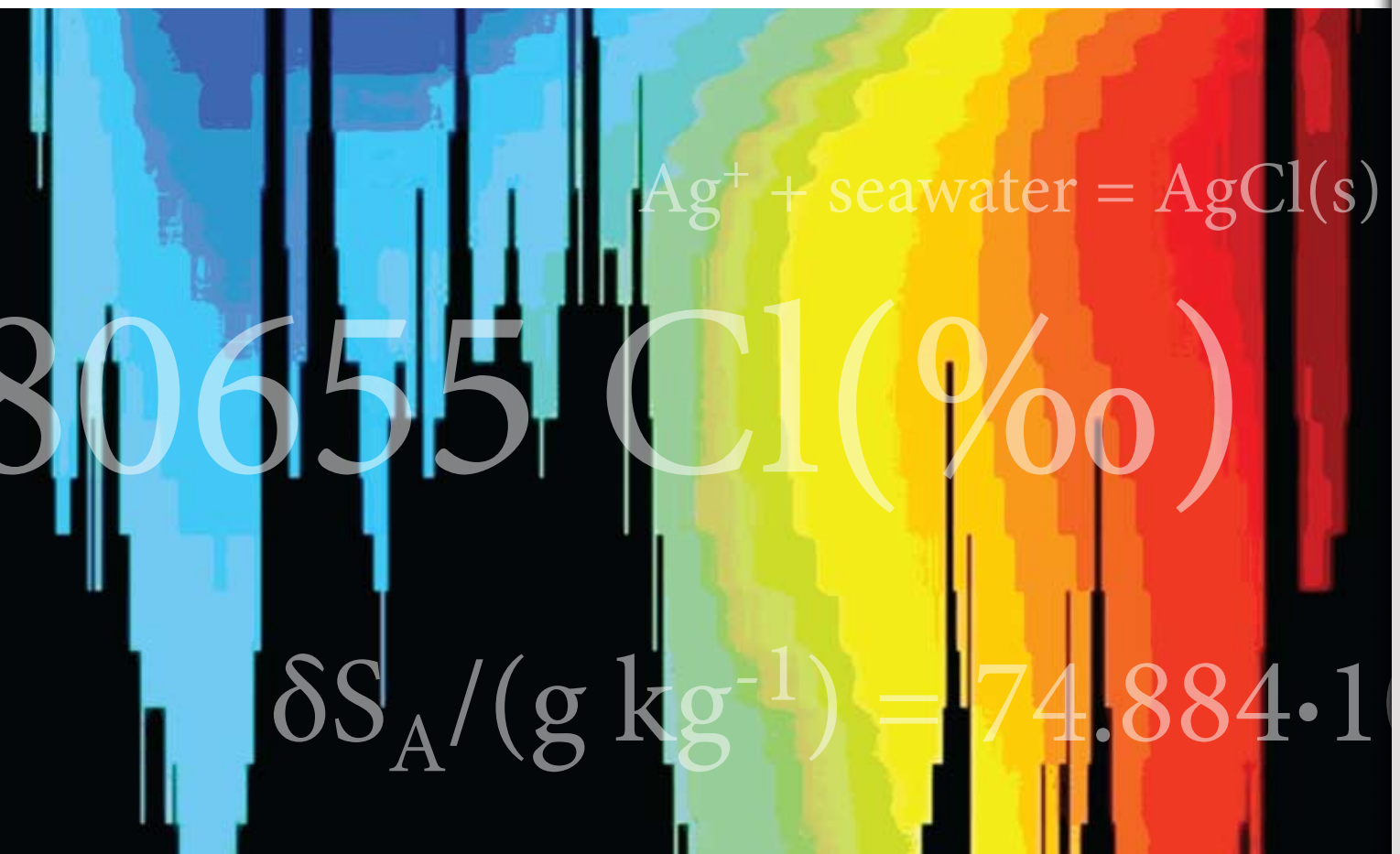


BY FRANK J. MILLERO

# HISTORY OF THE Equation of State of Seawater



“ TO EXAMINE THE THERMODYNAMIC PROPERTIES OF SEAWATER, ONE MUST KNOW THE CONCENTRATION OF THE MAJOR COMPONENTS OF OCEAN WATER. ”

