the equation of state derived from these sound measurements is presented.

3. The equation of state from sound speeds

The equation of state is in the form of a second degree secant bulk modulus equation (equation 21). Differentiating equation (21) with respect to pressure gives:

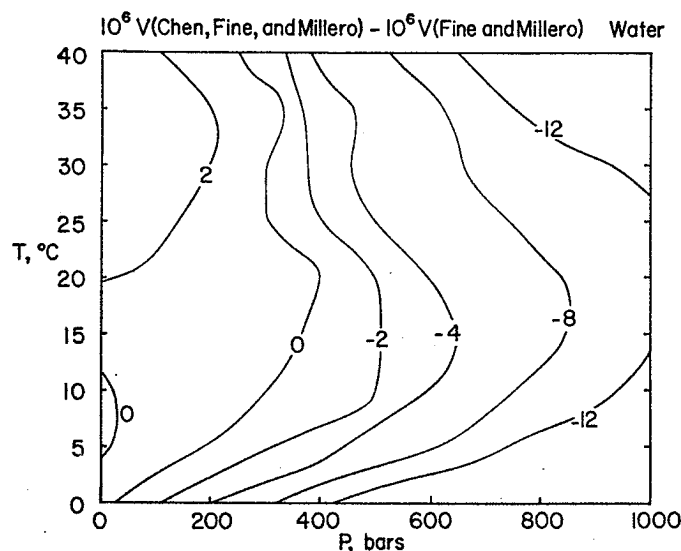$$-(\partial V/\partial P)^P = V^0 (K^0 - BP^2)/(K^0 + AP + BP^2)^2 \tag{34}$$

Figure 5. Comparisons of the specific volumes of pure water obtained by Chen, Fine and Millero (1977) and Fine and Millero (1973).

The pressure derivative of the specific volume is related to the speed of sound by (Wang and Millero, 1973):

$$-(\partial V/\partial P)^P = (V^P/U^P)^2 + T(\alpha^P V^P)^2/Cp^P \tag{35}$$

where T is the absolute temperature, α^P is the thermal expansibility at applied pressure P, and Cp^P is the specific heat at constant pressure at applied pressure P. Values of Cp^P can be calculated from the equation (Fofonoff, 1962):

$$Cp^P = Cp^0 - T \int_0^P (\partial^2 V/\partial T^2)\, dP \tag{36}$$

where Cp^0 is the specific heat at 1-atm (Millero *et al.*, 1973).

The K^0 term in equation (21) and equation (34) was determined by setting $P = 0$ bars applied pressure (1-atm). For $P = 0$ bars, equation (34) becomes

$$-\left(\frac{\partial V}{\partial P}\right)^0 = V^0/K^0 \tag{37}$$

and equation (35) becomes

$$-\left(\frac{\partial V}{\partial P}\right)^0 = (V^0/U^0)^2 + T(\alpha^0 V^0)^2/Cp^0 \tag{38}$$

Equations (37) and (38) can be combined to calculate K^0:

$$K^0 = V^0/[(V^0/U^0)^2 + T(\alpha^0 V^0)^2/Cp^0] \tag{39}$$

where values of V^0, U^0, α^0, and Cp^0 are all readily available. An iterative computer

technique [with equations (34) and (35)] was used to determine A and B. As the first step, an arbitrary equation of state was used to generate $\partial^2 V/\partial T^2$ (which was used to calculate Cp^P), V^P and α^P. Values of Cp^P, V^P and α^P generated were combined with the sound speeds obtained by Chen and Millero (1977b) to calculate $(\partial V/\partial P)^P$ from equation (35). The values of $(\partial V/\partial P)^P$ obtained at various concentrations, temperatures, and pressures were fit to an equation similar to equation (34):

$$- (\partial V/\partial P)^P = V^0(K^0 - B'P^2)/(K^0 + AP + BP^2)^2 \qquad (40)$$

where B' was an arbitrary function of concentration and temperature. A least squares program developed by Mehr (personal communication, 1974) and Fine (personal communication, 1976) was used in the fitting of the values of $(\partial V/\partial P)^P$ in order to determine the A and B terms, thus obtaining an equation of state. The newly obtained equation of state was then used to calculate Cp^P, V^P, and α^P, which were again combined with the sound speeds to calculate $(\partial V/\partial P)^P$ from equation (35).

Values of $(\partial V/\partial P)^P$ obtained were again fit to equation (40) (where the B' term was replaced by the B term obtained from the previous least squares fit) to generate new A and B terms. The same processes were repeated until the newly generated values of $(\partial V/\partial P)^P$ agreed with the previous values to within $0.01 \times 10^{-6}\text{bar}^{-1}$ at each concentration, temperature, and pressure level.

Using the iterative program and the 1-atm thermal expansibility and specific volume data of Millero *et al.* (1976), and the specific heat data of Millero *et al.* (1973), the temperature dependent parameters [equation (21)] were calculated

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

$$- 5.107 \times 10^{-5}t^3 \qquad (41)$$

$$b = 0.2322 - 4.838 \times 10^{-3}t \qquad (42)$$

$$c = 4.692 \times 10^{-3} - 8.387 \times 10^{-5}t + 4.68 \times 10^{-7}t^2 \qquad (43)$$

$$d = -1.332 \times 10^{-4} \qquad (44)$$

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

$$- 1.551 \times 10^{-9}t^2 \qquad (45)$$

The precision of the equation of state is $\pm 0.008 \times 10^{-6}\text{bar}^{-1}$ in isothermal compressibility. The maximum error is $0.03 \times 10^{-6}\text{bar}^{-1}$ at the temperature and pressure extremes. The precision of the specific volume is estimated to be better than $\pm 10 \times 10^{-6}\text{cm}^3\text{g}^{-1}$, and the thermal expansibility estimated to be reliable to within $\pm 2 \times 10^{-6}\text{deg}^{-1}$.

