



Thermodynamic properties of standard seawater: extensions to high temperatures and pressures

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Received: 26 February 2009 – Published in Ocean Sci. Discuss.: 17 April 2009

Revised: 17 June 2009 – Accepted: 24 June 2009 – Published: 7 July 2009

Abstract. Measurements of (p , ρ , T) properties of standard seawater with practical salinity $S \approx 35$, temperature $T = (273.14$ to $468.06)$ K and pressures, p , up to 140 MPa are reported with the reproducibility of the density measurements observed to be in the average percent deviation range $\Delta\rho/\rho = \pm(0.01$ to $0.03)\%$. The measurements are made with a newly constructed vibration-tube densimeter which is calibrated using double-distilled water, methanol and aqueous NaCl solutions. Based on these and previous measurements, an empirical expression for the density of standard seawater has been developed as a function of pressure and temperature. This equation is used to calculate other volumetric properties including isothermal compressibility, isobaric thermal expansibility, differences in isobaric and isochoric heat capacities, the thermal pressure coefficient, internal pressure and the secant bulk modulus. The results can be used to extend the present equation of state of seawater to higher temperatures for pressure up to 140 MPa.

1 Introduction

The majority of water on earth is seawater, a solution of salts of nearly constant composition (Millero et al., 2008), dis-

solved in water. The variable concentration of salts is represented by the mass fraction of dissolved salt in solution, referred to as absolute salinity. For scientific investigations and design of many natural and technical processes which have to do with seawater, it is of great importance to have a reliable base of thermodynamic data. The most recent standard formulation (IAPWS, 2008) for seawater is restricted in its range of applicability due to a lack of density measurements at higher temperatures and elevated pressures (IAPWS Certified Research Need #16, 2007). The present work therefore fills an essential data gap. In particular, it provides important information for evaporating tropical estuaries and technical applications such as those associated with desalination plants.

In 2006, as a successor of the Joint Panel on Oceanographic Tables and Standards (JPOTS), the Working Group 127 (WG127) was established by the International Association for the Physical Sciences of the Ocean (IAPSO) and the Scientific Committee on Oceanic Research (SCOR). Its main objective is an updated evaluation of the standards for seawater thermodynamics and, if necessary, the recommendation of improved formulations. Among the reasons for this revision is the need for consistency between seawater properties and the more accurate recent international standards for temperature (ITS-90) and for properties of pure water (IAPWS-95) (Wagner and Prüß, 2002). As a result, the International Association for the Properties of Water and Steam in cooperation with WG127 endorsed a new joint seawater



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formulation on the occasion of its international conference in September 2008 in Berlin (IAPWS, 2008). This formulation is also expected to be adopted internationally for oceanography (McDougall et al., 2009).

The present international standard for the representation of the properties of seawater is the 1980 International Equation of State of Seawater (EOS-80), released by JPOTS and published by Millero et al. (1980). It is based on the temperature scale IPTS-68 and on the Practical Salinity Scale 1978, PSS-78 (Lewis and Perkin, 1981). It is noteworthy that, since the evaluation of EOS-80, there have been only few new experimental (p , ρ , T) measurements made available (Feistel, 2003, 2008) and until 2009 no more recent standard EOS has been officially adopted for the calculation of the thermodynamic properties of standard seawater.

The purpose of the present study is the construction of a comprehensive and accurate thermodynamic equation of state for seawater over a wider range of temperature and pressure (and eventually salinity) than was possible based on earlier work. This will be useful for modeling and industrial process applications involving seawater at high temperatures and pressures.

In this research work, we describe the experimental results for standard seawater, $S \approx 35$, corresponding to an absolute salinity $S_A \approx 35.16504 \text{ g/kg}$ on the new Reference-Composition Salinity Scale (Millero et al., 2008) which extends the current Practical Salinity Scale PSS-78 to temperatures higher than 40°C. This work is the first step in expanding the present equation of state of seawater to higher temperature and pressure values. Work on salinities different from $S=35$ is in preparation.

As a first step, the most important literature works have been reviewed.

Tait (1888) was the first scientist, who studied the volumetric properties of seawater. From the results of his investigations, the “Tait equation” was developed for describing the density (or specific volume) of liquids at high pressures and temperatures. His measured compressibility results were at temperatures $T=(273.15 \text{ to } 288.15) \text{ K}$ and pressures $p=(0.101 \text{ to } 50) \text{ MPa}$.

Ekman (1908) measured the compressions of seawater for $T=(273.15 \text{ to } 293.15) \text{ K}$, $p=(0.101 \text{ to } 60) \text{ MPa}$, at salinities $S=(31.13 \text{ and } 38.53)$. Higashi et al. (1931) measured the specific gravity and the vapor pressure of concentrated seawater at concentrations varying from that of ordinary seawater up to values close to the saturation point of NaCl for temperatures in the range $T=(273.15 \text{ to } 448.15) \text{ K}$.

Newton and Kennedy (1965) determined the (p , v , T) properties of seawater for $T=(273.15 \text{ to } 298.15) \text{ K}$, $p=(0.101 \text{ to } 130) \text{ MPa}$ and $S=(0, 30.52, 34.99 \text{ and } 41.03)$. The apparatus used to make their measurements consisted of a piston-and-cylinder volumeter for measuring volume changes, supplemented by a pycnometer to determine the specific volumes at $p=0.101 \text{ MPa}$. A sample of standard seawater with salinity $S=34.99\%$ (so-called Copenhagen seawater) was re-

ported as 35.01‰ on the Point Loma bridge – giving an apparent accuracy of 2 parts in 10^5 . The average uncertainty of specific volume measurements was estimated to be $\pm 7 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$.

Wilson and Bradley (1966, 1968) measured the specific volumes of seawater for $T=(274.38 \text{ to } 313.54) \text{ K}$, $p=(0.101 \text{ to } 96.526) \text{ MPa}$ and for a range of S between 0 and 40.37. The seawater samples used in this study were supplied by the Navy Oceanographic Office; they were natural seawater taken from the Bermuda-Key West Region of the Atlantic Ocean. Biological material was removed prior to the salinity measurements. The sample salinity was varied by adding distilled water, or by evaporation, to obtain representative values near $S=10, 20, 30, 35, \text{ and } 40$. The salinity was determined before and after each set of measurements. The uncertainties of these measurements of specific volume were estimated as $\pm 1 \times 10^{-5} \text{ cm}^3 \text{ g}^{-1}$.

Bradshaw and Schleicher (1970) measured the thermal expansion of seawater for $T=(271.15 \text{ to } 303.15) \text{ K}$, $p=(0.8 \text{ to } 100.1) \text{ MPa}$ and $S=(30.5, 35 \text{ and } 39.5)$. A direct measurement technique was used in which the change of volume of a water sample in a dilatometer was measured with the sample maintained at constant pressure and subjected to a temperature change. Temperature derivatives of specific volume were derived; it is estimated that the data are accurate to within $\pm 3 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1} \text{ deg}^{-1}$.

Duedall and Paulowich (1973) reported isothermal compressibility values of seawater with a precision of $\pm 0.07 \times 10^{-6} \text{ bar}^{-1}$. The measurements were performed at $T=(283.15 \text{ and } 288.15) \text{ K}$, $p=(0.101 \text{ to } 90.12) \text{ MPa}$ and $S=35$.

