

The specific volume of seawater at high pressures*

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Abstract—The high pressure specific volumes of seawater (relative to pure water and 1 atm) have been measured from 0 to 40°C, 0 to 1000 bars and 5 to 40‰ salinity with a high pressure magnetic float densimeter (MILLERO, KNOX and EMMET, *Journal of Solution Chemistry*, 1, 173–186, 1972). The results of the measurements have been fitted to 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 measured specific volumes of seawater at applied pressure zero and P , respectively, $K^0 = 1/\beta^0$, the reciprocal of the isothermal compressibility at atmospheric pressure, A and B are all salinity- and temperature-dependent parameters. The specific volumes have been fitted to this equation with a standard deviation of 7 ppm (on the measurement residuals) over the entire salinity, temperature and pressure range. The fitted relative specific volumes ($V^P - V^0$) are in excellent agreement (within ± 5 ppm) with the sound-derived data of WANG and MILLERO (*Journal of Geophysical Research*, 78, 7122–7128, 1973) over the oceanographic range of salinity, temperature and pressure. The derived P – V – T properties have been compared with the experimental work of Ekman (*Publications de circonstance. Conseil permanent international pour l'exploration de la mer*, 43, 1–47, 1908); WILSON and BRADLEY (*Deep-Sea Research*, 15, 355–363, 1968); BRADSHAW and SCHLEICHER (*Deep-Sea Research*, 17, 691–706, 1970; personal communication 1974); DUEDELL and PAULOWICH (*Review of Scientific Instruments*, 44, 120–127, 1973); EMMET and MILLERO (*Journal of Geophysical Research*, 79, 3463–3472, 1974) and the sound-derived data of WANG and MILLERO (1973); FINE, WANG and MILLERO (*Journal of Marine Research*, 32, 433–456, 1974).

INTRODUCTION

IN RECENT years there has been a lot of controversy (FINE, WANG and MILLERO, 1974) concerning the equation of state of seawater. In order to clear up the controversy and obtain a reliable equation of state, two independent approaches are under way in our laboratory. The first approach is to derive the P – V – T properties from sound speeds (MILLERO and KUBINSKI, 1975). The second approach is to make direct measurements on the specific volume of seawater with a high pressure magnetic float densimeter (EMMET and MILLERO, 1974). In the present paper, we present an equation of state of seawater which is derived from our directly measured specific volume data and is good over a wide salinity, temperature and pressure range. The accurate specific volume data obtained should prove useful in interpreting the movement and stratification of deep water masses in the ocean. The isothermal compressibility will be useful in the calculation of N , the Brunt–Väisälä frequency (WANG, 1974). The thermal expansibility repre-

sented as a function of pressure will be useful in the calculation of the adiabatic temperature gradient. Higher derivatives of the equation of state may be used to calculate other interesting thermodynamic quantities such as the pressure dependence of specific heat of seawater at constant pressure (C_p), and the Joule–Thompson coefficient. The accurate specific volume data will also be useful for the determination of partial molal volumes as a function of temperature, pressure and salinity. The partial molal volumes can then be used to calculate the effect of temperature and pressure on the equilibria of importance in the marine environment.

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EXPERIMENTAL

Experimental apparatus

The high pressure magnetic float densimeter used in this study has been described in detail elsewhere (MILLERO, KNOX and EMMET, 1972; EMMET and MILLERO, 1974). It consists essentially of a 1-atm densimeter (MILLERO, 1967) enclosed in a non-magnetic bomb with optical ports to observe the motion of the float. The apparatus consists of a pressure bomb, a magnetic float and auxiliary measuring and control systems.

The pressure bomb used in this study was machined from Carpenter 20 stainless steel. The bomb is cylindrical with top and bottom plugs sealed with O-rings to form a vessel of 170 cm³. The bottom plug contains an insert plug that supports a solenoid. The windows in the bomb are 30° cones machined from cast Plexiglas rod. The magnetic floats are made of thick wall Pyrex glass and contain a permanent magnet (sealed with silastic R-T-V sealer). The volume of the floats used in this study were 59.8 cm³ at 0° and 1 atm. The pressure bomb was completely immersed in a 30-litre constant temperature bath controlled to $\pm 0.001^\circ\text{C}$ with a Hallikainen Thermotrol. The temperature of the bath was set to $\pm 0.002^\circ\text{C}$ with a platinum resistance thermometer (calibrated by the National Bureau of Standards, IPTS 1968 temperature scale) and a G-2 Mueller Bridge. The temperature of the bath was monitored to $\pm 0.001^\circ\text{C}$ during an experimental run with a Hewlett-Packard quartz crystal thermometer (also calibrated with the platinum resistance thermometer). A temperature variation of $\pm 0.002^\circ\text{C}$ is equivalent to ± 1 ppm in specific volume which is within our experimental error.

The pressure generating system has been described in detail elsewhere (MILLERO, KNOX and EMMET, 1972). A Enerpac hand pump was used to generate the pressure which was set and held with a Harwood Engineering dead weight tester. An oil water separator was used to separate the pressure-generating system from the solution in the bomb. The volume capacity of the oil water separator is seven times the volume change that occurs during compression of distilled water to 1000 bars. The dead weight tester is a piston

inserted into a close fitting cylinder. Weights are loaded on the top of the piston (which rotates) and are supported by the hydraulic fluid pressure applied to the bottom. The weight of the weights (and piston) divided by the cross-sectional area of the piston gives the pressure. The cross-sectional area of the piston (measured at 20°C) was corrected for the film thickness, effects of temperature and pressure to give the exact pressure to ± 0.1 bar at 1000 bars. The dead weight system (and weights) has been calibrated by the manufacturer (traceable to the National Bureau of Standards). The weights were determined from the measured masses by using the local acceleration of gravity. An error of ± 0.1 bar at 1000 bars is equivalent to an error of $\pm 4 \times 10^{-6}$ cm³ g⁻¹ in specific volume. Since the system is calibrated with water using the same weights used in the experimental runs on seawater, the errors in the relative specific volumes $V_{sw} - V_w$ at a given pressure are quite small.

Materials

The water used in the calibrations and in diluting the standard seawater was 18 M Ω ion exchanged (Millipore Super-Q system) Miami tap water. As discussed elsewhere (MILLERO and EMMET, 1976) the Miami ion exchanged water used in the calibrations had a specific volume that is 1×10^{-6} cm³ g⁻¹ higher than SMOW (standard mean ocean water); this did not affect the relative specific volumes $V_{sw} - V_w$.

The standard seawater (P-57, 6/8, 1972, Cl‰ = 19.3755) used in these studies was weight diluted or evaporated (at 30°C) to prepare the solutions at low and high salinities. The relationship (UNESCO, 1966) was used to convert the chlorinity into the salinity.

$$S(\text{‰}) = 1.80655 \text{ Cl}(\text{‰}). \quad (1)$$

The errors in this method of preparing the samples by weight is less than $\pm 0.001\text{‰}$ in salinity. The salinities of a number of the samples were checked by measuring the conductivity with a Beckman salinometer calibrated by weight diluting and evaporating a number of samples of standard seawater (MILLERO, GONZALEZ and

WARD, 1976). The conductivity salinities agree with the weight diluted or evaporated values to $\pm 0.003\%$ (the precision of the salinometer). This error in salinity is equivalent to $\pm 2 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in the specific volume.

Calibration and measurement procedures

If a weighted magnetic float in a magnetic field is completely immersed in a solution, the hydrostatic equilibrium is given by (MILLERO, 1967)

$$d(V_f + m/d_{\text{Pt}}) = M + m + fi, \quad (2)$$

where d is the density of the solution (the reciprocal of the specific volume, V), V_f is the volume of the float, m is the mass of platinum on the float, d_{Pt} is the density of platinum, M is the mass of the float, f is the magnetic interaction factor and i is the equilibrium current necessary to just hold the float on the bottom of the solution container. Rearrangement of equation (2) gives the linear equation (expressed in specific volumes)

$$m(1 - V_{\text{Pt}}/V) = -fi + (V_f/V - M), \quad (3)$$

which can be used to determine the volume of the float (V_f) and the magnetic interaction factor (f) by measuring the equilibrium current with two or more platinum weights on the float in a solution of known specific volume. As shown elsewhere (MILLERO, KNOX and EMMET, 1972), this equation holds over a wide pressure and temperature range in water to a precision of $\pm 4 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in V .

The densimeter was calibrated (CHEN, 1974) in water using the specific volumes, determined from the equation of state of FINE and MILLERO (1973), which have been derived from the high pressure sound speed measurements of WILSON (1959) by the methods of WANG and MILLERO (1973). These specific volumes are thought to be accurate to $\pm 16 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

The densities (or specific volumes) of platinum were calculated from the equation

$$d_{\text{Pt}} = d_{\text{Pt}}(25^\circ\text{C}, 1 \text{ atm}) / [1 + \alpha_{\text{Pt}}(t - 25) - \beta_{\text{Pt}}P], \quad (4)$$

where the compressibility of platinum (BRIDGEMAN, 1958), $\beta_{\text{Pt}} = 3.59 \times 10^{-7} \text{ bar}^{-1}$; the expansibility of platinum (*Handbook of chemistry and physics*, 1961), $\alpha_{\text{Pt}} = 2.65 \times 10^{-5} \text{ deg}^{-1}$ and the density of

platinum at 25°C and 1 atm (MACINNES, DAYHOFF and RAY, 1952), $d_{\text{Pt}} = 21.428 \text{ g cm}^{-3}$. The platinum mass was held on the float with a bridle made of thin platinum wire. The error in the platinum densities at a given pressure and temperature is $\pm 0.001 \text{ g cm}^{-3}$ which is equivalent to an error of $1 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ in specific volume.