The specific volume (V^P), thermal expansibility $\alpha^P = 1/V^P (\partial V/\partial T)^P$, and isothermal compressibility $\beta^P = -1/V^P (\partial V/\partial P)^P$ can be determined from

$$V^P = V^0 - \frac{V^0 P}{K^0 + AP + BP^2} \qquad (46)$$

$$\alpha^P = \frac{1}{V^P}\left(\frac{\partial V}{\partial T}\right)^0 - \frac{P(\partial V/\partial T)^0}{V^P(K^0 + AP + BP^2)}$$

$$+ PV^0 \frac{(\partial K^0/\partial T)_P + P(\partial A/\partial T)_P + P^2(\partial B/\partial T)_P}{V^P(K^0 + AP + BP^2)^2} \qquad (47)$$

$$\beta = \frac{V^0(K^0 - BP^2)}{V^P(K^0 + AP + BP^2)^2} \qquad (48)$$

using equations (21) to (28) and (41) to (45). Some check values are given below:

At 0‰, 10°C, and 0 bars: $V = 1.0003004$ cm^{3}g^{-1}, $\alpha = 87.957 \times 10^{-6}$deg^{-1}, $\beta = 47.810 \times 10^{-6}$bar^{-1}.

At 35‰, 10°C, and 0 bars: $V = 0.9737545$ cm^{3}g^{-1}, $\alpha = 166.828 \times 10^{-6}$deg^{-1}, $\beta = 44.058 \times 10^{-6}$bar^{-1}.

At 0‰, 10°C, and 1000 bars: $V = 0.9589935$ cm^{3}g^{-1}, $\alpha = 273.544 \times 10^{-6}$ deg^{-1}, $\beta = 37.167 \times 10^{-6}$bar^{-1}.

At 35‰, 10°C, and 1000 bars: $V = 0.9364213$ cm^{3}g^{-1}, $\alpha = 308.261 \times 10^{-6}$ deg^{-1}, $\beta = 34.697 \times 10^{-6}$bar^{-1}.

4. Results and discussion

The sound derived equation of state for seawater is valid over the salinity range of 0 to 40‰, temperature range of 0 to 40°C, and pressure range of 0 to 1000 bars. This makes the equation of state valid not only for oceanographic calculations, but also for the calculations concerning the processes in the estuaries and coastal zones such as in the salt water intrusion studies. The validity of the seawater equation of state at the low salinity range (Chen and Millero, 1977b,c) would make it useful in studies of deep well injection and studies on the salt water overlay and convection motions in the aquifers. It should be pointed out that the sound determined seawater equation of state obtained in this study covers wider ranges of salinity, temperature, and pressure than most of the equations developed by other workers (Table 4). However, it has the same number of terms as the equations developed in the past few years.[5] Values of specific volume, thermal expansibility, and isothermal compressibility for 35‰ salinity seawater are given in Tables 5 through 7.

The specific volumes calculated from eq. (46) are compared with the data of various workers in Figures 6, 7, and 8. In Figure 6, comparisons are made with the corrected and refitted specific volume data of Chen and Millero (1976a). Over most of the temperature and pressure space the sound derived specific volumes agree

5. It should be pointed out that the high pressure coefficients used for pure water are valid from 0 to 100°C (Chen, Fine and Millero, 1977). By confining the temperature range from 0 to 40°C, it is probably possible to eliminate a few terms.

Table 4. Number of terms and range covered of various equations of state.

Investigator	Number of terms		Range covered
	1-atm density	pressure effect	
Direct PVT measurements:			
Knudsen-Ekman*	16	32	31.13 and 38.53‰ S, 0 to 20°C, 0 to 600 bars
Bradshaw and Schleicher (1970, 1976)	13	32	30 to 40‰ S, −2 to 30°C, 0 to 1000 bars
Chen and Millero** (1976a)	21	27	0 to 40‰ S, 0 to 40°C, 0 to 1000 bars
Chen and Millero (1977a)	12	12	30 to 40‰ S, −2 to 38°C, 0 to 1000 bars
Sound speed derived equations:			
Wang and Millero (1973)	25	22	30 to 40‰ S, 0 to 30°C, 0 to 1000 bars
Fine, Wang and Millero (1974)	24	26	30 to 40‰ S, 0 to 30°C, 0 to 1000 bars
Chen and Millero (this study)	20	29	0 to 40‰ S, 0 to 40°C, 0 to 1000 bars

* Knudsen (1901), Ekman (1908).
** Chen and Millero (1976a). The new equation presented in this study has 20 1-atm density terms and 28 pressure effect terms.

with the direct measurements to within $20 \times 10^{-6} cm^3 g^{-1}$ from 5 to 40‰ salinity. It is interesting to note that the published equations of Chen and Millero (1976a, 1977a) yield specific volumes that agree to within $\pm 10 \times 10^{-6} cm^3 g^{-1}$ with the sound derived data over the oceanic ranges of pressure, temperature, and salinity (see Figure 8). This agreement at 35‰ salinity is fortuitous since the equations are in error at low salinities. The larger differences that occur at higher temperatures (30 to 40°C) and pressures (500 to 1000 bars) are probably due to errors in the direct measurements caused by the movement of the magnet in the magnetic float. Changes in the ultrasonic absorption of $MgSO_4$ at high pressures and temperature could also lead to the differences. Comparisons in Figure 7 are made with the direct measurements of Bradshaw and Schleicher at 15, 30, 35, and 40‰ salinity. Over most of the pressure and temperature space, the agreement is within $10 \times 10^{-6} cm^3 g^{-1}$. (The high pressure specific volumes of Bradshaw and Schleicher were obtained by integration, using their 10°C compression data and 1970 and 1977 expansion measurements.) The agreement of the sound derived specific volumes and the direct measurements of Chen and Millero and Bradshaw and Schleicher confirm the validity of the method used to determine an equation of state from sound speeds and the reliability of the results.