**ABSTRACT.** As one of few who have been involved in the equation of state of seawater over the last 40 years, I was invited to review some of the history behind its early development and also the more recent thermodynamic equation of state. The article first reviews early (late 1800s) work by Knudsen and others in defining the concept of salinity. This summary leads into the development of the practical salinity scale. Our studies at the University of Miami Rosenstiel School, along with the work of Alain Poisson's group at Laboratoire de Physique et Chimie, Université Pierre et Marie Curie, and that of Alvin Bradshaw and Karl Schleicher at Woods Hole Oceanographic Institution, were instrumental in deriving the 1980 equation of state (EOS-80) that has been used for 30 years. The fundamental work of Ranier Feistel at Leibniz Institute for Baltic Sea Research led to the development of a Gibbs free energy function that is the backbone of the new thermodynamic equation of state (TEOS-10). It can be used to determine all of the thermodynamic properties of seawater. The salinity input to the TEOS-10 Gibbs function requires knowledge of the absolute salinity of seawater ( $S_A$ ), which is based upon the reference salinity of seawater ( $S_R$ ). The reference salinity is our best estimate of the absolute salinity of the seawater that was used to develop the practical salinity scale ( $S_p$ ), the equation of state, and the other thermodynamic properties of seawater. Reference salinity is related to practical salinity by

$$S_R = S_p (35.16504/35.000) \text{ g kg}^{-1}$$

and absolute salinity is related to reference salinity by

$$S_A = S_R + \delta S_A,$$

where  $\delta S_A$  is due to the added solutes in seawater in deep waters resulting from the dissolution of  $\text{CaCO}_3(\text{s})$  and  $\text{SiO}_2(\text{s})$ ,  $\text{CO}_2$ , and nutrients like  $\text{NO}_3$  and  $\text{PO}_4$  from the oxidation of plant material. The  $\delta S_A$  values due to the added solutes are estimated from the differences between the measured densities of seawater samples compared with the densities calculated from the TEOS-10 equation of state ( $\Delta\rho$ ) at the same reference salinity, temperature, and pressure, using

$$\delta S_A = \Delta\rho/0.75179 \text{ g kg}^{-1}.$$

The values of  $\delta S_A$  in the ocean can be estimated for waters at given longitude, latitude, and depth using correlations of  $\delta S_A$  and the concentration of  $\text{Si}(\text{OH})_4$  in the waters. The  $S_A$  values can then be used to calculate all the thermodynamic properties of seawater in the major oceans using the new TEOS-10. It will be very useful to modelers examining the entropy and enthalpy of seawater.

## EARLY DAYS IN SCIENCE

I got into the equation of state business 43 years ago. After receiving my BS degree at Ohio State in physical chemistry in 1961 and before going to graduate school, I took a summer job at the National Bureau of Standards (now the National Institute of Standards and Technology) in Washington, DC, in the Electrochemical Division headed by Roger Bates (1973). This summer job introduced me to the thermodynamic chemistry of solutions, and I met a number of other famous solution chemists (such as Robert Robinson and Roger Stokes, 1959) while enjoying afternoon tea-break discussions. My summer work, which involved studies of the density and viscosity of electrolytes in a nonaqueous solvent, changed the direction of my later studies.

Upon arrival at Carnegie Mellon University, I began PhD work under the direction of Loren Hepler, a graduate of the University of California, and the Gilbert N. Lewis and Merle Randall "School of Thermodynamics" (Lewis and Randall, 1961). Hepler was a student of W.M. Latimer, who wrote a book on the oxidation states of elements (Latimer, 1952). My thesis work involved thermodynamic studies of the dissociation of organic acids in aqueous solutions. Unbeknownst to my major advisor, I had a night bartending job (9 p.m. to 2 a.m.) at a local college bar. It was a place to remember, since I met my wife

Judy there one evening. I saved enough money from this night job to tour Europe for three months after receiving my PhD. Upon returning from Europe, I joined the motor fuels section of ESSO in Linden, New Jersey, working on automobile pollution, catalytic muffler testing, and evaporation of gasoline from the gas tank and the carburetor (and enjoying being close to New York City).

After getting married, I yearned to get back to an academic environment and out of Elizabeth, NJ. While reading *Chemical Engineering News* one afternoon, I saw an advertisement for an employment opportunity to examine the physical chemistry of seawater at the Marine Laboratory (now the Rosenstiel School) at the University of Miami, studies supported by the US Office of Desalination. I applied for the position, outlining all my PhD work on thermodynamics and my brief summer work at the National Bureau of Standards. I was sent plane tickets within a week and left snowy New Jersey for a trip to Miami. After being wined, dined, and offered a position with a starting salary of \$9,000, I called my wife and told her to start packing. We left New Jersey for Miami in August 1966 and spent a week exploring all the beaches from New Jersey to Miami. Forty-three years later, I am still enjoying the sunshine and work at the University of Miami.