The densimeter was calibrated (CHEN, 1974) in water from 0 to 40°C (5° intervals) and 0 to 1000 bars (200-bar intervals) by using three masses of platinum on the float. The results at a given pressure and temperature were fitted to equation (3) by using a least squares method. A summary of the calibration results are given in Table 1. Although the pressure dependence of V_f and f were found to be nearly linear in pressure (in agreement with early studies, MILLERO, KNOX and EMMET, 1972; EMMET and MILLERO, 1974), we have not used smoothed values of V_f and f in determining the specific volumes of the seawater solutions. The average differences (ΔV) between the smoothed specific volumes (determined with the least squares values of V_f and f) and the volumes used in the calibrations are also given in Table 1. These values of ΔV represent the reproducibility or precision of the densimeter. The average ΔV over the entire temperature and pressure range was $\pm 3.5 \text{ ppm}$ (with a maximum of $\pm 9.4 \text{ ppm}$).

The errors involved in using the densimeter on the seawater solution from

$$1/V = (M + m + fi) / (V_f + m/d_{\text{Pt}}) \quad (5)$$

can be examined by considering the errors in quantities $V_f (\pm 0.0002 \text{ cm}^3)$, $m (\pm 0.0001 \text{ g})$, $M (\pm 0.0001 \text{ g})$, $d_{\text{Pt}} (\pm 0.001 \text{ g cm}^{-3})$, $f (\pm 0.001 \text{ g A}^{-1})$ and $i (\pm 0.00001 \text{ amp})$ at a given pressure and temperature. (As discussed earlier the errors in V due to variations in T , P and salinity are within $\pm 3 \text{ ppm}$). The maximum probable error estimated at 1000 bars is found to be $\pm 11 \text{ ppm}$ in specific volume. The errors in the magnetic interaction factor are the largest source of errors in the measured specific volumes (a maximum error of $\pm 6.5 \text{ ppm}$ at 1000 bars). The error f determined at a given P and T is largely due to the non-elastic properties of the magnetic

Table 1. Calibration for the high pressure magnetic float.

Pressure (bars)	V_f^a (cm ³)	f^a (g/amp)	$\pm \Delta V^b$ (ppm)	V_f (cm ³)	f (g/amp)	$\pm \Delta V$ (ppm)	V_f (cm ³)	f (g/amp)	$\pm \Delta V$ (ppm)
<u>0°C</u>									
0.00	59.85198	5.8781	1.7	59.85791	5.8763	7.5	59.86456	5.8748	3.8
199.66	59.69086	5.8821	0.1	59.69750	5.8845	4.3	59.70509	5.8856	5.0
399.33	59.52905	5.8860	0.7	59.53642	5.8900	4.2	59.54507	5.8938	3.0
599.00	59.36681	5.8896	1.4	59.34545	5.8979	4.8	59.38272	5.8960	4.9
798.67	59.20363	5.8903	3.2	59.21274	5.9033	2.9	59.22020	5.9018	2.1
998.34	59.04057	5.8978	1.0	59.04981	5.9090	3.9	59.05622	5.9047	4.4
<u>15°C</u>									
0.00	59.87002	5.8622	2.7	59.87618	5.8664	0.1	59.88053	5.8676	4.3
199.66	59.70989	5.8736	1.4	59.71616	5.8741	0.3	59.72065	5.8715	6.5
399.33	59.54903	5.8807	0.2	59.55477	5.8780	0.0	59.56021	5.8728	5.8
599.00	59.38807	5.8887	3.6	59.39288	5.8819	0.3	59.39847	5.8747	4.2
798.67	59.22668	5.8980	3.4	59.23013	5.8867	1.6	59.23606	5.8750	4.2
998.34	59.06397	5.9033	7.1	59.06746	5.8921	0.4	59.07284	5.8776	6.9
<u>30°C</u>									
0.00	59.88598	5.8611	0.2	59.89125	5.8289	9.4	59.89744	5.8367	0.4
199.66	59.72689	5.8701	2.8	59.73187	5.8598	3.0	59.73696	5.8561	5.1
399.33	59.56780	5.8810	4.7	59.57253	5.8711	4.6	59.57671	5.8601	1.5
599.00	59.40806	5.8893	4.7	59.41229	5.8759	1.3	59.41619	5.8657	0.6
798.67	59.24917	5.9013	1.0	59.25309	5.8892	3.4	59.25592	5.8747	7.0
998.34	59.09119	5.9165	2.9	59.09141	5.8930	8.3	59.09454	5.8801	8.6

(a) V_f and f are the volume of the float and the magnetic interaction factor respectively, determined from equation (3) by a least squares method and are based on at least 3 separate calibrations with 3 platinum weights on the float.

(b) Average deviation between the back calculated specific volumes of water (obtained by using the measured currents and the least squared values of V_f and f) and the specific volumes of water given by FINE and MILLERO (1973). The average deviation is a measure of the reproducibility of the magnetic float system.

float and pressure bomb (i.e. the distance between the bottom of the magnet in the float and the solenoid). As discussed elsewhere (MILLERO, 1967), by using the magnetic float system to measure the relative densities of a solution to pure water ($d - d_w$) and to 1 atm ($d^P - d^0$), the

systematic errors (due to errors in P , T and S_{∞}) essentially cancel and the errors in the relative densities approach the precision or reproducibility of the densimeter (± 3.5 ppm).

The specific volume measurements on the seawater solutions at a given pressure and

temperature were determined from the measured equilibrium current using equation (5) and the values of V_f and f given in Table 1. The precision or reproducibility of i at a given P and T was $\pm 1 \times 10^{-5}$ amps (which is equivalent to ± 1 ppm in V).

RESULTS

The specific volumes of seawater (5 to 40‰ at 5‰ increments) have been measured over the temperature range of 0 to 40°C at 5°C increments and over the pressure range of 0 to 1000 bars at 200-bar increments (100-bar increments for 30, 35 and 40‰ salinity seawater). Table 2 gives the measured specific volumes. The seawater specific volumes have been used to determine the secant bulk modulus, K , defined by

$$K = \frac{V^0 P}{V^0 - V^P} \quad (6)$$

V^0 and V^P are the specific volumes of seawater at applied pressure zero and P , respectively.

The pressure dependence of the secant bulk modulus for 35‰ salinity seawater at various temperatures is shown in Fig. 1. The secant bulk

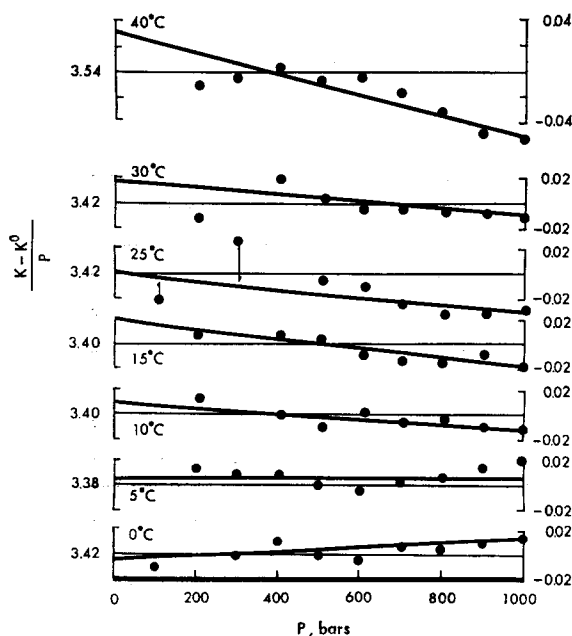


Fig. 1. $(K - K^0)/P$ versus pressure for 35‰ salinity seawater at various temperatures, lines are determined by a linear least squares fit of the data.

modulus at 1 atm, K^0 , is equal to the reciprocal of the isothermal compressibility (β^0). The values of $K^0 = 1/\beta^0$ for this illustration were taken from the work of MILLERO and KUBINSKI (1975). The values of $(K - K^0)/P$ for 35‰ salinity seawater are a linear function of pressure over the entire temperature range (within the experimental error of the measurements). Similar results are found for seawaters at other salinities. Between 0 and 5°C the values of $(K - K^0)/P$ increase with increasing pressure, while at higher temperatures the values decrease with increasing pressure. The values of $(K - K^0)/P$ at a fixed pressure decrease with increasing temperature at temperatures below 5°C, while at higher temperatures the values increase with increasing temperatures. From these results it is clear that the secant bulk modulus of seawater can be represented by a second degree function of pressure (WANG and MILLERO, 1973; FINE and MILLERO, 1973; FINE, WANG and MILLERO, 1974; EMMET and MILLERO, 1974). This finding is in contrast with the work of HAYWARD (1967) who found that K is a linear function of pressure. Since the slope of $(K - K^0)/P$ versus P is small, it is not surprising that a linear function can be used to represent the less precise P - V - T data of the early workers.