Table 5. The specific volumes of seawater at 35‰ salinity and various temperatures and pressures.

$V(\text{cm}^3\text{g}^{-1})$

P(bars)	0°C	5°C	10°C	15°C	20°C
0	0.972664	0.973070	0.973754	0.974685	0.975835
100	0.968227	0.968750	0.969527	0.970530	0.971735
200	0.963926	0.964558	0.965423	0.966493	0.967751
300	0.959754	0.960489	0.961435	0.962570	0.963877
400	0.955707	0.956538	0.957560	0.958755	0.960108
500	0.951779	0.952699	0.953793	0.955044	0.956440
600	0.947965	0.948968	0.950128	0.951432	0.952869
700	0.944260	0.945340	0.946563	0.947916	0.949391
800	0.940661	0.941812	0.943092	0.944491	0.946002
900	0.937162	0.938379	0.939713	0.941154	0.942698
1000	0.933761	0.935038	0.936421	0.937902	0.939476

	25°C	30°C	35°C	40°C
0	0.977189	0.978732	0.980455	0.982349
100	0.973129	0.974699	0.976437	0.978336
200	0.969182	0.970778	0.972531	0.974434
300	0.965344	0.966965	0.968732	0.970640
400	0.961610	0.963253	0.965034	0.966946
500	0.957974	0.959640	0.961433	0.963350
600	0.954433	0.956119	0.957925	0.959846
700	0.950983	0.952688	0.954505	0.956429
800	0.947620	0.949343	0.951170	0.953097
900	0.944340	0.946080	0.947915	0.949845
1000	0.941140	0.942895	0.944738	0.946669

Table 6. The thermal expansibilities of seawater at 35‰ salinity and various temperatures and pressures.