Emmet and Millero (1974) measured the specific volume of $S=35$ salinity seawater at $T=(271.15 \text{ to } 313.15) \text{ K}$, $p=(0.101 \text{ to } 99.533) \text{ MPa}$. The specific volume of standard seawater with 19.3755‰ chlorinity was measured with a high-pressure magnetic float densimeter. The specific volumes were fitted to an equation having a standard deviation of $\pm 11 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

Bradshaw and Schleicher (1976) measured the compressibility of distilled water and seawater for $T=283.15 \text{ K}$, $p=(0.8 \text{ to } 100) \text{ MPa}$ and $S=(30.705, 34.891 \text{ and } 38.884)$ using the well known dilatometer method. Diluted and evaporated samples derived from Copenhagen Standard Seawater with $S=34.912$ were used for these experiments. The average uncertainty of the reported specific volume data has been estimated as $\pm 15 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

Chen and Millero (1976) reported the specific volume of seawater for $T=(273.15 \text{ to } 313.15) \text{ K}$, $p=(0.101 \text{ to } 100) \text{ MPa}$ and $S=(5 \text{ to } 40)$. The specific volume of a standard seawater sample (P-57, 6/8, 1972, Cl‰=19.3755) was measured with a high-pressure magnetic float densimeter. The uncertainty of the specific volume measurements was $\pm 4 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$.

Caldwell (1978) measured the temperature-pressure-salinity points of maximum density for $T=(267.07 \text{ to }$

276.99) K, pressures $p=(0.101$ to 38.09) MPa and $S=(0$ to 29.84). In this paper a method is described for finding maximum density points by determining points where adiabatic expansion or compression can affect no change in the temperature of the fluid. The zero-crossing of the adiabatic lapse rate, which estimates the maximum density point, was measured and the dependence on pressure, salinity and temperature was determined. A total of 67 measurements were used, 36 with pure water and the rest at $S=10.45$, 10.46 , 20.10 , 25.16 , and 29.84 , from which the maximum-density-point estimates were produced. The precision of the measurements was thus about 0.01°C in temperature and about 0.2 bar in pressure.

Based on the analysis of all experimental results on (p, v, T) behavior, isothermal compressibility and thermal expansion available in 1979, Millero et al. (1980) determined the equation of state referred to as EOS-80.

After the publication and international agreement on EOS-80, the highly accurate IAPWS 1995 Formulation for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use, which is in the form of a fundamental equation for the Helmholtz free energy, was developed and published by Wagner and Prüß (2002). A Gibbs function for seawater covering the standard oceanic range of salinities, temperatures and pressures was developed by Feistel and Hagen (1995) and by Feistel (1993, 2003, 2008). The more recent versions (Feistel, 2003, 2008) are based on the IAPWS-95 formulation for pure water in combination with extended sets of different theoretical and experimental data for standard seawater relative to pure water, and are expressed in terms of the ITS-90 temperature scale. This work extends the EOS-80 formulation to include equations for the entropy, enthalpy and chemical potential, and corrects a systematic error in high-pressure sound speeds that is present in EOS-80.

The results of the above investigations have demonstrated the important roles of pressure, temperature and salinity in determining the thermophysical properties of seawater, which are required for a wide range of state parameters. The temperature interval of EOS-80 covers $T=(271.15$ to 313.15) K but is still not large enough for some oceanographic and engineering applications. It is therefore important to improve EOS-80, using the new density data for pure water (IAPWS-95) (Wagner and Prüß, 2002) and (p, ρ, T) measurements of seawater with various salinities. These should cover the broadest possible range of pressure, temperature and salinity. The present investigation of the (p, ρ, T) properties of standard seawater extends previously measured results to the range $T=(273.14$ to 468.06) K and $p=(0.101$ to 140) MPa. An additional reason for this ongoing revision process is the requirements for consistent representations of seawater properties in terms of the more accurate recent international ITS-90 standard for temperature.

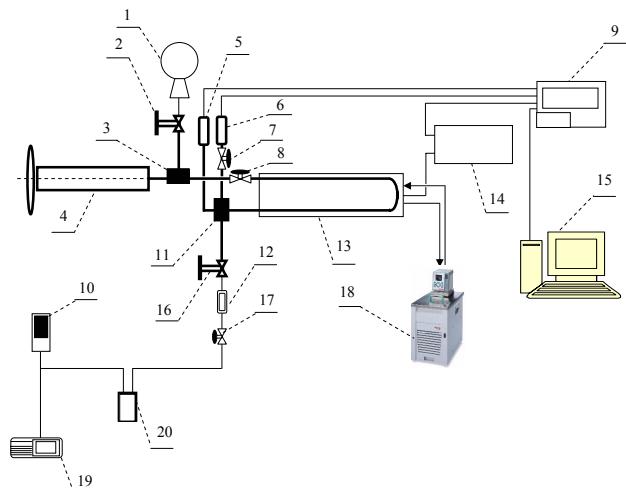


Fig. 1. A new modernized high pressure – high temperature vibrating tube densimeter DMA HPM: 1 – flask for the probe; 2, 7, 16, 17 – valves; 3, 11 – fitting; 4 – pressure intensifier; 5 – pressure sensor HP-1; 6 – pressure sensor P-10; 8 – valve for the closing of system during the experiments; 9 – evaluation unit mPDS2000V3 for the temperature and period control; 10 – vacuum indicator; 12 – visual window; 13 – vibration tube; 14 – interface module; 15 – PC; 18 – thermostat F32-ME; 19 – vacuum pump; 20 – thermos for cooling.

2 Experimental

The (p, ρ, T) measurements were carried out using a recently developed high pressure – high temperature vibrating tube densimeter DMA HPM (Anton-Paar, Austria). A sketch of the instrument is shown in Fig. 1. Density measurements made with a vibrating tube are based on the dependence of the period of oscillation of a unilaterally fixed Hastelloy C-276 U-tube on its mass. The behavior of the vibrating tube can be described by a simple mathematical-physical mass-spring-damper model (Kratky et al., 1969), where the mass of the vibration tube m is equal to the sum of the mass of the tube in vacuum plus the mass of liquid contained in it. The frequency of oscillation is given in s^{-1} by

$$f(T, p) = \frac{\omega_0}{2\pi} = \frac{1}{2\pi} \sqrt{\frac{k}{m_0 + \rho(T, p)V(T, p)}}, \quad (1)$$

where ω is the angular frequency in rad s^{-1} ; k is the force constant (or spring constant) of the tube material in N m^{-1} , which depends on the size and shape of the tube and is proportional to the Young's modulus of the tube material, m_0 is the mass of the evacuated vibration tube in kg; $V(T, p)$ is the volume of the vibration tube in m^3 ; $\rho(T, p)$ is the density of the liquid inside of the vibration tube in kg m^{-3} . At given force constant k the sensitivity increases with increasing ratio of the mass of fluid to that of the tube, $(\rho V/m_0)$. For a glass tube, the sensitivity is large, while for tubes made of stainless steel or alloys the sensitivity is lower.

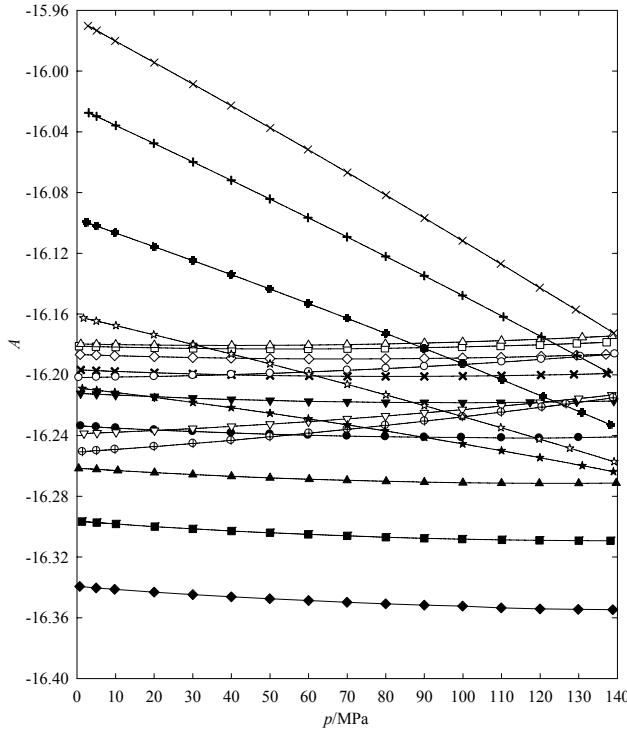


Fig. 2. Plot of calibration coefficient A of Eq. (4) of standard seawater vs. pressure p : \blacklozenge , 273.17 K; \blacksquare , 278.15 K; \blacktriangle , 283.15 K; \bullet , 288.16 K; \blacktriangledown , 293.15 K; \times , 298.18 K; \lozenge , 303.18 K; \square , 308.15 K; \triangle , 313.15 K; \circ , 333.15 K; \triangledown , 353.16 K; \oplus , 373.15 K; \star , 393.17 K; \star , 413.15 K; \blacklozenge , 433.18 K; $+$, 453.17 K; x , 468.03 K.