Figure 2 shows the salinity dependence of the secant bulk modulus of seawater at 1000 bars and various temperatures. The secant bulk modulus of

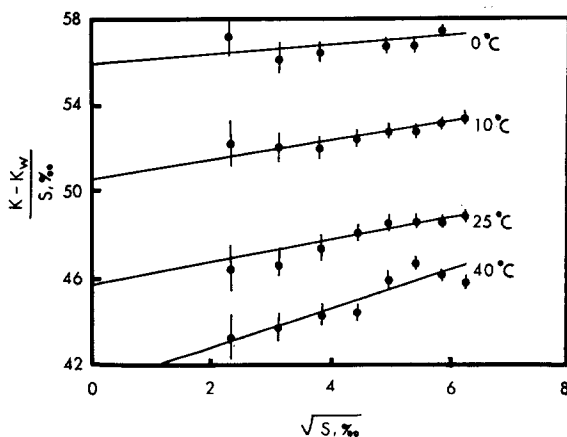


Fig. 2. $(K - K_w)/S(\%)$ versus $S(\%)^{1/2}$ at 1000 bars and various temperatures, lines are determined by a linear least squares fit of the data.

Table 2. The measured specific volumes of seawater at various salinities, temperatures and pressures.

$V(\text{cm}^3 \text{ g}^{-1})$									
5.467°/‰ Salinity									
P (bars)	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0.00	0.995718	0.995697	0.996041	0.996703	0.997647	0.998844	1.000273	1.001918	1.003787
199.66	0.986078	0.986360	0.986934	0.987793	0.988873	0.990179	0.991687	0.993376	0.995263
399.33	0.977044	0.977580	0.978372	0.979390	0.980600	0.981999	0.983580	0.985321	0.987234
599.00	0.968558	0.969322	0.970290	0.971455	0.972785	0.974273	0.975914	0.977697	0.979628
798.67	0.960583	0.961536	0.962663	0.963957	0.965381	0.966952	0.968650	0.970466	0.972414
998.34	0.953079	0.954198	0.955461	0.956855	0.958365	0.959996	0.961746	0.963599	0.965562
9.989°/‰ Salinity									
0.00	0.992115	0.992162	0.992565	0.993275	0.994253	0.995476	0.996923	0.998577	1.000437
199.66	0.982626	0.982960	0.983577	0.984475	0.985591	0.986915	0.988440	0.990132	0.992017
399.33	0.973706	0.974300	0.975123	0.976178	0.977419	0.978833	0.980425	0.982162	-----
599.00	0.965350	0.966155	0.967162	0.968349	0.969694	0.971195	0.972847	0.974622	0.976550
798.67	0.957485	0.958476	0.959634	0.960942	0.962389	0.963958	0.965664	0.967481	0.969416
998.34	0.950076	0.951223	0.952510	0.953921	0.955450	0.957076	0.958832	0.960676	0.962628
14.949°/‰ Salinity									
P (bars)	0°C	5°C	10°C	15°C	20°C ^a	25°C ^a	30°C ^a	35°C ^a	40°C ^a
0.00	0.988195	0.988319	0.988783	0.989542	0.990495	0.991746	0.993211	0.994878	0.996733
199.66	0.978855	0.979261	0.979940	0.980872	0.981962	0.983303	0.984832	0.986540	0.988427
399.33	0.970092	0.970731	0.971603	0.972688	0.973894	0.975328	0.976919	0.978667	0.980568
599.00	0.961861	0.962717	0.963749	0.964960	0.966275	0.967785	0.969433	0.971216	0.973138
798.67	0.954115	0.955135	0.956321	0.957650	0.959060	0.960641	0.962342	0.964166	0.966101
998.34	0.946811	0.947984	0.949292	0.950721	0.952221	0.953852	0.955599	0.957442	0.959388
20.082°/‰ Salinity									
0.00	0.984175	0.984376	0.984900	0.985706	0.986759	0.988036	0.989521	0.991202	0.993068
199.66	0.974999	0.975465	0.976197	0.977166	0.978341	0.979710	0.981256	0.982973	0.984855
399.33	0.966387	0.967078	0.967990	0.969102	0.970389	0.971841	0.973445	0.975199	0.977102
599.00	0.958293	0.959173	0.960245	0.961483	0.962869	0.964393	0.966050	0.967836	0.969757
798.67	0.950662	0.951712	0.952922	0.954270	0.955757	0.957339	0.959050	0.960869	0.962815
998.34	0.943462	0.944664	0.945994	0.947439	0.948990	0.950649	0.952395	0.954230	-----
24.989°/‰ Salinity									
P (bars)	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0.00	0.980362	0.980632	0.981213	0.982057	0.983143	0.984445	0.985948	0.987643	0.989520
199.66	0.971335	0.971858	0.972634	0.973636	0.974841	0.976222	0.977791	0.979516	0.981423
399.33	0.962862	0.963605	0.964545	0.965681	0.966999	0.968470	0.970082	0.971843	0.973771
599.00	0.954887	0.955809	0.956915	0.958169	0.959586	0.961120	0.962779	0.964587	0.966530
798.67	0.947382	0.948455	0.949684	0.951059	0.952545	0.954149	0.955865	0.957707	0.959648
998.34	0.940280	0.941504	0.942855	0.944314	0.945874	0.947538	0.949293	0.951130	0.953104

Table 2. (continued)

30.003 ^o /oo Salinity									
P (bars)	-0.051°C	4.948°C	9.946°C	14.940°C	19.935°C	24.929°C	29.926°C	34.924°C	39.919°C
0.00	0.976490	0.976825	0.977457	0.978342	0.979459	0.980781	0.982302	0.984003	0.985885
99.83	0.971987	0.972439	0.973170	0.974137	0.975303	0.976673	0.978215	0.979942	0.981821
199.66	0.967612	0.968193	0.969019	0.970047	0.971272	0.972682	0.974251	0.975986	0.977876
299.50	0.963371	0.964069	0.964970	0.966071	0.967350	0.968793	0.970391	0.972142	0.974029
399.33	0.959268	0.960053	0.961039	0.962206	0.963541	0.965011	0.966637	0.968412	0.970306
499.16	-----	0.956164	0.957221	0.958447	0.959821	0.961339	0.962986	0.964763	0.966667
599.00	0.951409	0.952376	0.953509	0.954794	0.956221	0.957752	0.959425	0.961225	0.963139
698.83	0.947658	0.948704	0.949896	0.951241	0.952692	0.954272	0.955964	0.957785	0.959723
798.67	-----	0.945133	0.946390	0.947769	0.949266	0.950871	0.952585	0.954426	0.956377
898.50	0.940467	0.941652	0.942975	0.944399	0.945941	0.947559	0.949301	0.951154	0.953120
998.34	-----	0.938273	0.939632	0.941110	0.942691	0.944343	0.946105	0.947972	0.949940
35.003 ^o /oo Salinity									
P (bars)	0.000°C	4.948°C	9.946°C	14.940°C	19.935°C	24.929°C	29.926°C	34.924°C	39.919°C
0.00	0.972666	0.973074	0.973755	0.974676	0.975826	0.977175	0.978716	0.980434	0.982325
99.83	0.968237	0.968761	0.969536	0.970531	0.971732	0.973124	0.974686	0.976418	0.978320
199.66	0.963951	0.964576	0.965437	0.966498	0.967759	0.969186	0.970774	0.972518	0.974423
299.50	0.959780	0.960512	0.961464	0.962587	0.963887	0.965355	0.966962	0.968738	0.970638
399.33	0.955744	0.956565	0.957587	0.958774	0.960127	0.961622	0.963267	0.965033	0.966960
499.16	0.951820	0.952728	0.953822	0.955069	0.956465	0.957992	0.959657	0.961446	0.963378
599.00	0.948010	0.948997	0.950169	0.951460	0.952895	0.954453	0.956143	-----	0.959896
698.83	0.944318	0.945372	0.946607	0.947946	0.949418	0.951003	0.952723	0.954540	0.956490
798.67	0.940720	0.941850	0.943144	0.944526	0.946030	0.947648	0.949387	0.951226	0.953181
898.50	0.937224	0.938428	0.939763	0.941203	0.942735	0.944379	0.946137	0.947987	0.949944
998.34	0.933845	-----	0.936474	0.937947	0.939523	0.941195	0.942959	0.944835	0.946792
39.864 ^o /oo Salinity									
P (bars)	-0.051°C	4.948°C	9.946°C	14.940°C	19.935°C	24.929°C	29.926°C	35.000°C ^b	40.000°C ^b
0.00	0.968951	0.969420	0.970146	0.971109	0.972283	0.973655	0.975209	0.976994	0.978907
99.83	0.964593	0.965173	0.965987	0.967023	0.968245	0.969661	0.971232	0.973033	0.974952
199.66	0.960367	0.961051	0.961954	0.963054	0.964331	0.965767	0.967372	0.969180	0.971108
299.50	0.956265	0.957057	0.958029	0.959192	0.960514	0.961983	0.963611	0.965446	0.967369
399.33	0.952293	0.953159	0.954208	0.955434	0.956794	0.958295	0.959952	0.961804	0.963731
499.16	0.948427	0.949380	0.950497	0.951774	0.953181	0.954716	0.956397	0.958263	0.960189
599.00	0.944679	0.945704	0.946889	0.948223	0.949661	0.951222	0.952932	0.954806	0.956737
698.83	0.941031	0.942138	0.943376	0.944747	0.946227	0.947822	0.949548	0.951443	0.953372
798.67	0.937497	0.938662	0.939955	0.941368	0.942885	0.944509	0.946259	0.948151	0.950090
898.50	-----	0.935278	0.936625	0.938077	0.939640	0.941276	0.943046	0.944946	0.946887
998.34	-----	0.931986	0.933381	0.934869	0.936459	0.938130	0.939904	0.941806	0.943758