$10^6 \, \alpha(\text{deg}^{-1})$

| P(bars)	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	51.74	113.45	166.83	214.18	257.15	296.85	334.03	369.17	402.53
100	79.29	135.68	184.73	228.51	268.47	305.63	340.64	373.89	405.60
200	105.27	156.72	201.73	242.16	279.33	314.10	347.05	378.53	408.69
300	129.74	176.61	217.87	255.17	289.70	322.23	353.26	383.06	411.74
400	152.76	195.39	233.15	267.54	299.60	330.03	359.24	387.45	414.74
500	174.39	213.09	247.61	279.27	309.03	337.47	364.97	391.68	417.64
600	194.66	229.76	261.26	290.39	317.98	344.57	370.44	395.72	420.42
700	213.63	245.41	274.14	300.90	326.47	351.30	375.64	399.56	423.05
800	231.35	260.09	286.25	310.82	334.49	357.67	380.55	403.18	425.50
900	247.85	273.82	297.61	320.15	342.05	363.67	385.17	406.56	427.76
1000	263.10	286.64	308.26	328.91	349.16	369.31	389.49	409.69	429.80
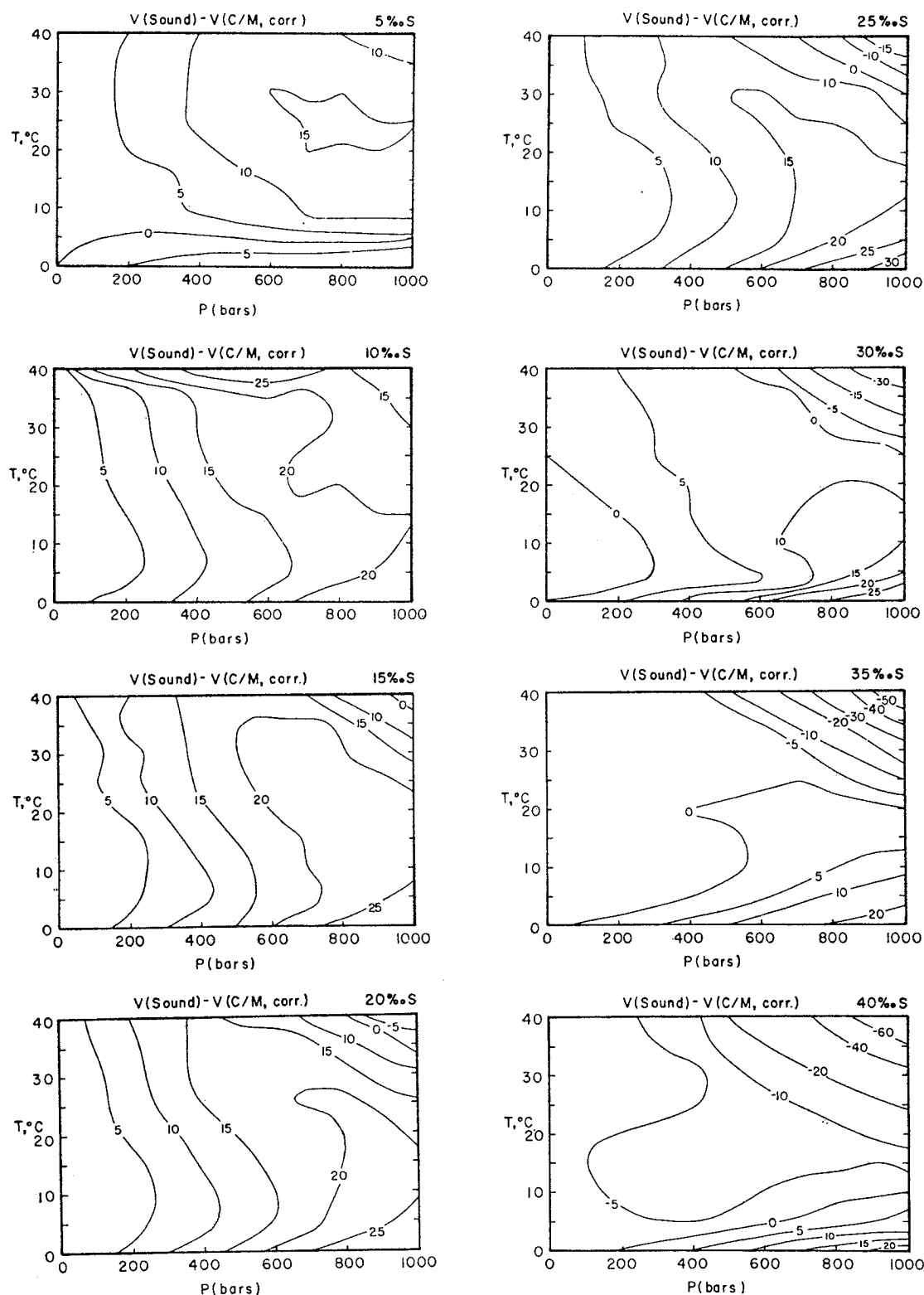
Figure 6. Contour diagrams of the differences in the relative specific volumes ($V^P - V^0$ in cm³g⁻¹, normalized at 1-atm) obtained in this study and the corrected and refitted data of Chen and Millero (1976a) for various salinities.
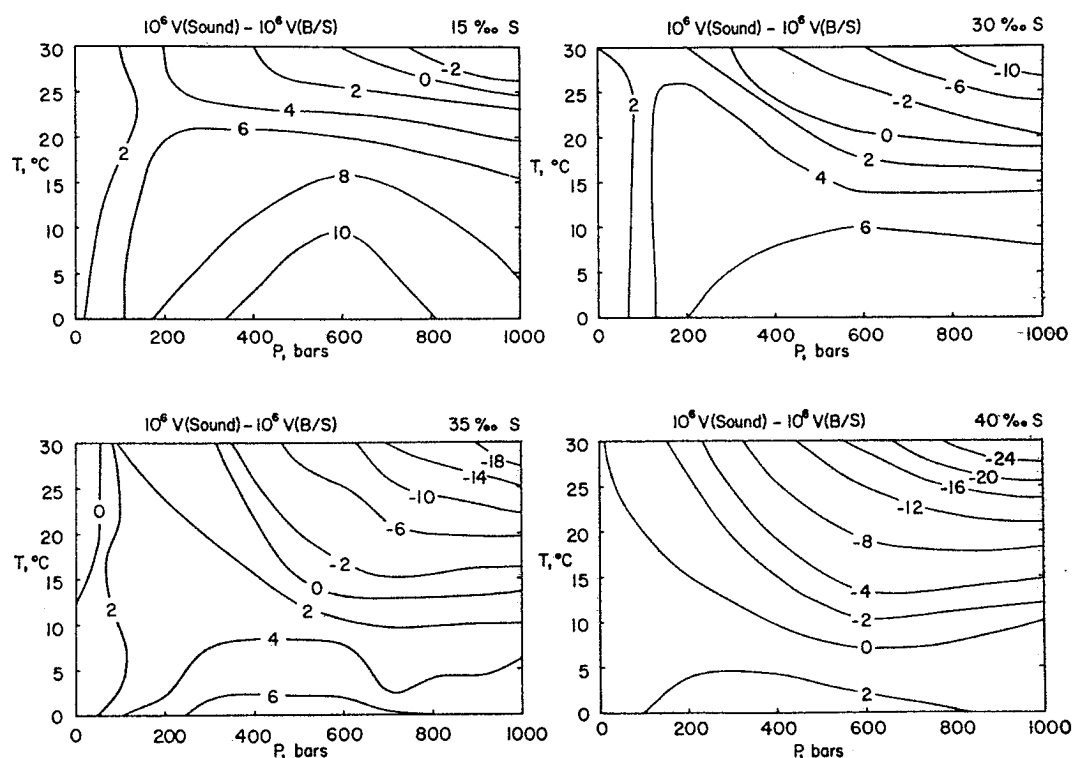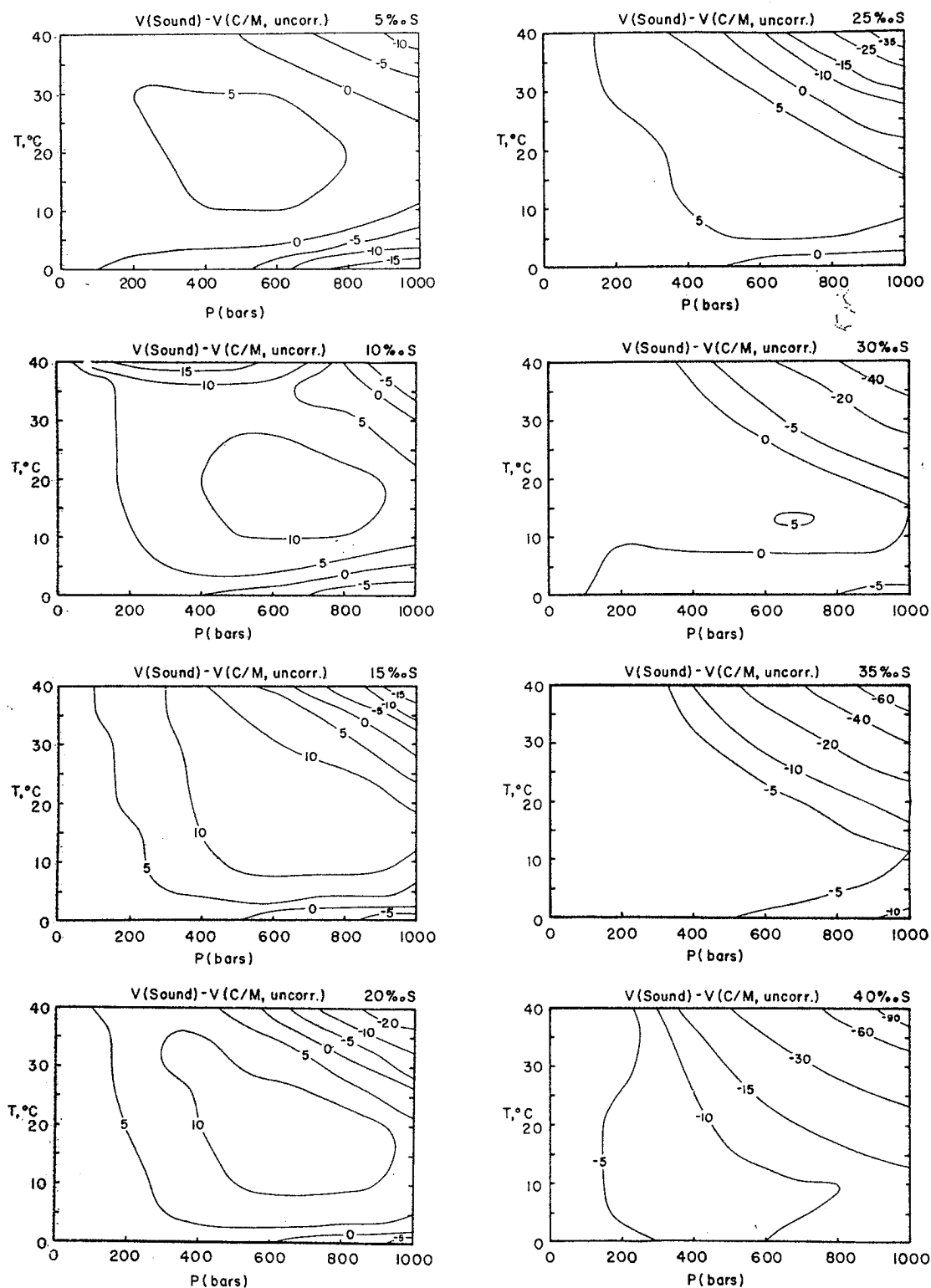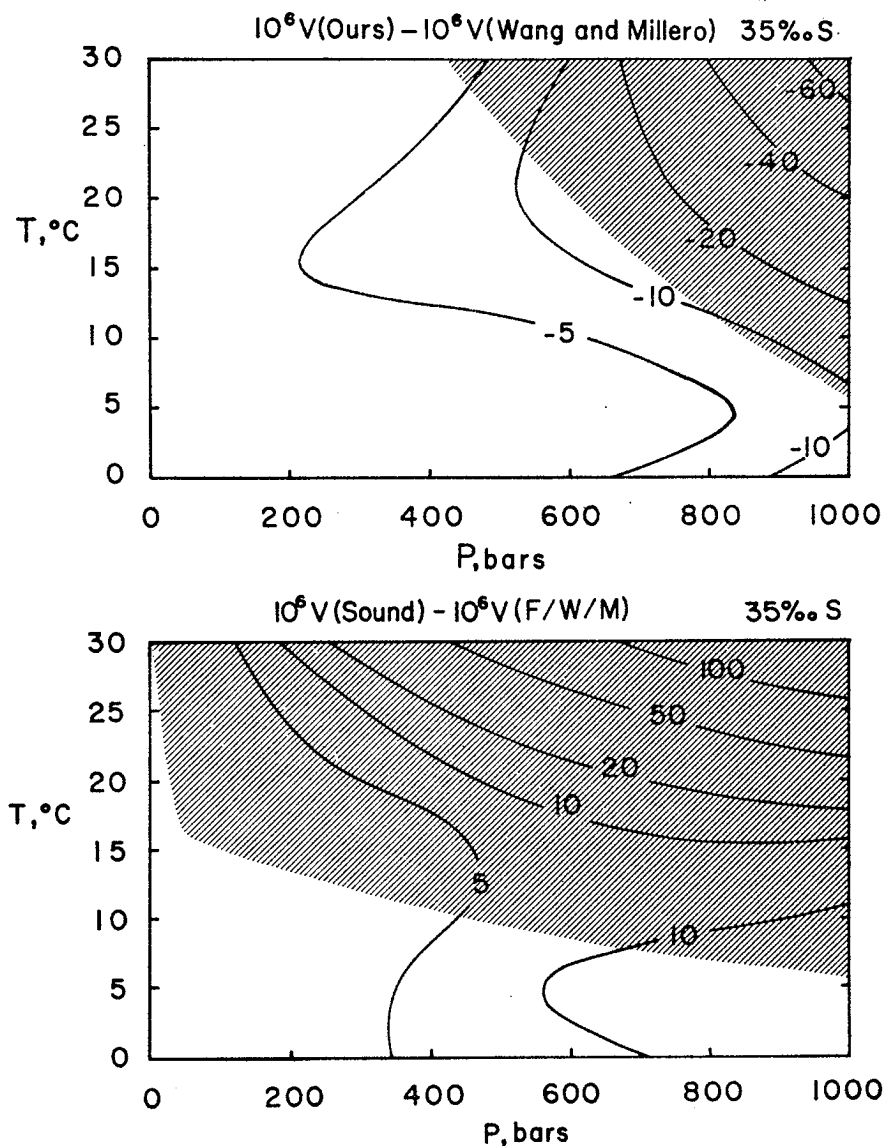
Figure 7. Contour diagrams of the differences in the relative specific volumes ($V^P - V^0$ in cm^3g^{-1}, normalized at 1-atm) obtained in this study and the data of Bradshaw and Schleicher (B/S) for various salinities.