Measurement of the mass of the liquid inside of the vibration tube is difficult but it can be achieved by measuring the period of vibration of the tube. From Eq. (1):

$$\tau(T, p) = 2\pi \sqrt{\frac{m_0 + \rho(T, p)V(T, p)}{k}}. \quad (2)$$

The period depends on the elasticity and length of the tube. From Eq. (2) it is seen that the period of vibration of the vibration tube can be directly related to the density of the fluid:

$$\rho(T, p) = A_1(T, p) - B_1(T, p)\tau^2(T, p), \quad (3)$$

where $A_1(T, p) = -\frac{m_0}{V(T, p)}$ and $B_1(T, p) = -\frac{k}{4\pi^2 V(T, p)}$.

The parameters $A_1(T, p)$ and $B_1(T, p)$ do not depend on the properties of the fluid to be measured. The instrument may thus be calibrated by measuring the period of oscillation for at least two substances of known density as calibration samples. In this work, water (twice-distilled) (Wagner and Prüß, 2002), methanol (Osada et al., 1999; Yokoyama and Uematsu, 2003; de Reuck and Craven, 1993) and NaCl (aq) (Hilbert, 1979; Archer, 1992) of various molalities were used as reference substances to calibrate the vibrating tube densitometer.

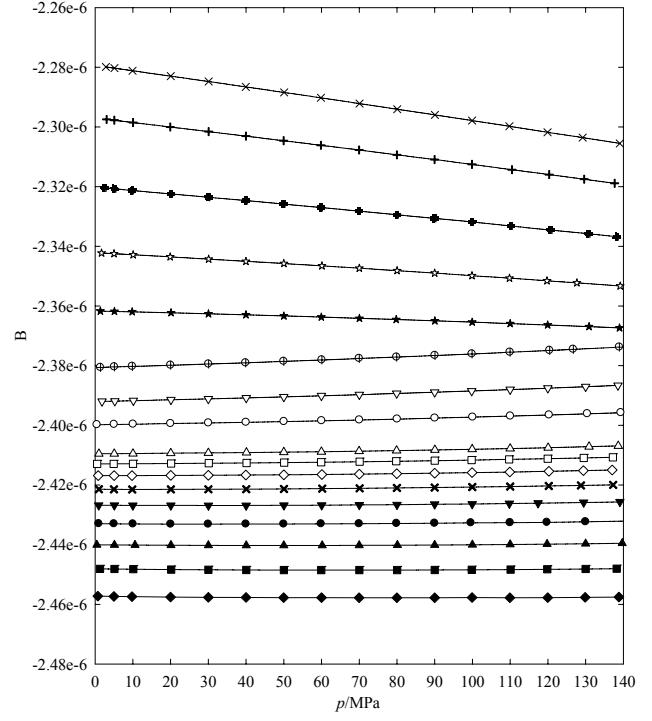


Fig. 3. Plot of calibration coefficient B of Eq. (5) of standard seawater vs. pressure p : \blacklozenge , 273.17 K; \blacksquare , 278.15 K; \blacktriangle , 283.15 K; \bullet , 288.16 K; \blacktriangledown , 293.15 K; \times , 298.18 K; \lozenge , 303.18 K; \square , 308.15 K; \triangle , 313.15 K; \circ , 333.15 K; \triangledown , 353.16 K; \oplus , 373.15 K; \star , 393.17 K; \star , 413.15 K; \blacklozenge , 433.18 K; $+$, 453.17 K; x , 468.03 K.

Unfortunately, the parameters $A_1(T, p)$ and $B_1(T, p)$ are strongly temperature and pressure dependent. Therefore, the parameters must be determined for each temperature and pressure separately and the classical Eq. (3) must be extended by additional temperature and pressure-dependent terms. For measurements at $T=(273.14$ to 468.06) K and pressures up to $p=140$ MPa the following calibration equation containing 14 adjustable parameters has been employed (Ihmels and Gmehling, 2001):

$$A_1(T, p) = \sum_{i=0}^3 d_i(T/K)^i + \sum_{j=1}^2 e_j(p/\text{MPa})^j + f(T/K)(p/\text{MPa}), \quad (4)$$

$$B_1(T, p) = \sum_{i=0}^3 h_i(T/K)^i + \sum_{j=1}^2 l_j(p/\text{MPa})^j + n(T/K)(p/\text{MPa}), \quad (5)$$

where d_0 , d_1 , d_2 , d_3 , e_1 , e_2 , f , h_0 , h_1 , h_2 , h_3 , l_1 , l_2 and n are parameters to be determined. The calculated values of $A_1(T, p)$ and $B_1(T, p)$ are shown in Figs. 2 and 3. The fitted calibration Eqs. (4) and (5) represent the results for pure water from the IAPWS-95 formulation, and NaCl (aq) from Hilbert (1979) and Archer (1992) with $\Delta\rho/\rho=\pm 0.02\%$ average deviation. The (p, ρ, T) measurements of pure water were carried out using this

calibration method and $\Delta\rho/\rho=\pm 0.01\%$ average deviation was obtained from the IAPWS-95 formulation of water. The results of the pure-water measurements obtained with the calibration (4), (5) are available from the digital supplement of this paper (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>) for alternative adjustments if this is required for certain purposes. The average percent deviation is calculated as:

$$APD, \% = \frac{\sum \left| \frac{100(\rho_{exp} - \rho_{fit})}{\rho_{exp}} \right|}{n}, \quad (6)$$

where ρ_{exp} is the experimental density; ρ_{fit} is the density obtained from the IAPWS-95 formulation and n is the number of experimental points. This type of uncertainty measure is used extensively in the discussion of our results in the next section.

The oscillation period, τ , of the vibration tube was determined with a digital counter using the vibration tube installation with the temperature control implemented inside the DMA HPM control system. This consists of a measuring cell (13 on Fig. 1) and a modified evaluation unit mPDS2000V3 for the temperature and frequency control (9) connected to a PC (15) via an interface module (14). The interface module measures both the period of oscillation and the temperature of the sample. The temperature in the measuring cell was monitored using an (ITS-90) Pt100 thermometer (AOIP PN 5207) with an experimental error of $\pm 15\text{ mK}$ and it was controlled using a thermostat (18) F32-ME (Julabo, Germany) with an uncertainty of $\pm 10\text{ mK}$. Pressure was adjusted with a pressure intensifier (4) (Type 37-6-30, HIP, USA) and measured by two different pressure manometers [HP-1 (5) and P-10 (6), WIKA Alexander Wiegand GmbH & Co., Germany] with experimental uncertainties of ± 0.5 and $\pm 0.1\%$ from a measured value, respectively. The pressure was kept constant during the experimental measurements. All high pressure valves (2, 7, 8, 16, 17), tubes, fittings (3 and 11) etc. were supplied by SITEC and NOVA (Switzerland).

The mPDS2000V3 evaluation unit displays the vibration period to seven digits. According to the specifications of Anton-Paar and the results of our calibration procedures, the reproducibility of the density measurements for temperatures in the range $T=(273.14\text{ to }468.06)\text{ K}$ and absolute pressures up to 140 MPa is within $\Delta\rho=\pm(0.1\text{ to }0.3)\text{ kg m}^{-3}$ or $\Delta\rho/\rho=\pm(0.01\text{ to }0.03)\%$.