(h) 39.827‰ salinity.

pure water, K_w , was calculated from the work of FINE and MILLERO (1973). The values of $(K - K_w)/S(\%)$ are linear functions of $S(\%)^{1/2}$ (within the experimental error of the measurements). This linear relationship holds over the entire temperature and pressure range of the studies. The slope of the linear equations increase with increasing temperature. At a fixed salinity the values of $(K - K_w)/S(\%)$ decrease with increasing temperature. From these results it is clear that the secant bulk modulus, like other thermodynamic properties of seawater (LEPPLE and MILLERO, 1971; MILLERO and LEPPLE, 1973; MILLERO, 1973, 1974, 1976; MILLERO and KUBINSKI, 1975), is a function of $S(\%)$ and $S(\%)^{3/2}$. The intercepts of the $(K - K_w)/S(\%)$ versus $S(\%)^{1/2}$ plots are related to the effect of pressure on the ion-water interactions of the major sea salts and the slopes are related to the effect of pressure on the ion-ion interactions (MILLERO, 1974).

The equation of state selected to fit our specific volume measurements is in the form

$$K = \frac{V^0 P}{V^0 - V^P} = K^0 + AP + BP^2, \quad (7)$$

where K^0 , the secant bulk modulus at 1 atm, A and B are all temperature- and salinity-dependent parameters. Since all of our measurements were made relative to pure water, we have determined the salinity and temperature dependence of the relative secant bulk modulus $(K - K_w)$. The salinity dependence of $(K - K_w)/S(\%)$ was assumed to be a function of $S(\%)^{1/2}$. Thus, the values of K^0 , A and B can be represented by

$$K^0 = K_w^0 + a S(\%) + b S(\%)^{3/2} \quad (7a)$$

$$A = A_w + c S(\%) + d S(\%)^{3/2} \quad (7b)$$

$$B = B_w + e S(\%) + f S(\%)^{3/2}, \quad (7c)$$

where the values of K_w^0 , A_w and B_w are for pure water (taken from the work of FINE and MILLERO, 1973), a , b , c , d , e and f (which was found to be zero) are all temperature-dependent parameters.

The advantage of formulating the equation of state of seawater in this manner is that it can be easily adjusted should more reliable P - V - T data become available for pure water over the T - P space of our investigation and the results are consistent with an infinite dilution standard state for the thermodynamic properties of seawater (MILLERO, 1976).

A least squares program was used to fit the secant bulk modulus $(K - K_w)$ data (on a UNIVAC 1106 computer) to equation (7). The final salinity and temperature form of the values of K^0 , A and B was arrived at by using the F -test for various polynomial forms. The distribution of the residuals between the measured and calculated [equation (8)] relative specific volumes ($V^P - V^0$) as a function of salinity, temperature and pressure are shown in Figs. 3, 4 and 5. These residuals are non-systematic although Fig. 5 shows that the residuals increase slightly with increasing pressure. The overall standard deviation of these residuals is 7 ppm in specific volume.

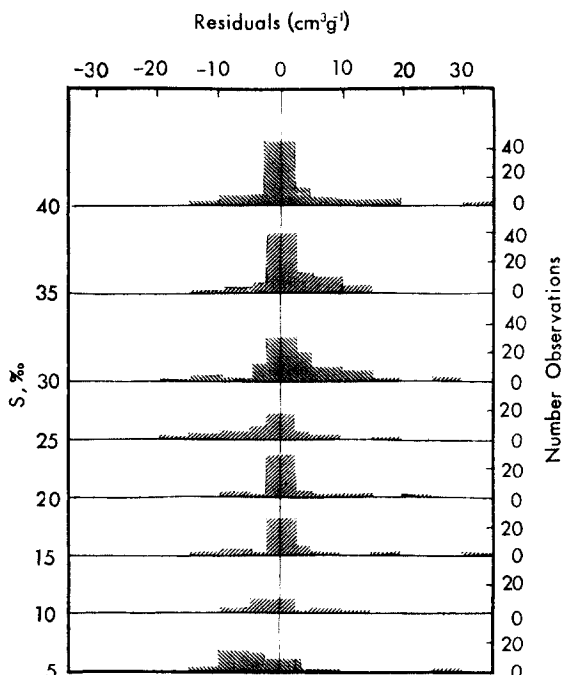


Fig. 3. The residuals between the relative specific volumes ($V^P - V^0$) calculated from equation (8) and the direct measurements at various salinities, the unit of the residual is $10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

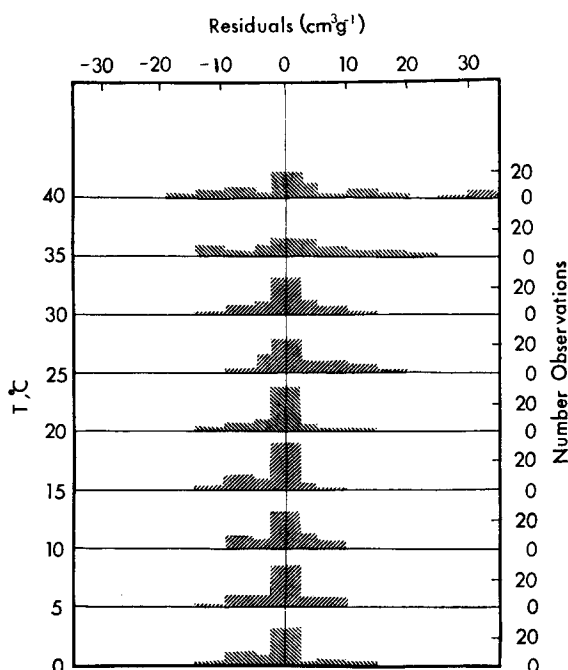


Fig. 4. The residuals between the relative specific volumes ($V^P - V^0$) calculated from equation (8) and the direct measurements at various temperatures, the unit of the residual is $10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

The standard deviation is 5 ppm over the oceanographic range.

Since the high pressure magnetic float densimeter was originally designed to study the effect of pressure on the specific volume of solutions up to very high pressures, we have been able to obtain very precise specific volumes relative ($V^P - V^0$) to the 1-atm volumes. Therefore, to obtain reliable values of V^P from our fitted values of the secant bulk modulus (or $V^P - V^0$) we have selected the more reliable values (± 3 ppm) of V^0 determined by MILLERO, GONZALEZ and WARD (1976). It should be pointed out that the values of V^0 given in Table 2 agree on the average to ± 4.5 ppm with those determined from the equation of MILLERO, GONZALEZ and WARD (1976). The specific volume of seawater solutions at any pressure (V^P) can be determined from the rearranged form of equation (7)

$$V^P = V^0 - \frac{V^0 P}{K^0 + AP + BP^2} \quad (8)$$

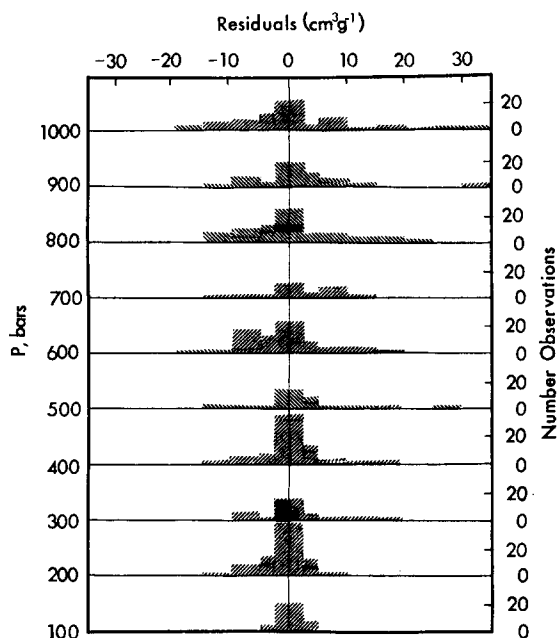


Fig. 5. The residuals between the relative specific volumes ($V^P - V^0$) calculated from equation (8) and the direct measurements at various pressures, the unit of the residual is $10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