Table 7. The isothermal compressibilities of seawater at 35‰ salinity and various temperatures and pressures.

$$10^6 \, \beta(bar^{-1})$$

P(bars)	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	46.34	45.07	44.06	43.25	42.62	42.14	41.80	41.57	41.45
100	45.12	43.92	42.96	43.19	41.59	41.13	40.79	40.57	40.44
200	43.94	42.81	41.90	41.17	40.59	40.15	39.83	39.61	39.48
300	42.81	41.74	40.88	40.19	39.64	39.22	38.90	38.69	38.56
400	41.72	40.71	39.90	39.24	38.72	38.31	38.01	37.81	37.69
500	40.66	39.72	38.95	38.33	37.83	37.45	37.16	36.96	36.85
600	39.65	38.76	38.04	37.45	36.98	36.61	36.34	36.15	36.04
700	38.67	37.84	37.16	36.61	36.16	35.81	35.56	35.38	35.27
800	37.72	36.95	36.31	35.79	35.37	35.04	34.80	34.63	34.54
900	36.81	36.09	35.49	35.00	34.61	34.30	34.07	33.91	33.83
1000	35.92	35.26	34.70	34.24	33.87	33.58	33.37	33.23	33.15

Figure 8. Contour diagrams of the differences in the relative specific volumes ($V^P - V^0$ in cm^{3}g^{-1}, normalized at 1-atm) obtained in this study and the uncorrected results of Chen and Millero (1976a, 1977a) for various salinities.

Figure 9. Contour diagrams of the differences in the relative specific volumes ($V^P - V^0$ in cm³g⁻¹, normalized at 1-atm) obtained in this study and other work using the sound data of Wilson (Wang and Millero, 1973) and Del Grosso (Fine, Wang and Millero, 1974) at 35‰ salinity.

Our specific volumes agree (Fig. 9) with the work of Wang and Millero (1973) to within ± 10 × 10⁻⁶cm³g⁻¹ over the limits of their equation (to 600 bars at 20°C and to 400 bars at 30°C), and agree with the work of Fine, Wang and Millero (1974) to within ± 15 cm³g⁻¹ over the range of their study (to 400 bars at 10°C and to 200 bars at 15°C).

The relative thermal expansibilities ($\alpha^P - \alpha^0$ in 10⁻⁶deg⁻¹) at 10 and 35‰
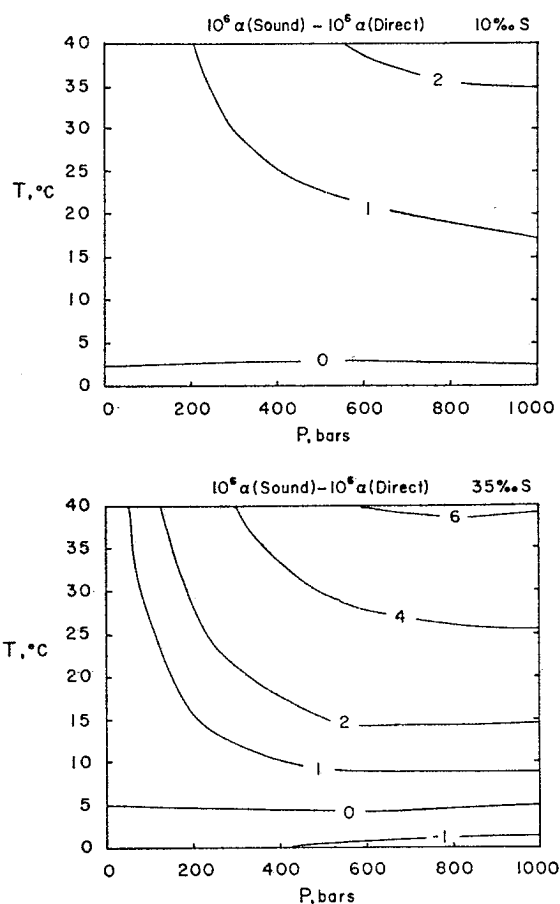
Figure 10. Contour diagrams of the differences in the relative thermal expansibilities $(\alpha^P - \alpha^0$ in deg^{-1}, normalized at 1-atm) obtained from this study and the refitted data of Chen and Millero for 10 and 35‰ salinity seawater.

salinity calculated from the temperature derivative of eq. (21) are compared with the refitted direct measurements of Chen and Millero (1976a) in Figure 10. At 10‰ salinity, the agreement is within ± 2 × 10^{-6}deg^{-1} over the entire temperature and pressure range. At 35‰ salinity, our thermal expansibilities are higher than those of Chen and Millero by up to 6 × 10^{-6}deg^{-1} at the high temperature and pressure range. Our values agree with the work of Wang and Millero and Fine, Wang and Millero (Fig. 11) to within ± 3 × 10^{-6}deg^{-1} over the valid range of their equations of state. The work of Bradshaw and Schleicher (refitted by Bryden, 1973) agrees with our values to within ± 4 × 10^{-6}deg^{-1} (Fig. 11).