Before each of the experiments, the installation was washed with water and then acetone and finally dried in a vacuum system. The valve of the flask (1) is closed. Vacuum is applied over 3 to 4 h using a vacuum pump (19) (Model S 1.5, Leybold, Germany) until a minimal pressure of 3 to 5 Pa is reached (measured with a digital vacuum indicator (10) THERMOVAC TM 100 (Leybold, Germany)). The valve (17) is closed and the valve of the flask is opened so that the measuring system is filled with the substance to be

investigated. A special window (12) was constructed in order to trace the flow of the measured samples between valves (16) and (17). After filling of the system, the valves (2) and (16) were closed. The high pressure region is located between these two valves (indicated by heavier lines in Fig. 1). The experiments were usually started at low pressure [(0.8 to 1.0) MPa] in the measured cell. For temperature stabilization the waiting time is about one hour. The period of oscillation of the vibration tube is taken from the display of the evaluation unit mPDS2000V3 (9).

3 Results and discussion

The (p, ρ, T) data of the standard seawater samples ($S=34.993$, $k_{15}=0.99982$, 10 October 2006 and $S=34.994$, $k_{15}=0.99984$, 5 October 2007, OSIL Laboratory, UK) were measured for $T=(273.14\text{ to }468.06)\text{ K}$ and pressures up to $p=140\text{ MPa}$. Based on the results, a new equation of state for standard seawater is reported. The temperature and pressure steps in the experiments were in the ranges $T=(5\text{ to }20)\text{ K}$ and $p=(5\text{ to }10)\text{ MPa}$, respectively. Obtained values were compared with the available literature results for standard seawater with temperatures in the range 273.15 K to 313.15 K and pressures up to 130 MPa. As discussed below, the current results are in good agreement with previously published results over this range. The obtained (p, ρ, T) results are listed in the Supplementary material (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>).

The measured densities as a function of pressure and temperature were fitted to the equation of state (1) from Safarov (2003):

$$p/\text{MPa} = A(\rho/\text{g cm}^{-3})^2 + B(\rho/\text{g cm}^{-3})^8 + C(\rho/\text{g cm}^{-3})^{12}, \quad (7)$$

where the coefficients of Eq. (7) are polynomial functions of temperature.

$$A(T) = \sum_{i=1}^4 a_i T^i, B(T) = \sum_{i=0}^3 b_i T^i, C(T) = \sum_{i=0}^3 c_i T^i. \quad (8)$$

The coefficients a_i , b_i and c_i for Eqs. (7) and (8) are given in Table 1. The Eqs. (7–8) describe the experimental results obtained for the density of standard seawater with an average percent deviation of $\Delta\rho/\rho=\pm 0.006\%$ and standard and maximum absolute deviations of 0.084 kg m^{-3} and 0.280 kg m^{-3} , respectively. The measured (p, ρ, T) values of pure water were also fitted to the equation of state (1) from Safarov (2003) and $\Delta\rho/\rho=\pm 0.007\%$ average deviation was found. The coefficients a_i , b_i and c_i of Eqs. (7) and (8) for the pure water are given in Table 2.

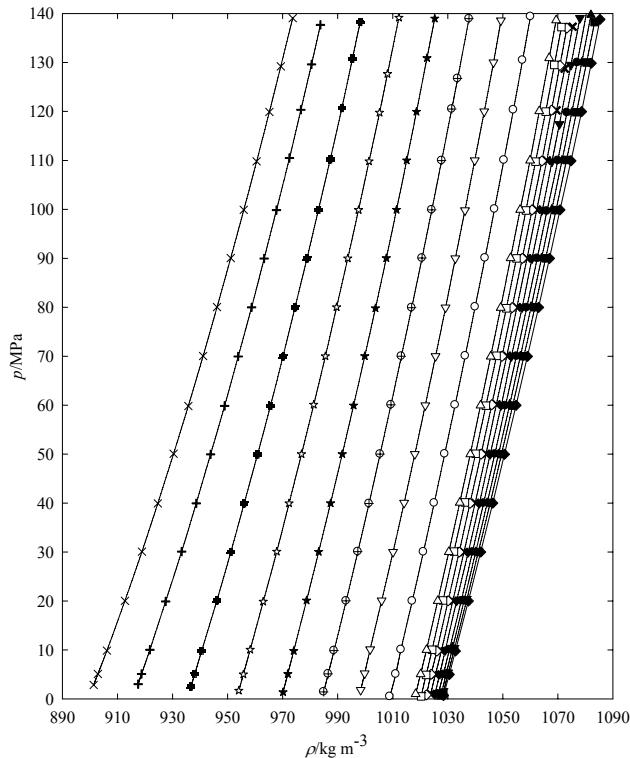
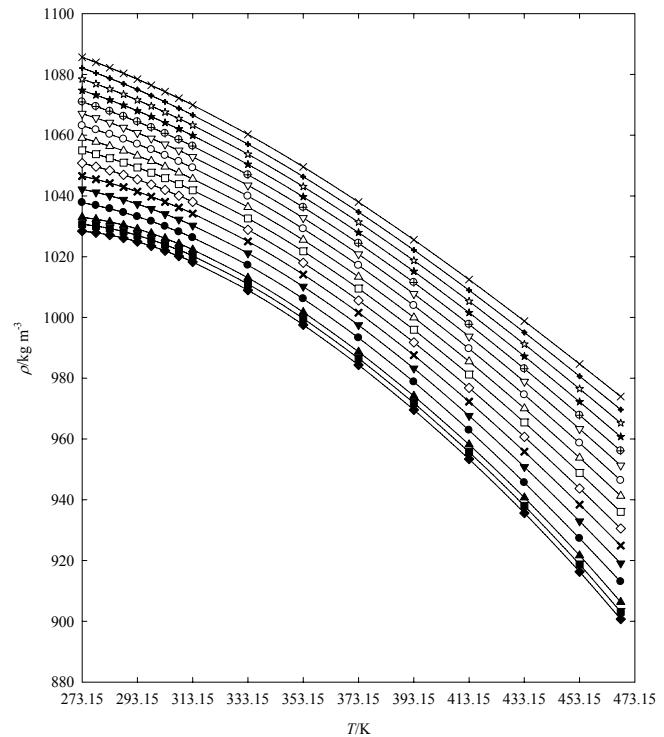
Figures 4–6 show plots of the pressure p of standard seawater vs. density ρ , the density ρ of standard seawater vs. temperature T calculated by Eqs. (7–8), and the percent deviations $(\rho_{exp} - \rho_{cal})/\rho_{exp}$ vs. pressure, where ρ_{exp} is the experimentally determined density of standard seawater and ρ_{cal} is the value determined from Eqs. (7–8).

Table 1. Values of the coefficients a_i , b_i and c_i in Eqs. (7–8) for the standard seawater.

a_i	b_i	c_i
$a_1 = -2.157761589$	$b_0 = 3638.11368199$	$c_0 = -2235.76774015$
$a_2 = -0.10341365 \times 10^{-2}$	$b_1 = -27.97107636$	$c_1 = 17.6361364636$
$a_3 = 0.103809737 \times 10^{-4}$	$b_2 = 0.0815083395$	$c_2 = -0.04771579895$
$a_4 = -0.305662763 \times 10^{-8}$	$b_3 = -0.74604739 \times 10^{-4}$	$c_3 = 0.4100691661 \times 10^{-4}$

Table 2. Values of the coefficients a_i , b_i and c_i in Eqs. (7–8) for the pure water.

a_i	b_i	c_i
$a_1 = -3.3758451745$	$b_0 = 3955.4195315463$	$c_0 = -2447.6394165082$
$a_2 = 0.6419188921 \times 10^{-2}$	$b_1 = -27.1994626242$	$c_1 = 17.32571704$
$a_3 = -0.23686189346 \times 10^{-5}$	$b_2 = 0.07206343975153$	$c_2 = -0.04210264822$
$a_4 = 0.225027523061 \times 10^{-8}$	$b_3 = -0.598096050112 \times 10^{-4}$	$c_3 = 0.31913365 \times 10^{-4}$

**Fig. 4.** Plot of pressure p of standard seawater vs. density ρ : ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◇, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; +, 433.18 K; +, 453.17 K; x, 468.03 K calculated by Eqs. (7–8).**Fig. 5.** Plot of density ρ of standard seawater vs. temperature T calculated by Eqs. (7–8): ◆, 0.101 MPa (after $T=373.15\text{ K}$ – p_s of water); ■, 5 MPa; ▲, 10 MPa; ●, 20 MPa; ▼, 30 MPa; ✕, 40 MPa; ◇, 50 MPa; □, 60 MPa; △, 70 MPa; ○, 80 MPa; ▽, 90 MPa; ⊕, 100 MPa; ★, 110 MPa; ☆, 120 MPa; +, 130 MPa; x, 140 MPa.