The constants for equation (8) are given below

$$V^0 = 1/d^0 \text{ (MILLERO, GONZALEZ and WARD, 1976)} \quad (8a)$$

$$\begin{aligned} d^0 = & (0.9998396 + 1.8224944 \times 10^{-2}t \\ & - 7.922210 \times 10^{-6}t^2 - 5.544846 \times 10^{-8}t^3 \\ & + 1.497562 \times 10^{-10}t^4 - 3.932952 \times 10^{-13}t^5) / \\ & (1 + 1.8159725 \times 10^{-2}t) + (8.25915 \times 10^{-4} \\ & - 4.44897 \times 10^{-6}t + 1.04850 \times 10^{-7}t^2 \\ & - 1.25795 \times 10^{-9}t^3 + 3.3154 \times 10^{-12}t^4) \\ & \cdot S(\text{‰}) + (-6.3376 \times 10^{-6} + 2.8441 \times 10^{-7}t \\ & - 1.6871 \times 10^{-8}t^2 + 2.8325 \times 10^{-10}t^3) \\ & \cdot S(\text{‰})^{3/2} + (5.4704 \times 10^{-7} - 1.9797 \times 10^{-8}t \\ & + 1.6641 \times 10^{-9}t^2 - 3.1203 \times 10^{-11}t^3) S(\text{‰})^3 \end{aligned} \quad (8b)$$

$$\begin{aligned} K^0 = & 19654.32 + 147.037t - 2.21554t^2 + 1.04780 \\ & \times 10^{-2}t^3 - 2.2789 \times 10^{-5}t^4 + (51.2614 \\ & - 0.45222t + 2.6834 \times 10^{-3}t^2) S(\text{‰}) \\ & + (0.66286 + 7.281 \times 10^{-3}t) S(\text{‰})^{3/2} \end{aligned} \quad (8c)$$

$$A = 3.2891 - 2.3910 \times 10^{-3}t + 2.8446 \times 10^{-4}t^2 - 2.8200 \times 10^{-6}t^3 + 8.477 \times 10^{-9}t^4 + (4.93050 \times 10^{-3} - 1.74067 \times 10^{-4}t + 3.7712 \times 10^{-6}t^2) S(\text{‰}) + (-2.932 \times 10^{-4}) S(\text{‰})^{3/2} \quad (8d)$$

$$B = 6.2450 \times 10^{-5} - 3.913 \times 10^{-6}t - 3.499 \times 10^{-8}t^2 + 7.942 \times 10^{-10}t^3 - 3.299 \times 10^{-12}t^4 + (-1.17249 \times 10^{-6} + 1.40136 \times 10^{-7}t - 2.26045 \times 10^{-9}t^2) S(\text{‰}). \quad (8e)$$

Values of the specific volumes for 35‰ salinity seawater are given in Table 3.

The expansibility of seawater at any salinity and temperature and pressure can be determined by differentiating equation (8) with respect to temperature

$$\alpha = \frac{1}{V^P} \left(\frac{\partial V^P}{\partial T} \right)_P = \frac{1}{V^P} \left(\frac{\partial V^0}{\partial T} \right)_P - \frac{P (\partial V^0 / \partial T)}{V^P (K^0 + AP + BP^2)} + PV^0 \frac{(\partial K^0 / \partial T)_P + P(\partial A / \partial T)_P + P^2(\partial B / \partial T)_P}{V^P (K^0 + AP + BP^2)^2}. \quad (9)$$

The isothermal compressibility of seawater can be obtained by differentiating equation (8) with respect to pressure

$$\beta_T = -\frac{1}{V^P} \left(\frac{\partial V^P}{\partial P} \right)_T = \frac{V^0 (K^0 - BP^2)}{V^P (K^0 + AP + BP^2)^2}. \quad (10)$$

Values of the thermal expansibility and isothermal compressibility of 35‰ salinity seawater are given in Tables 4 and 5. Two simple equations have been determined from the α 's and β 's generated from equations (9) and (10) and can easily be used to generate thermal expansibilities and isothermal compressibilities at any salinity, temperature or pressure

$$\alpha = \alpha_w + A S(\text{‰}) + B S(\text{‰})^{3/2} \quad (11)$$

$$\alpha_w = -6.80977 \times 10^{-5} + 1.82945 \times 10^{-5}t - 3.2519 \times 10^{-7}t^2 + 6.4062 \times 10^{-9}t^3 - 8.8997 \times 10^{-11}t^4 + 5.846 \times 10^{-13}t^5 + (3.7409 \times 10^{-7} - 1.5881 \times 10^{-8}t + 2.9713 \times 10^{-10}t^2 - 3.5431 \times 10^{-12}t^3 + 1.741 \times 10^{-14}t^4)P + (-9.6658 \times 10^{-11} + 4.8741 \times 10^{-12}t - 1.0169 \times 10^{-13}t^2 + 9.941 \times 10^{-16}t^3)P^2 + 4.75 \times 10^{-16}P^3 \quad (11a)$$

$$A = 4.04385 \times 10^{-6} - 1.3990 \times 10^{-7}t + 1.727 \times 10^{-9}t^2 - 1.944 \times 10^{-11}t^3 + (-3.2190 \times 10^{-9} + 1.0353 \times 10^{-10}t - 8.365 \times 10^{-13}t^2)P + (7.183 \times 10^{-13} - 1.636 \times 10^{-14}t)P^2 \quad (11b)$$

$$B = -1.058 \times 10^{-7} + 1.308 \times 10^{-9}t + 2.125 \times 10^{-11}t^2 + 1.69 \times 10^{-12}t^3 + (8.446 \times 10^{-11} - 1.88 \times 10^{-12}t)P. \quad (11c)$$

The standard deviation is $\pm 0.40 \times 10^{-6} \text{deg}^{-1}$.
Check value:

$$\text{at } 35\text{‰}, 10^\circ\text{C}, 1000 \text{ bars} \\ \alpha = 306.0 \times 10^{-6} \text{deg}^{-1}$$

$$\beta = \beta_w + A S(\text{‰}) + B S(\text{‰})^{3/2} + C S(\text{‰})^2 \quad (12)$$

$$\beta_w = 5.08768 \times 10^{-5} - 3.76611 \times 10^{-7}t + 7.8394 \times 10^{-9}t^2 - 8.269 \times 10^{-11}t^3 + 4.597 \times 10^{-13}t^4 + (-1.4446 \times 10^{-8} + 2.1204 \times 10^{-10}t - 5.0987 \times 10^{-12}t^2 + 5.073 \times 10^{-14}t^3 - 3.00 \times 10^{-16}t^4)P + (2.5985 \times 10^{-12} - 2.6109 \times 10^{-14}t + 7.069 \times 10^{-16}t^2)P^2 - 3.068 \times 10^{-18}P^3 \quad (12a)$$

$$A = -1.3737 \times 10^{-7} + 3.5304 \times 10^{-9}t - 8.399 \times 10^{-11}t^2 + 9.822 \times 10^{-13}t^3 - 2.276 \times 10^{-15}t^4 + (5.8856 \times 10^{-11} - 1.3667 \times 10^{-12}t + 1.441 \times 10^{-14}t^2)P - 1.010 \times 10^{-14}P^2 \quad (12b)$$

$$B = 2.489 \times 10^{-10} - 1.465 \times 10^{-10}t + 5.516 \times 10^{-12}t^2 - 8.02 \times 10^{-14}t^3 + (1.13 \times 10^{-13} + 1.57 \times 10^{-14}t)P \quad (12c)$$

Table 3. The specific volumes of seawater at 35‰ salinity and various temperatures and pressures.

P (bars)	$v(\text{cm}^3 \text{ g}^{-1})$								
	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	0.972664	0.973069	0.973754	0.974684	0.975834	0.977186	0.978729	0.980452	0.982346
100	0.968228	0.968751	0.969529	0.970531	0.971735	0.973127	0.974696	0.976433	0.978331
200	0.963927	0.964561	0.965425	0.966495	0.967751	0.969181	0.970776	0.972528	0.974431
300	0.959757	0.960492	0.961438	0.962572	0.963877	0.965343	0.966963	0.968730	0.970640
400	0.955711	0.956541	0.957563	0.958757	0.960109	0.961610	0.963254	0.965036	0.966953
500	0.951784	0.952702	0.953795	0.955045	0.956441	0.957975	0.959643	0.961441	0.963365
600	0.947971	0.948971	0.950130	0.951434	0.952871	0.954437	0.956127	0.957939	0.959871
700	0.944267	0.945343	0.946565	0.947918	0.949394	0.950990	0.952702	0.954528	0.956467
800	0.940669	0.941815	0.943095	0.944494	0.946007	0.947631	0.949363	0.951203	0.953149
900	0.937171	0.938383	0.939716	0.941159	0.942707	0.944356	0.946108	0.947960	0.949914
1000	0.933770	0.935044	0.936427	0.937910	0.939489	0.941163	0.942933	0.944797	0.946756

Table 4. The expansibilities of seawater at 35‰ salinity and various temperatures and pressures.