The isothermal compressibilities at 10 and 35‰ salinity calculated from the pressure derivative of equation (21) are compared with the refitted direct measurements of Chen and Millero (1976a) in Figure 12. The agreement is within ± 0.05 × 10^{-6}bar^{-1} over most of the temperature and pressure space of both studies. At higher salinities, temperatures, and pressures, the sound determined isothermal com-
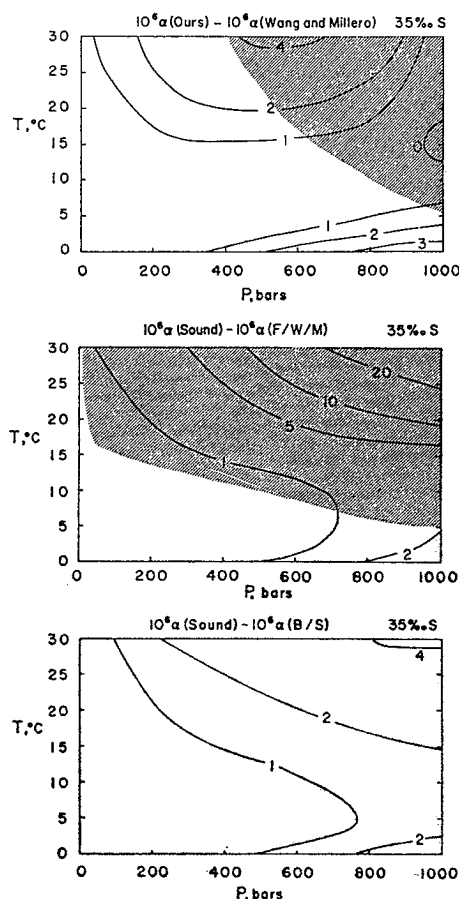
Figure 11. Contour diagrams of the differences in the relative thermal expansibilities $(\alpha^P - \alpha^\bullet$ in deg^{-1}, normalized at 1-atm) obtained from this study and the data of various workers for 35‰ salinity seawater.

pressibilities are higher than the direct measurements. The agreement with the data of Wang and Millero (Fig. 13) and Fine, Wang, and Millero (Fig. 13) are within ± 0.02 × 10^{-6}bar^{-1} over the valid range of the latter two equations of state (normalized to agree with our value at 1-atm). The work of Bradshaw and Schleicher (Fig. 13) (normalized at 1-atm) agrees with our results to within ± 0.05 × 10^{-6}bar^{-1} over most of the range of their study.

5. Conclusion

A precise equation of state for seawater was determined from the sound speeds with a maximum error of ± 0.03 × 10^{-6}bar^{-1} in isothermal compressibility. The equation of state can be used to calculate reliable specific volumes (± 10 × 10^{-6}cm^{3}g^{-1}) and thermal expansibilities (± 2 × 10^{-6}deg^{-1}) over the range of 0 to 40‰ salinity, 0 to 40°C, and 0 to 1000 bars. The equation agrees with the re-fitted direct measurements of Chen and Millero (1976a) to within ± 20 × 10^{-6}cm^3
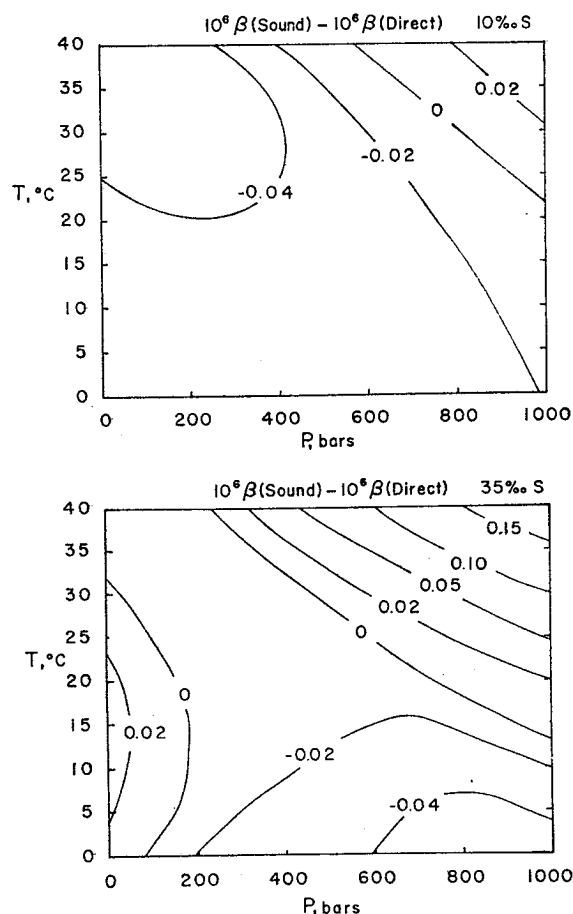
Figure 12. Contour diagrams of the differences in the isothermal compressibilities ($\beta^P - \beta^0$ in bar^{-1}) obtained from this study and the refitted data of Chen and Millero for 10 and 35‰ salinity seawater.

g^{-1} in specific volume, $\pm 4 \times 10^{-6}$deg^{-1} in thermal expansibility, and $\pm 0.05 \times 10^{-6}$bar^{-1} in isothermal compressibility over most of the space studied. The results of Bradshaw and Schleicher (1970, 1976) agrees with ours to within $\pm 10 \times 10^{-6}$cm^{3}g^{-1} in specific volume, $\pm 4 \times 10^{-6}$deg^{-1} in thermal expansibility and $\pm 0.05 \times 10^{-6}$bar^{-1} in isothermal compressibility. The agreement with the two other sound determined equations of state of Wang and Millero (1973) and Fine, Wang, and Millero (1974) is within $\pm 15 \times 10^{-6}$cm^{3}g^{-1} in specific volume, $\pm 2 \times 10^{-6}$deg^{-1} in thermal expansibility, and $\pm 0.02 \times 10^{-6}$bar^{-1} in isothermal compressibility.