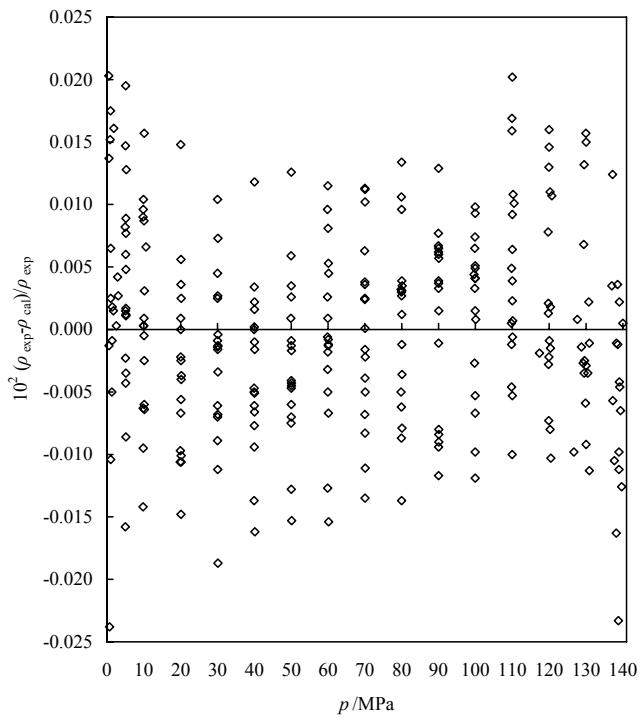


Fig. 6. Plot of deviations of experimental density ρ_{exp} of the investigated standard seawater from the calculated by Eqs. (7–8) density ρ_{cal} vs. pressure p at $T=(273.14$ to $468.06)$ K.

The isothermal compressibility k_T / MPa^{-1} of the standard seawater is a measure of its relative volume change in response to a pressure change at constant temperature:

$$k_T = (1/\rho)(\partial p/\partial\rho)_T^{-1}. \quad (9)$$

The (hydrostatic) pressure experienced by fluid parcels in the ocean increases by about one atmosphere for every 10 m of depth. The full pressure range found in the ocean basins is from approximately 0.1 MPa at the sea surface to about 108.6 MPa at the bottom of the Mariana Trench (11 022 m), over 1000 times the atmospheric pressure at the sea surface.

The isothermal compressibility of seawater can be calculated from the experimental (p, ρ, T) results of the standard seawater using Eqs. (7) and (9) according to:

$$k_T = 1/[2A(T)\rho^2 + 8B(T)\rho^8 + 12C(T)\rho^{12}]. \quad (10)$$

The calculated values of the isothermal compressibility are given in the Supplementary material and shown in Fig. 7 as a function of pressure and in Fig. 8 as a function of temperature.

Another thermal property that can be calculated from Eqs. (7–8) is isobaric thermal expansibility α_p / K^{-1} , which is the tendency of matter to change in volume in response to a change in temperature at constant pressure, i.e., the degree of expansion divided by the change in temperature,

$$\alpha_p = (1/\rho)(\partial p/\partial T)_\rho(\partial p/\partial\rho)_T^{-1}, \quad (11)$$

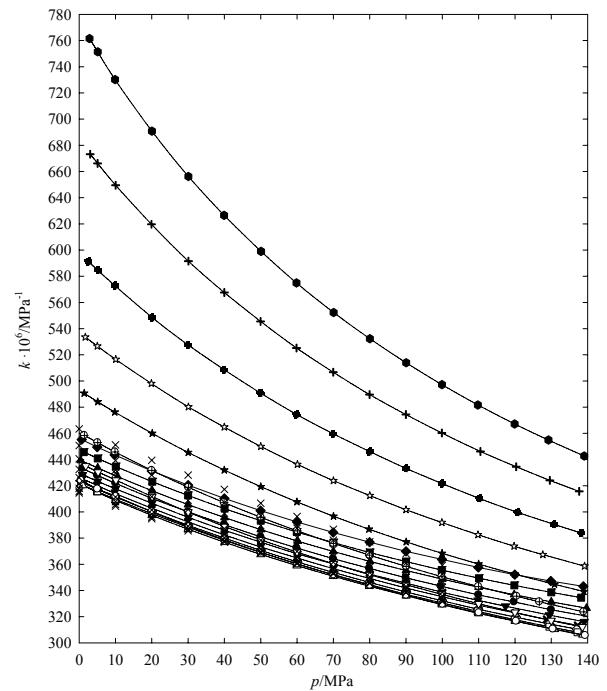


Fig. 7. Plot of isothermal compressibility $k_T \times 10^6 / \text{MPa}^{-1}$ of standard seawater vs. pressure p : ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◇, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ∇, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; +, 433.18 K; +, 453.17 K; ◑, 468.03 K; x (Millero et al., 1980).

which varies with temperature, pressure and salinity. Samples that contract with an increase in temperature are rather uncommon; for seawater, this effect occurs only at low salinities and below the temperature of maximum density (Caldwell, 1978).

The known temperature range, which occurs in natural seawater extends from the freezing point to a maximum value in the approximate range $T=(303.15$ to $313.15)$ K. At active ridge systems (2000 to 3000 m below the sea surface) the temperatures can be extremely hot as seawater gushes out of fissures in the underlying rocks (473.12 K to 673.15 K) (Sun, 2008). These temperatures decrease quickly as the hot waters mix with the surrounding cold water with temperatures typically ranging from 276.15 K to 277.15 K. It is important to know the isobaric thermal expansibility of seawater at these temperatures and pressures and to be able to calculate it from the constructed equation of state. From Eq. (11) this quantity can be calculated from the experimental (p, ρ, T) results of the standard seawater using Eqs. (7–8):

$$\alpha_p = \left[A'(T) + B'(T)\rho^6 + C'(T)\rho^{10} \right] / \left[2A(T) + 8B(T)\rho^6 + 12C(T)\rho^{10} \right], \quad (12)$$