P (bars)	$10^6 \alpha (\text{deg}^{-1})$								
	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	51.5	113.5	166.8	214.0	257.0	296.7	333.9	369.2	402.6
100	79.1	135.6	184.4	227.9	267.6	304.6	339.4	372.5	404.1
200	104.8	156.4	201.1	241.2	277.9	312.3	344.9	376.1	405.8
300	129.0	176.1	217.0	253.8	287.9	319.9	350.4	379.7	407.9
400	151.6	194.5	232.0	265.9	297.4	327.3	355.9	383.4	410.1
500	172.7	211.9	246.2	277.4	306.6	334.4	361.2	387.2	412.4
600	192.6	228.3	259.6	288.3	315.3	341.2	366.4	390.9	414.8
700	211.1	243.7	272.3	298.7	323.7	347.8	371.4	394.5	417.2
800	228.5	258.2	284.3	308.5	331.7	354.2	376.3	398.1	419.6
900	244.8	271.8	295.6	317.8	339.2	360.2	380.9	401.5	421.9
1000	260.1	284.6	306.3	326.6	346.3	365.8	385.3	404.7	424.0

Table 5. The isothermal compressibilities of seawater at 35‰ salinity and various temperatures and pressures.

P (bars)	$10^6 \beta \text{ (bar}^{-1}\text{)}$								
	0°C	5°C	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	46.33	45.05	44.03	43.23	42.60	42.14	41.80	41.59	41.47
100	45.11	43.91	42.94	42.18	41.58	41.12	40.79	40.57	40.44
200	43.93	42.80	41.89	41.17	40.59	40.15	39.82	39.59	39.46
300	42.80	41.74	40.88	40.19	39.64	39.21	38.89	38.66	38.51
400	41.70	40.71	39.90	39.24	38.72	38.30	37.99	37.76	37.61
500	40.65	39.72	38.96	38.33	37.83	37.43	37.12	36.90	36.75
600	39.64	38.76	38.04	37.45	36.97	36.59	36.29	36.07	35.92
700	38.66	37.84	37.16	36.60	36.14	35.78	35.49	35.28	35.13
800	37.71	36.94	36.30	35.77	35.34	34.99	34.72	34.52	34.37
900	36.80	36.08	35.47	34.97	34.57	34.24	33.98	33.78	33.64
1000	35.92	35.24	34.67	34.20	33.82	33.51	33.26	33.08	32.95

$$C = 1.63 \times 10^{-10}. \quad (12d)$$

The standard deviation is $\pm 0.0045 \times 10^{-6} \text{ bar}^{-1}$.
Check value:

$$\begin{aligned} &\text{at } 35\text{‰}, 10^\circ\text{C}, 1000 \text{ bars} \\ &\beta = 34.677 \times 10^{-6} \text{ bar}^{-1}. \end{aligned}$$

COMPARISONS

The comparisons of the relative specific volumes ($V^P - V^0$) for 35‰ salinity seawater calculated from equation (8) with data of various workers are shown in Fig. 6. Over most of the oceanographic range (denoted by the broken line) our specific volume agree with the work of WANG and MILLERO (1973, based on the sound speed data of WILSON, 1960) to within ± 5 ppm; with the work of FINE, WANG and MILLERO (1974, based on the work of DEL GROSSO and MADER, 1972) to within ± 20 ppm; with the work of Bradshaw and Schleicher (the high pressure specific volumes were obtained by integration, using their recent 10°C compression data and 1970 expansion measurements) to within ± 5 ppm; with the work

of EMMET and MILLERO (1974) to within ± 30 ppm; with the work of EKMAN (1908) to within ± 60 ppm and with the work of WILSON and BRADLEY (1968) to within ± 60 ppm. Similar deviations occur at 30 and 40‰ salinity.

These comparisons indicate that the direct measurements made in this study agree with the sound-derived equation of state of Wang and Millero to within ± 5 ppm over the oceanographic range of salinity, temperature and pressure. The apparent disagreement between the direct measurements and sound-derived data at higher temperatures (above 30°C) and pressures are due to the limits of the Wang and Millero equation of state (to 600 bars at 20°C and to 400 bars at 30°C). The comparisons with the sound-derived equation of state obtained from the measurements of Del Grosso and Mader indicate that Wilson's sound data are more reliable at high pressures. Although this conjecture could be attributed to the fact that our measurements are made relative to the pure water sound data of Wilson, the results of Bradshaw and Schleicher (which are in excellent agreement with our results) support this finding.

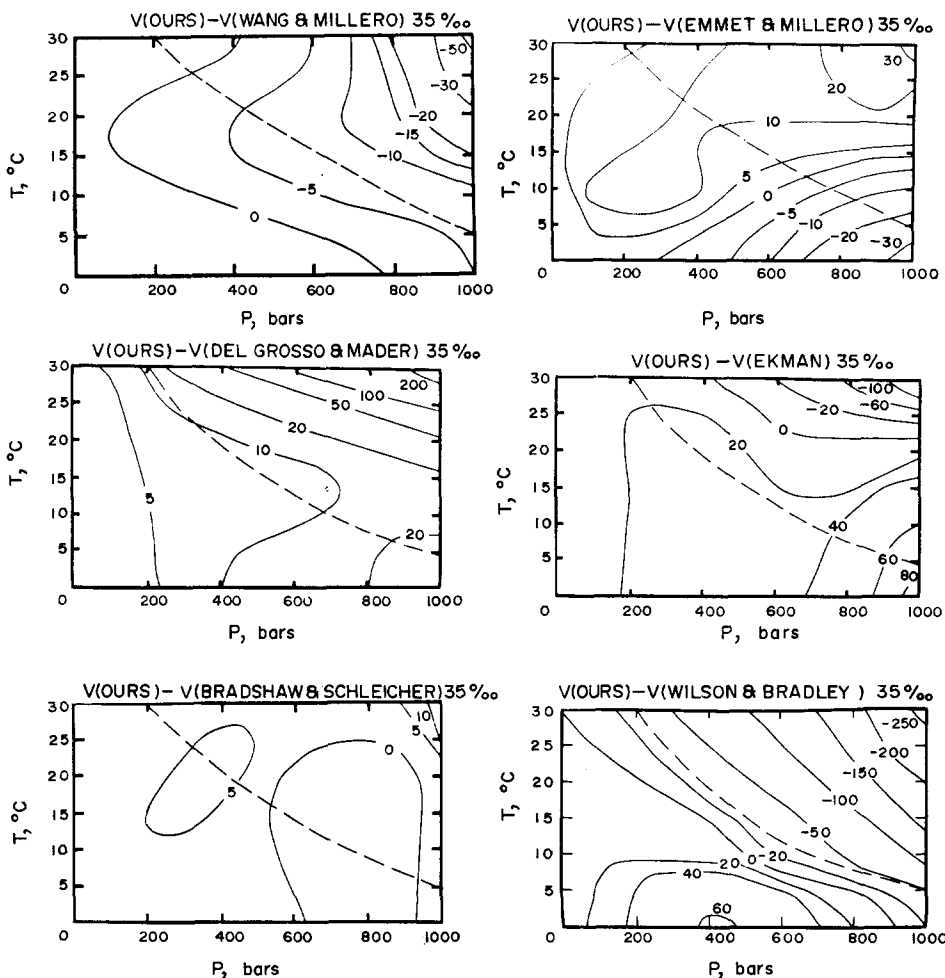


Fig. 6. The contour diagrams of the differences in the relative specific volumes ($V^P - V^0$ in ppm) obtained from our results and the data of various workers for 35‰ salinity seawater from 0 to 30°C and from 0 to 1000 bars. The broken line indicates the boundary of the oceanographic range.

It, thus, appears that although Wilson's sound speeds for water (FINE and MILLERO, 1973), deuterium oxide (FINE and MILLERO, 1975) and seawater (MILLERO and KUBINSKI, 1975) at 1 atm are in error, his high pressure measurements are reliable to $\pm 0.3 \text{ m s}^{-1}$ (BARLOW and YAZGEN, 1969). We are presently making high pressure sound speed measurements on these systems in an attempt to further elucidate these differences.

Since all of the recent high pressure work on the P - V - T properties of seawater indicate that the earlier measurements of Ekman are in error

in specific volume by as much as 60 ppm, we feel that the equation of state based on these measurements should be abandoned.