APPENDIX

The sound derived equation of state of seawater is given by

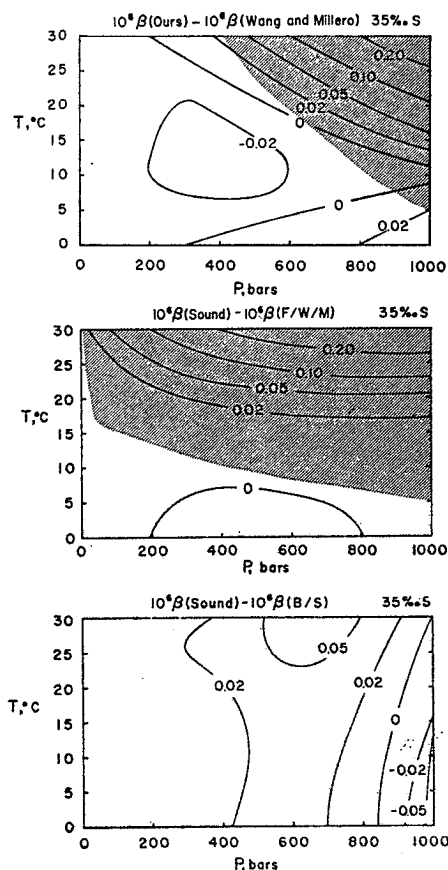$$K = \frac{V^0 P}{V^0 - V^P} = K^0 + AP + BP^2$$

Figure 13. Contour diagrams of the differences in the relative isothermal compressibilities $(\beta^P - \beta^0$ in bar^{-1}, normalized at 1-atm) obtained from this study and the data of various workers for 35‰ salinity seawater.

in which V^0 is the specific volume (cm^{3}g^{-1}) at sea level, V^P is the specific volume at applied pressure P (bars), K^0, A and B are functions of temperature (t°C) and salinity (S in ‰)

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

$$A = A_W + c\ S(\text{‰}) + d\ S(\text{‰})^{3/2}$$

$$B = B_W + e\ S(\text{‰})$$

The coefficients for the various terms are given by

$$V^0 = 1/\rho^0$$

$$\begin{aligned}
\rho^0 &= 0.9998395 + 6.7914 \times 10^{-5}t - 9.0894 \times 10^{-6}t^2 \\
&\quad + 1.0171 \times 10^{-7}t^3 - 1.2846 \times 10^{-9}t^4 + 1.1592 \times 10^{-11}t^5 \\
&\quad - 5.0125 \times 10^{-14}t^6 + (8.25917 \times 10^{-4} - 4.4490 \times 10^{-6}t \\
&\quad + 1.0485 \times 10^{-7}t^2 - 1.2580 \times 10^{-9}t^3 + 3.315 \times 10^{-12}t^4) \\
&\quad S(\text{‰}) + (-6.33761 \times 10^{-6} + 2.8441 \times 10^{-7}t \\
&\quad - 1.6871 \times 10^{-8}t^2 + 2.83258 \times 10^{-10}t^3)\ S(\text{‰})^{3/2} \\
&\quad + (5.4705 \times 10^{-7} - 1.97975 \times 10^{-8}t + 1.6641 \times 10^{-9}t^2 \\
&\quad - 3.1203 \times 10^{-11}t^3)\ S(\text{‰})^2
\end{aligned}$$

$$K_w{}^0 = 19652.17 + 148.183t - 2.29995t^2 + 0.012810t^3$$
$$- 4.91564 \times 10^{-5}t^4 + 1.03553 \times 10^{-7}t^5$$

$$A_w = 3.26138 + 5.223 \times 10^{-4}t + 1.324 \times 10^{-4}t^2$$
$$- 7.655 \times 10^{-7}t^3 + 8.584 \times 10^{-10}t^4$$

$$B_w = 7.2061 \times 10^{-5} - 5.8948 \times 10^{-6}t + 8.699 \times 10^{-8}t^2$$
$$1.010 \times 10^{-9}t^3 + 4.322 \times 10^{-12}t^4$$

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

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

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

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

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

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).

V^P FOR PURE WATER

$(S = 0‰)$ AT 0°C AND 25°C

P	V^P (0°C)	V^P (25°C)
0	1.0001605	1.0029639
100	0.9951545	0.9984935
200	0.9903103	0.9941540
300	0.9856212	0.9899394
400	0.9810810	0.9858440
500	0.9766835	0.9818624
600	0.9724232	0.9779897
700	0.9682944	0.9742209
800	0.9642922	0.9705518
900	0.9604116	0.9669779
1000	0.9566481	0.9634954

V^P FOR 35(‰) SALINITY

P	V^P (0°C)	V^P (25°C)
0	0.9726638	0.9771887
100	0.9682268	0.9731289
200	0.9639255	0.9691824
300	0.9597541	0.9653442
400	0.9557069	0.9616095
500	0.9517788	0.9579739
600	0.9479649	0.9544330
700	0.9442604	0.9509829
800	0.9406610	0.9476197
900	0.9371624	0.9443401
1000	0.9337607	0.9411404

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