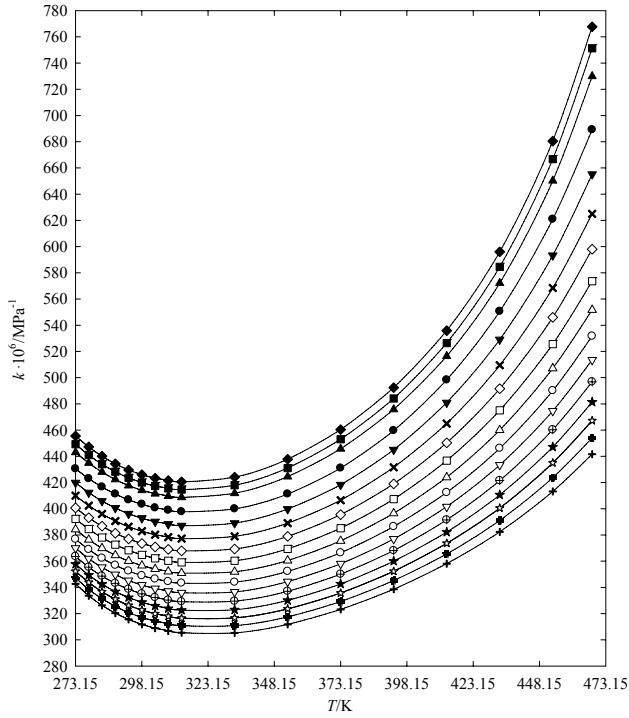


Fig. 8. Plot of isothermal compressibility $k_T \times 10^6/\text{MPa}^{-1}$ of standard seawater vs. temperature T : ◆, 0.101 MPa (after $T=373.15\text{ K}$ p_s of water); ■, 5 MPa; ▲, 10 MPa; ●, 20 MPa; ▼, 30 MPa; ✕, 40 MPa; ◇, 50 MPa; □, 60 MPa; △, 70 MPa; ○, 80 MPa; ▽, 90 MPa; +, 100 MPa; ★, 110 MPa; ☆, 120 MPa; +, 130 MPa; x, 140 MPa.

where A , B , and C are the derivatives of the A , B , and C defined by Eq. (8):

$$\begin{aligned} A'(T) &= \sum_{i=1}^4 i a_i T^{i-1}, \quad B'(T) = \sum_{i=1}^3 i b_i T^{i-1}, \\ C'(T) &= \sum_{i=1}^3 i c_i T^{i-1}. \end{aligned} \quad (13)$$

The calculated values of the isobaric thermal expansibility are given in the Supplementary material (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>) and shown in Fig. 9.

The next important parameter for the investigation of the thermodynamic properties of seawater is the difference between the specific heat capacities determined at constant pressure and constant volume. Measuring the heat capacity at constant volume can be prohibitively difficult for liquids. It is easier to measure the heat capacity at constant pressure and solve for the heat capacity at constant volume using mathematical relationships derived from basic thermodynamic laws:

$$c_p = c_v + T \frac{(\partial p / \partial T)^2}{\rho^2 (\partial p / \partial \rho)_T}, \quad (14)$$

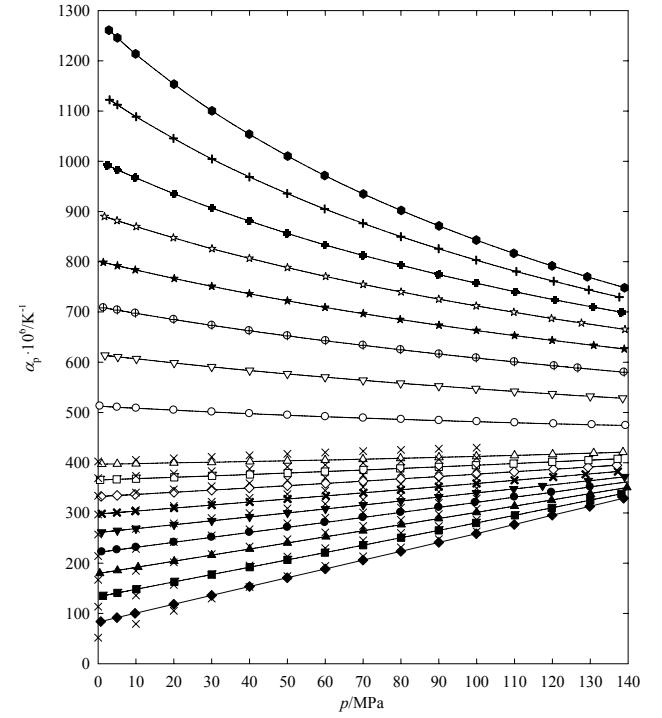


Fig. 9. Plot of isobaric thermal expansibility $\alpha_p \times 10^6/\text{K}^{-1}$ of standard seawater vs. pressure p : ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◇, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; +, 373.15 K; ★, 393.17 K; ☆, 413.15 K; +, 433.18 K; x, 453.17 K; ◑, 468.03 K; x (Millero et al., 1980) for $T=(273.15 \text{ to } 313.15)\text{ K}$.

where c_p and c_v are the heat capacities at constant pressure and volume, respectively, with units of $\text{Jkg}^{-1}\text{K}^{-1}$. Using Eqs. (9) and (11), we obtain the following relationship:

$$c_p - c_v = \frac{\alpha_p^2 T}{\rho k_T}, \quad (15)$$

which can be evaluated using Eqs. (10), (12) and (14). The resulting values of the differences in specific heat capacities of the standard seawater are given in the Supplementary material (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>) and are shown in Fig. 10.

The thermal pressure coefficient γ/MPaK^{-1} is calculated as the ratio of the isobaric thermal expansibility to the isothermal compressibility at the same state parameters S , T and p :

$$\gamma = \frac{\alpha_p}{k_T}. \quad (16)$$

The calculated values of the thermal pressure coefficient of the standard seawater are given in the Supplementary material (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>) and shown in Fig. 11.

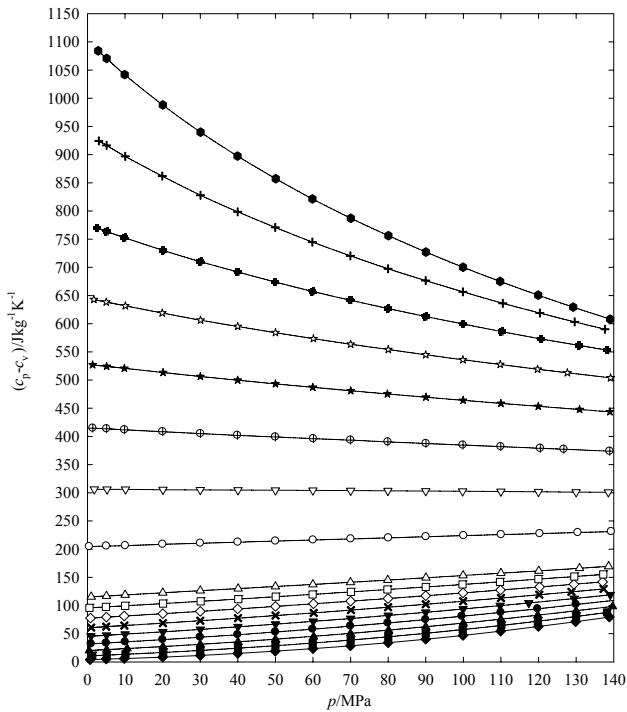


Fig. 10. Plot of difference in isobaric and isochoric heat capacities $(c_p - c_v) / \text{J kg}^{-1} \text{K}^{-1}$ of standard seawater vs. pressure p : ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◇, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; +, 433.18 K; +, 453.17 K; ◦, 468.03 K.

The internal pressure, $p_{\text{int}} / \text{MPa}$ is related to thermal pressure coefficient, γ , and defined by the following relationship:

$$p_{\text{int}} \equiv \left(\frac{\partial U}{\partial V} \right)_T = T \left(\frac{\partial p}{\partial T} \right)_p - p = T\gamma - p = \frac{T\alpha_p}{k_T} - p. \quad (17)$$

The calculated values of the internal pressure of the standard seawater are given in the Supplementary material (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>) and shown in Fig. 12.

Next, consider the secant bulk modulus of standard seawater. Thermodynamically stable substances diminish in volume when exposed to a uniform, externally applied pressure. The secant bulk modulus K / MPa is the product of the original fluid volume and the slope of the line drawn from the origin to any specified point on the plot of pressure versus specific volume (the slope of the secant line to the point). That is, the secant bulk modulus, K , is

$$K = \frac{v^0 p}{v^0 - v^p}, \quad (18)$$

where v^0 is the specific volume at the reference temperature and pressure, v^p is the experimental value of specific volume at the reference temperature and pressure, and p is the experimental pressure.