Although the sound-derived equation of state of WANG and MILLERO (1973) is confined to the salinity range of 30 to 40‰, our directly measured results at low salinities, shown in Fig. 7, are in good agreement with the data derived from Wang and Millero's equation of state. WILSON and BRADLEY (1968) were the only workers to make measurements at low salinities and their specific volumes differ by as much as 80 ppm in the low

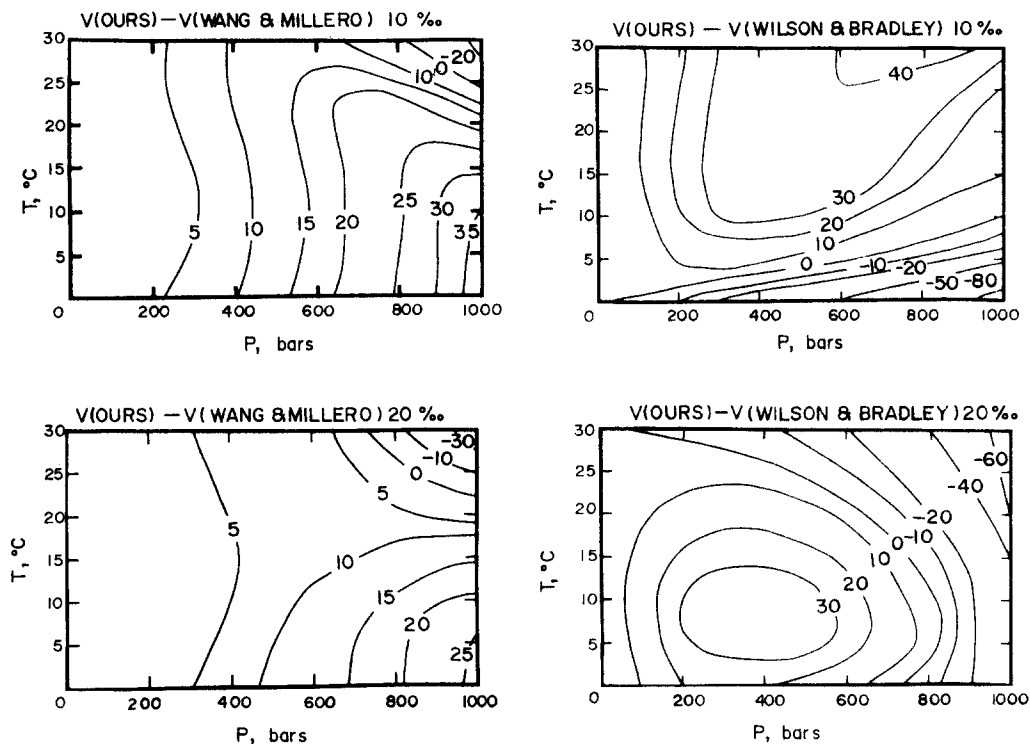


Fig. 7. The contour diagrams of the differences in the relative specific volumes ($V^P - V^0$ in ppm) obtained from our results and the data of WANG and MILLERO (1973) and WILSON and BRADLEY (1968) for 10 and 20‰ salinity seawater from 0 to 30°C and from 0 to 1000 bars.

temperature and high pressure range (Fig. 7).

The comparisons of the relative thermal expansibilities ($\alpha^P - \alpha^0$) at 35‰ salinity calculated from equation (9) with data of various workers are shown in Fig. 8. Over most of the oceanographic range, our results agree with the work of WANG and MILLERO (1973) to $\pm 2 \times 10^{-6} \text{deg}^{-1}$; with the work of FINE, WANG and MILLERO (1974) to $\pm 1 \times 10^{-6} \text{deg}^{-1}$; with the work of BRADSHAW and SCHLEICHER (1970) to $\pm 1 \times 10^{-6} \text{deg}^{-1}$ and with the work of EMMET and MILLERO (1974) to $\pm 2 \times 10^{-6} \text{deg}^{-1}$.

Figure 9 shows the comparisons of the thermal expansibility with the sound-derived data of Wang and Millero at lower salinities. The agreement is within $\pm 1 \times 10^{-6} \text{deg}^{-1}$ in the low temperature range and is within $\pm 5 \times 10^{-6} \text{deg}^{-1}$ over most of the temperature and pressure range.

The comparisons of the isothermal compressibilities at 35‰ salinity calculated from equation

(10) with those obtained by other workers are shown in Fig. 10. Our results are higher than those of WANG and MILLERO (1973) over most of the oceanographic range (the agreement is within $0.02 \times 10^{-6} \text{bar}^{-1}$) but lower than those of FINE, WANG and MILLERO (1974) ($-0.04 \times 10^{-6} \text{bar}^{-1}$). The reason that the results of this study are higher than those of Wang and Millero (WILSON's 1960 sound speeds) but lower than those of Fine, Wang and Millero (DEL GROSSO and MADER's 1972 sound speeds) is due to the differences in the sets of sound speed data. The large deviations shown in the high temperature and high pressure range are due to the limited range of the sound-derived equations. The compressibilities of BRADSHAW and SCHLEICHER (1974) and those of EMMET and MILLERO (1974) agree with ours to $\pm 0.05 \times 10^{-6} \text{bar}^{-1}$ over most of the T - P space. At low salinities, our compressibilities are also in good agreement with the sound-derived data of

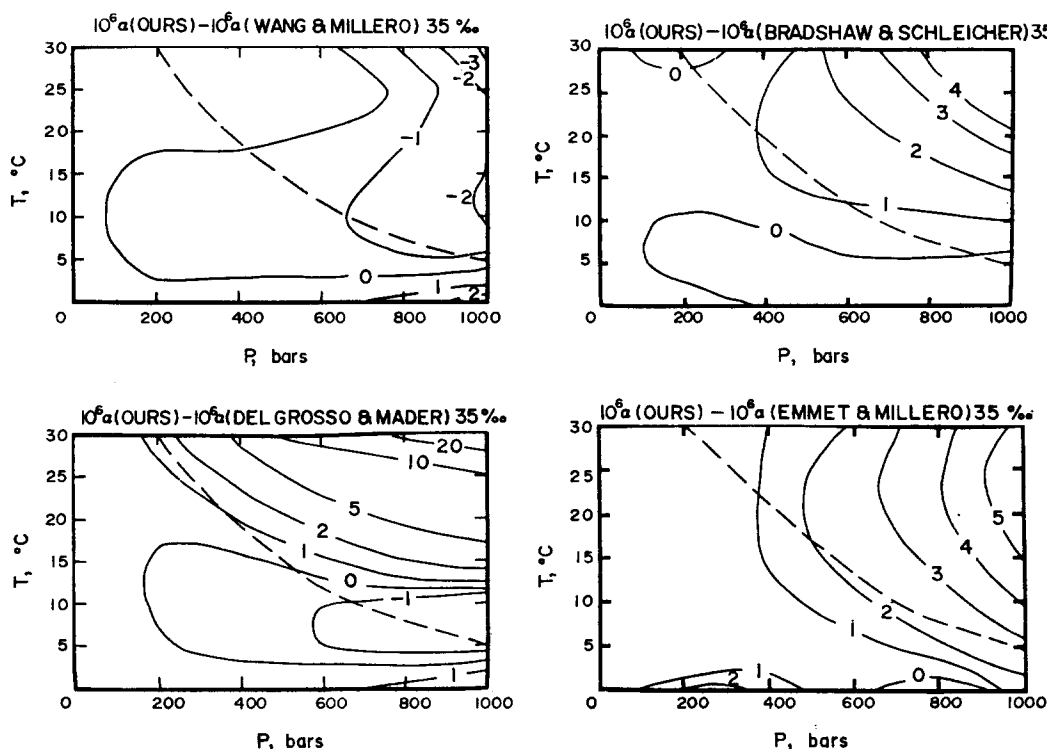


Fig. 8. The contour diagrams of the differences in the relative thermal expansibilities ($\alpha^P - \alpha^0$ in ppm per degree) obtained from our results and the data of various workers for 35‰ salinity seawater from 0 to 30°C and from 0 to 1000 bars. The broken line indicates the boundary of the oceanographic range.

WANG and MILLERO (1973) (Fig. 11). The agreement is within $\pm 0.06 \times 10^{-6} \text{ bar}^{-1}$ over the range of 0 to 20°C and 0 to 1000 bars.

Recently, DUEDALL and PAULOWICH (1973) constructed a bellows-type differential compressimeter to measure directly, to 900 bars, the differences between the isothermal compressibilities of 35‰ salinity seawater and distilled deionized water at 10 and 15°C to a precision which ranged from $\pm 0.03 \times 10^{-6}$ to $\pm 0.07 \times 10^{-6} \text{ bar}^{-1}$ over the pressure range of 100 to 900 bars. In Table 6 we have compared our results with those obtained by DUEDALL and PAULOWICH (1973) and by other workers. Our $\beta_W - \beta_{SW}$ values agree with the results of DUEDALL and PAULOWICH (1973) to an average deviation of $\pm 0.08 \times 10^{-6} \text{ bar}^{-1}$ at both temperatures. The agreement would be better (to an average deviation of $\pm 0.05 \times 10^{-6} \text{ bar}^{-1}$ at both temperatures) if we normalized their data to agree with ours at

1 atm. The comparisons with other workers agree to within an average deviation of $\pm 0.04 \times 10^{-6} \text{ bar}^{-1}$. From Table 6, we can see that EMMET and MILLERO's (1974) 1-atm compressibilities are probably in error (due to an improper extrapolation).

CONCLUSION

A comprehensive and precise study has been made on the high pressure P - V - T properties of seawater using a high pressure magnetic float densimeter. The relative specific volumes ($V^P - V^0$) determined from these direct measurements are more precise over the entire S - T - P space (with a standard deviation of 7 ppm over the range of 5 to 40‰, 0 to 40°C and 0 to 1000 bars), and in particular over the oceanographic range (5 ppm standard deviation) than any previous direct measurements. In addition, since this is the only precise study to date that covers the entire

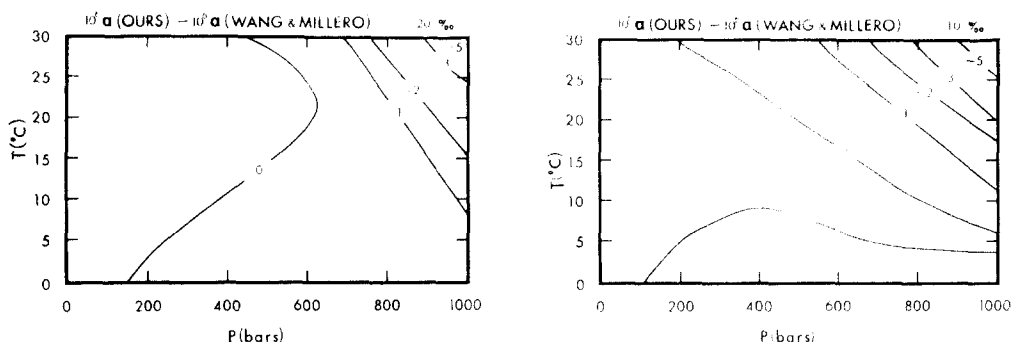


Fig. 9. The contour diagrams of the differences in the relative thermal expansibilities ($\alpha^P - \alpha^0$ in ppm per degree) obtained from our results and the data of WANG and MILLERO (1973) for 10 and 20‰ salinity seawater from 0 to 30°C and from 0 to 1000 bars.

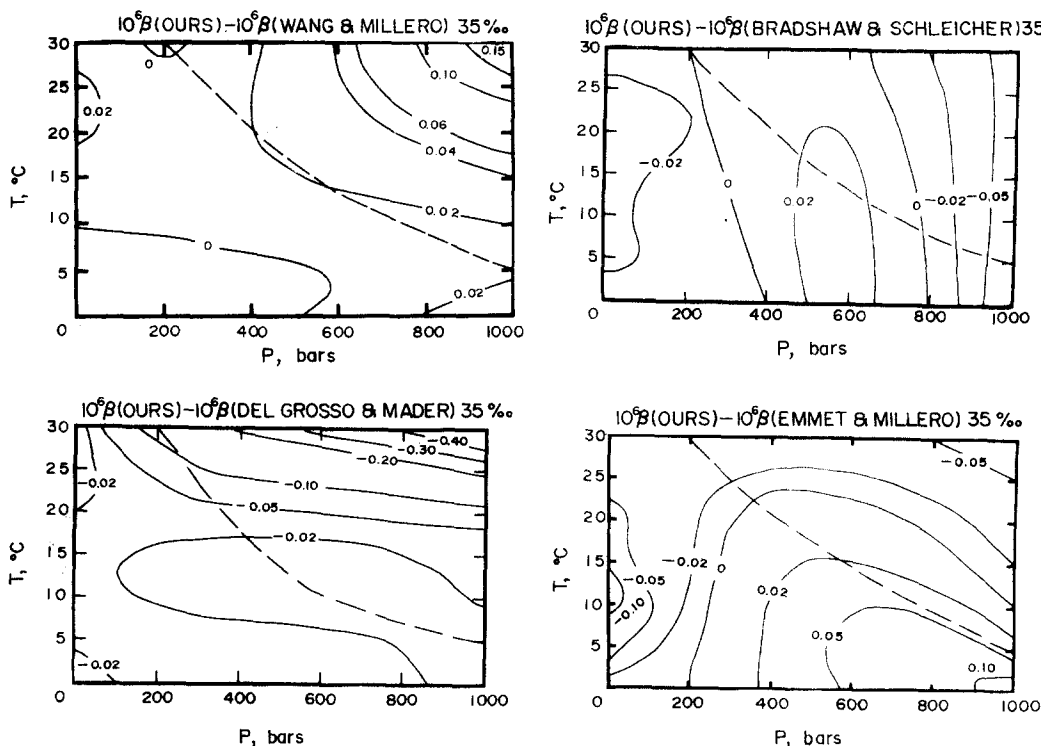


Fig. 10. The contour diagrams of the differences in the isothermal compressibilities (in ppm per bar) obtained from our results and the data of various workers for 35‰ salinity seawater from 0 to 30°C and from 0 to 1000 bars. The broken line indicates the boundary of the oceanographic range.

S - T - P space, it is important for theoretical thermodynamic calculations.

The direct experimental measurements confirm the validity of the seawater equation of state of WANG and MILLERO (1973) derived from the velocity of sound measurements of WILSON (1960). Their equation agrees with the experimental

measurements of this study in specific volume to within ± 5 ppm, in thermal expansibility to within $\pm 2 \times 10^{-6} \text{ deg}^{-1}$, and in isothermal compressibility to within $\pm 0.02 \times 10^{-6} \text{ bar}^{-1}$ over the oceanographic range. The P - V - T properties derived from the present work are in good agreement with the work based on the 1960

Table 6. Comparison of our $(\beta_w - \beta_{sw})$ and those obtained by other workers. The unit is 10^{-6} bar^{-1} .

P (bars)	10°C					15°C				
	Δ^a	Δ^b	Δ^c	Δ^d	Δ^e	Δ^a	Δ^b	Δ^c	Δ^d	Δ^e
0	-0.01	-0.03	0.02	0.11	0.12	-0.01	-0.03	0.03	0.09	-0.03
100	0.00	-0.03	0.02	0.06	0.08	-0.01	-0.02	0.02	0.05	-0.06
200	0.00	-0.02	0.01	0.02	0.06	-0.01	-0.01	0.01	0.02	-0.09
300	0.00	-0.01	0.00	-0.01	0.04	-0.01	-0.01	0.00	0.00	-0.10
400	0.00	-0.01	-0.01	-0.03	0.04	-0.01	-0.01	-0.01	-0.01	-0.10
500	-0.01	-0.01	-0.02	-0.05	0.04	-0.01	-0.01	-0.02	-0.02	-0.10
600	-0.01	-0.01	-0.02	-0.05	0.06	-0.02	-0.01	-0.02	-0.03	-0.09
700	-0.02	-0.01	-0.02	-0.05	0.07	-0.03	-0.01	-0.02	-0.02	-0.07
800	-0.01	-0.01	0.00	-0.04	0.10	-0.03	-0.02	0.00	-0.01	-0.02
900	-0.01	-0.02	0.02	-0.02	0.14	-0.03	-0.03	0.03	0.01	-0.02
1000	-0.01	-0.02	0.07	0.01	----	-0.04	-0.04	0.07	0.02	----
Ave. dev.	± 0.01	± 0.02	± 0.01	± 0.04	± 0.08	± 0.02	± 0.02	± 0.02	± 0.03	± 0.08

(a) Our results—Wang and Millero (using Wilson's sound speeds).

(b) Our results—Fine, Wang and Millero (using Del Grosso and Mader's sound speeds).

(c) Our results—Bradshaw and Schleicher.

(d) Our results—Emmet and Millero.

(e) Our results—Duedall and Paulowich.

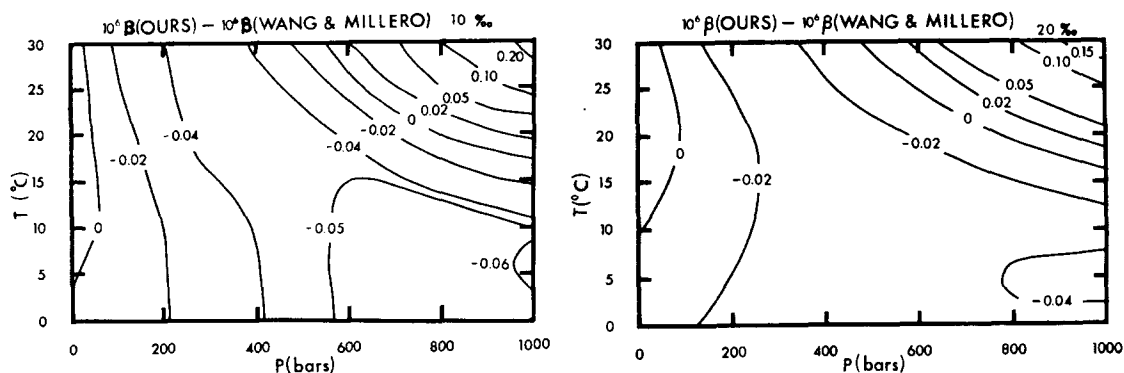


Fig. 11. The contour diagrams of the differences in the isothermal compressibilities (in ppm per bar) obtained from our results and the data of WANG and MILLERO (1973) for 10 and 20‰ salinity seawater from 0 to 30°C and from 0 to 1000 bars.

velocity of sound measurements of Wilson (WANG and MILLERO, 1973), whereas the P - V - T properties derived from the 1972 velocity of sound measurements of Del Grosso and Mader (FINE,

WANG and MILLERO, 1974) are not in as good agreement over the wider S - T - P space. These comparisons indicate that the sound speed measurements of Wilson at high pressures are

more reliable than the measurements of Del Grosso and Mader.

The independent direct measurements of BRADSHAW and SCHLEICHER (1973), DUEDALL and PAULOWICH (1973) and EMMET and MILLERO (1974) also agree with, and substantiate, this investigation. EKMAN (1908) and WILSON and BRADLEY's (1968) measurements show large deviations from this investigation.

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