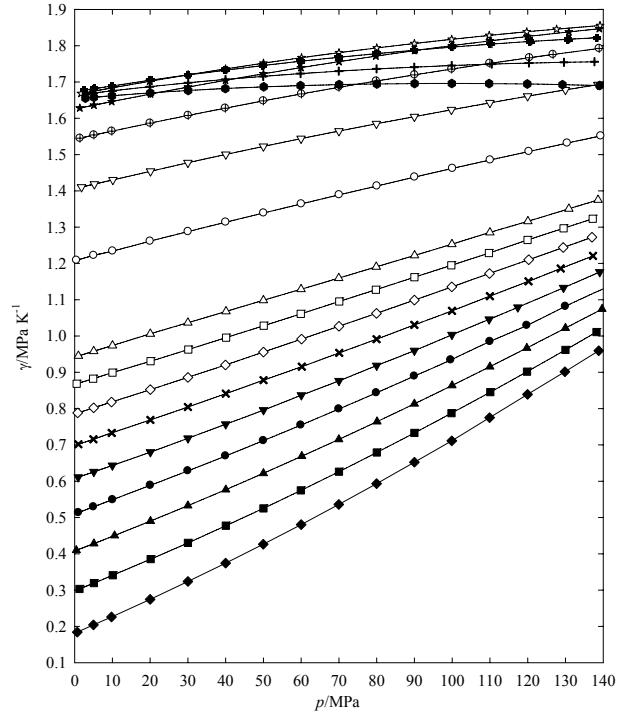


Fig. 11. Plot of thermal coefficient of pressure $\gamma / \text{MPa K}^{-1}$ of standard seawater vs. pressure p : ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◇, 303.18 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; +, 433.18 K; +, 453.17 K; ◦, 468.03 K.

The units of the bulk modulus are the same as those of pressure, MPa, and it can be interpreted as a measure of resistance to compressibility of a fluid. The calculated values of the secant bulk modulus, K / MPa , of the standard seawater are given in Supplementary material (see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf>) and the dependence on pressure is shown in Fig. 13. It is seen that the secant bulk modulus for standard seawater is approximately a linear function of pressure.

The measured (p, ρ, T) results for standard seawater were compared with the available literature results (Feistel, 2003; Newton and Kennedy, 1965; Wilson and Bradley, 1968; Emmet and Millero, 1974; Chen and Millero, 1976; Feistel and Hagen, 1995) and results are shown in Fig. 14, where the zero line indicates the experimental results of the present work. The experimental density results in these publications do not include all of the temperature and pressure values obtained here. Thus, the literature values were fitted to the equation of state (7–8) and average and maximum percent deviations were found over the range of the previous measurements. The results of these comparisons are discuss below.

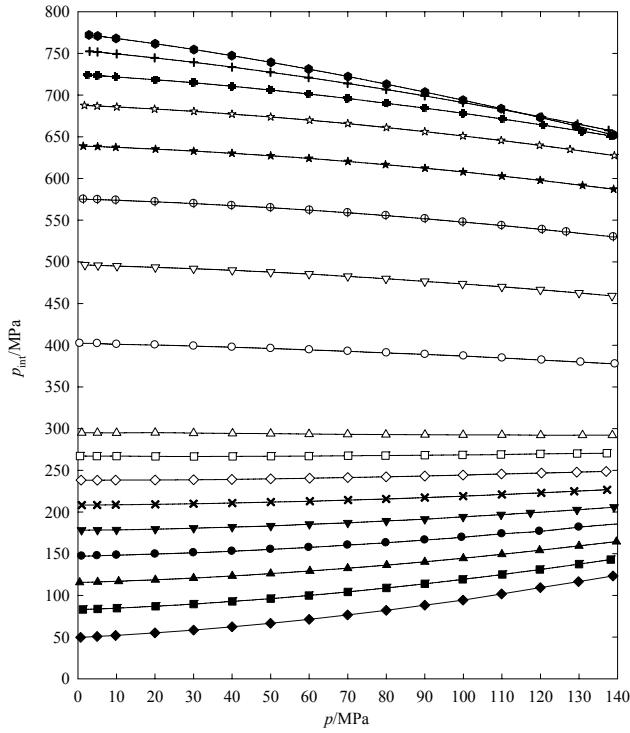


Fig. 12. Plot of internal pressure p_{int} /MPa of standard seawater vs. pressure p : ◆, 273.17 K; ■, 278.15 K; ▲, 283.15 K; ●, 288.16 K; ▼, 293.15 K; ✕, 298.18 K; ◇, 303.15 K; □, 308.15 K; △, 313.15 K; ○, 333.15 K; ▽, 353.16 K; ⊕, 373.15 K; ★, 393.17 K; ☆, 413.15 K; +, 433.18 K; +, 453.17 K; ◩, 468.03 K.

The 84 experimental (p , ρ , T) results for standard seawater at $S=34.99$, measured by Newton and Kennedy (1965), have $\Delta\rho/\rho=\pm 0.017\%$ average deviation from our experimental values. The maximum uncertainty of their results is $\Delta\rho/\rho=0.042\%$ at $T=293.15$ K and $p=120$ MPa. Their density results are typically smaller than ours for pressures up to about 40 MPa and higher than our results at higher pressures.

The 134 experimental (p , ρ , T) results of seawater at $S=35.568$, measured by Wilson and Bradley (1968), were also compared with our results measured at $S=34.993$ and $S=34.994$. Since the salinity of the seawater sample considered by Wilson and Bradley (1968) was higher than ours by $\Delta S=0.575$ and $\Delta S=0.574$, we expect their densities to also be higher. For temperatures in the range $T=(273.15$ to $313.15)$ K and pressures in the range $p=(0.101$ to $100)$ MPa the haline contraction coefficient is in the range 667.3357 to 780.2349, giving an expected density differences in the range $\Delta\rho=(0.24$ to $0.72)$ kg m $^{-3}$. The actual average deviation between the two sets of results is $\Delta\rho/\rho=0.046\%$, consistent with expectations. The maximum uncertainty of the results presented by Wilson and Bradley (1968) is $\Delta\rho/\rho=0.07\%$ at $T=283.30$ K and $p=0.101$ MPa.

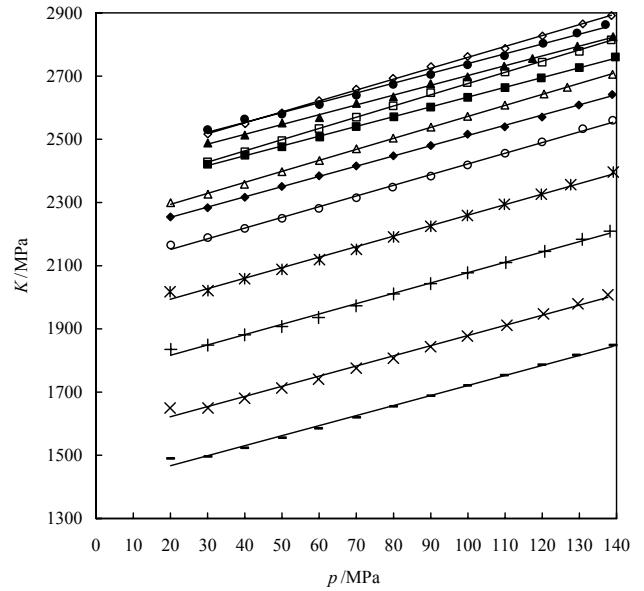


Fig. 13. Plot of calculated values of secant bulk modulus K /MPa of standard seawater vs. pressure p : ◆, 273.17 K; ■, 283.15 K; ▲, 293.15 K; ●, 303.18 K; ◇, 313.15 K; □, 353.16 K; △, 373.15 K; ○, 393.17 K; *, 413.15 K; +, 433.18 K; x, 453.17 K; -, 468.03 K.

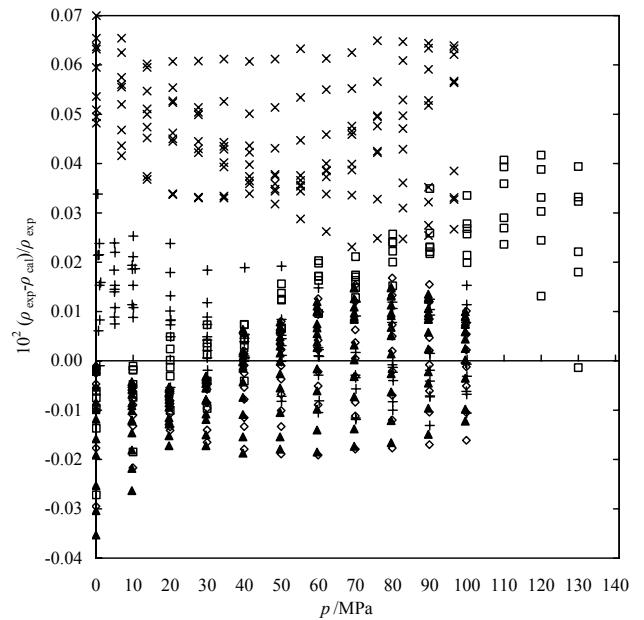


Fig. 14. Comparison of (p , ρ , T) results of standard seawater with various literature values: +, (Feistel, 2003; Feistel and Hagen, 1995); □, (Newton and Kennedy, 1965); x, (Wilson and Bradley, 1965); ▲, (Emmet and Millero, 1974); ◇, (Millero et al., 1980).

The 152 experimental (p , ρ , T) results for seawater at $S=35$, documented in Emmet and Millero (1974) have $\Delta\rho/\rho=\pm 0.009\%$ average deviation from our results and are typically smaller than our results up to pressures of about

40 MPa. The maximum uncertainty of density results of Emmet and Millero (1974) is $\Delta\rho/\rho=-0.035\%$ at $T=271.15\text{ K}$, $p=0.101\text{ MPa}$.

The 97 (p , ρ , T) results of Chen and Millero (1976) for seawater at $S=35.003$ were also compared with our results. The average deviation from our measurements is $\Delta\rho/\rho=\pm 0.008\%$. The density results of Chen and Millero are smaller than ours for pressures up to about 50 MPa and larger above this pressure. The maximum uncertainty of (p , ρ , T) results in Chen and Millero (1976) is $\Delta\rho/\rho=-0.03\%$ at $T=273.15\text{ K}$, $p=0.101\text{ MPa}$.

The 108 experimental density values for seawater in the temperature range $T=(273.14\text{ to }313.21)\text{ K}$ and for pressures up to 100 MPa were compared with calculated results using the formula of Feistel (2003). The average deviation between these calculated results and our measurements is $\Delta\rho/\rho=\pm 0.009\%$. The maximum uncertainty of (p , ρ , T) results in (Feistel, 2003) is $\Delta\rho/\rho=+0.034\%$ at $T=283.15\text{ K}$ and $p=0.465\text{ MPa}$.

We also compared our calculated results for isothermal compressibility (99 points) and isobaric thermal expansibility (99 points) with the calculated results of Chen and Millero (1976). The average deviation $\Delta k_{T\text{cal}}-\Delta k_{T\text{lit}}$ between the isothermal compressibility results is $\pm 2.7\times 10^{-6}\text{ MPa}^{-1}$ and the maximum uncertainty of $\Delta k_{T\text{cal}}-\Delta k_{T\text{lit}}$ is $-10.1\times 10^{-6}\text{ MPa}^{-1}$ at $T=288.14\text{ K}$ and $p=10\text{ MPa}$. The average deviation $\Delta\alpha_{p\text{cal}}-\Delta\alpha_{p\text{lit}}$ between the isobaric thermal expansibility results is $\Delta\alpha_p=\pm 9.8\times 10^{-6}\text{ K}^{-1}$ and the maximum uncertainty $\Delta\alpha_{p\text{cal}}-\Delta\alpha_{p\text{lit}}$ is $\Delta\alpha_p=41.56\times 10^{-6}\text{ K}^{-1}$ at $T=273.14\text{ K}$ and $p=0.101\text{ MPa}$.

Calculated values of the secant bulk modulus were compared with the same results from Millero et al. (1980). The differences $\Delta K_{\text{cal}}-\Delta K_{\text{lit}}$ between the calculated values is $\pm 24\text{ MPa}$ at $T=273.15\text{ K}$, $p=100\text{ MPa}$ and $\pm 22\text{ MPa}$ at $T=298.15\text{ K}$, $p=100\text{ MPa}$.

4 Conclusions

This study presents new (p , ρ , T) measurements for standard seawater samples over the extended temperature interval $T=(273.14\text{ to }468.06)\text{ K}$ and for pressures up to $p=140\text{ MPa}$. The results are used to derive an equation of state of seawater that is valid for higher temperatures and pressures than previously possible. The new equation of state has been used to calculate a number of thermal and caloric parameters.

From the analysis of the isothermal compressibility values of standard seawater, it is apparent that standard seawater has similar anomalies to those of pure water (Supplementary material, see <http://www.ocean-sci.net/5/235/2009/os-5-235-2009-supplement.pdf> and Figs. 4, 5, 7–12). This is not very surprising since the majority of standard seawater (appr. 96.5%) is pure water. In a typical liquid, the compressibility decreases as the structure becomes more compact due

to lowered temperature. In water and all aqueous salt solutions in which the concentration of water is very high, the cluster equilibrium shifts towards a more open structure (for example, expanded structure – ES) as the temperature is reduced due to preference for a more ordered structure (that is, ΔG for $\text{ES}\rightleftharpoons\text{CS}$ (collapsed structure) becomes more positive) (Chaplin, 2009). As the water structure is more open at these lower temperatures, the capacity for it to be compressed increases (Kell, 1975). Since the compressibility depends on fluctuations in the specific volume, these will be largest where water molecules have a more open structure. At high pressures (for example, $\sim 200\text{ MPa}$), this compressibility anomaly, although still present, is far less apparent (Kanno and Angell, 1979).

The isobaric thermal expansibility of seawater increases with increasing pressure up to about $T=313.15\text{ K}$ (for which the isobaric thermal expansibility is approximately constant) in contrast to most other liquids where thermal expansibility decreases with increased pressure. Above $T=313.15\text{ K}$, isobaric thermal expansibility of seawater decreases with increased pressure. This is due to the collapsed structure of water having a greater isobaric thermal expansibility than the expanded structure and the increasing pressure shifting the equilibrium towards a more collapsed structure.

More than 800 published values for density, isothermal compressibility, isobaric thermal expansibility and the secant bulk modulus have been compared with our results and, as already discussed, all previous results are in good agreement with our new results. We note however, that the results of Wilson and Bradley (1968) correspond to a salinity higher than that considered here so the average deviation between the two sets of results is higher than the experimental uncertainty in either data set.

The results obtained here were used for the development of a new equation of state for seawater which can be used for oceanographic calculations and marine research.

The (p , ρ , T) measurements of seawater with various salinities are critically required in order to extend the limits of validity of the currently available EOS80 or IAPWS08. We have already measured the (p , ρ , T) properties of seawater with the following salinities: $S=(2.524, 3.514, 5.087, 6.296, 7.577, 9.110, 10.925, 13.524, 15.351, 16.967, 20.174, 22.069, 23.818, 25.610, 28.757, 29.541, 31.535, 33.350, 37.791, 41.454, 45.902, 48.372, \text{ and } 50.531)$. These and other results will be discussed in our future publications.

Acknowledgements. The authors like to thank Daniel G. Wright (Bedford Institute of Oceanography, Dartmouth, Canada) for various helpful questions, comments, corrections, and editorial improvements of the manuscript. The authors appreciate financial support of this investigation by German Research Foundation (DFG). FJM wishes to acknowledge the support of the Oceanographic Section of the National Science Foundation and the National Oceanic and Atmospheric Administration.

Edited by: T. McDougall

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