## SALINITY OF SEAWATER

To examine the thermodynamic properties of seawater, one must know the concentration of the major components of ocean water. Over the years, this calculation has been done by considering the total mass of the dissolved salts in seawater (salinity) or some measure of

the total salts. Marcet (1819) was the first to suggest that the relative composition of seawater is constant. This assumption allows estimation of the total dissolved solids in seawater by measuring one of the major components. Some years ago, Dana Kester suggested that this is the First Law of Chemical Oceanography. Earlier workers attempted to determine the total solutes in average seawater (the absolute salinity,  $S_A$ ) by adding up all the individual components. Seawater's individual components were examined relative to seawater chlorinity, which was originally defined as the chlorine equivalent to total halides (Cl, Br in  $\text{g kg}^{-1}$  or parts per thousand) and determined by titrating the sample with  $\text{AgNO}_3$ :



Because changes in the atomic weights of Ag and Cl can occur, Jacobsen and Knudsen (1940) defined chlorinity as the mass in grams of pure silver necessary to precipitate the halides in 328.5234 grams of seawater:

$$\text{Cl}(\text{‰}) = 328.5234 \text{ Ag}(\text{‰}). \quad (2)$$

I should point out that the use of the ‰ symbol to denote parts per thousand has led some oceanographers to consider it a unit (Millero, 1993). It is actually a fraction and should have been denoted as the accepted unit  $\text{g kg}^{-1}$ . More will be said about this later when discussing absolute salinity ( $S_A$ ), which represents the total dissolved solids in seawater ( $\text{g kg}^{-1}$ ).

The International Council for the Exploration of the Sea (ICES) asked Knudsen (1903) to chair a commission to investigate and give advice on the definition of the salinity and density of seawater. Forch et al. (1902)

defined salinity as “the weight in grams of dissolved inorganic salts in one kilogram of seawater, when all bromides and iodides are replaced by an equivalent quantity of chlorides, and all the carbonates are replaced by an equivalent quantity of oxides.” The seawater sample was dried to constant weight at  $480^\circ\text{C}$ . Salinity was thus the weight of the dissolved solids minus the loss of  $\text{HCO}_3$ ,  $\text{CO}_3$ , and boric acid (Millero, 2006). Because the composition of seawater is nearly constant, the commission defined chlorinity, and suggested it could be used as a measure of salinity. Because changes can occur in the atomic weights of Ag and Cl, chlorinity was redefined in 1937 by Jacobsen and Knudsen as “...the mass in grams of pure silver necessary to precipitate the halogens in 328.5234 grams of seawater.” Measurements of the chlorinity and evaporation salinity were made on nine samples of seawater (two from the Baltic, two from the Atlantic, four from intermediate Baltic-North Sea waters, and one from the Red Sea). The results were fit to the equation (Knudsen, 1901)

$$S(\text{‰}) = 0.030 + 1.805 \text{ Cl}(\text{‰}). \quad (3)$$

The standard error was 0.01‰ and the largest deviation was 0.022‰. This formula was used in oceanography for about 65 years. The intercept was due to river salts with little Cl coming into the Baltic estuary (Millero and Kremling, 1976).

The development of precise

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conductivity bridges in the 1950s made it possible to determine conductivity salinities with great precision ( $\pm 0.003\text{‰}$ ). In 1961, commercial conductivity bridges became available. All of these bridges gave conductivity ratios between the sample and standard seawater used to calibrate the bridges. Although standard seawater was calibrated for chlorinity, it was not meant to be a standard for conductivity. The Joint Panel for Oceanographic Tables and Standards (JPOTS), sponsored by the United Nations Economic, Science, and Cultural Organization (UNESCO), ICES, the International Association of Physical Sciences of the Oceans (IAPSO), and the Scientific Committee on Oceanic Research (SCOR), was appointed to develop a conductivity standard for salinity.

A number of samples were collected from around the world and analyzed for their chemical composition, chlorinity, and conductivity ratios. The JPOTS panel decided to revise the old relationship between salinity and chlorinity as follows (Wooster et al., 1969):

$$S(\text{‰}) = 1.80655 \text{ Cl}(\text{‰}), \quad (4)$$

which is equivalent to the original definition at  $S = 35.000$  for  $\text{Cl} = 19.374$ . Near  $S(\text{‰}) = 35$ , the two equations are identical; however, at  $S(\text{‰}) = 32$  or  $38$ , the difference is  $0.003\text{‰}$ .

Cox et al. (1967) developed a relationship between the conductivity ratios of samples of seawater relative to standard seawater at  $15^\circ\text{C}$  as a function of chlorinity. Samples deeper than 200 m were deleted (due to the effect of added  $\text{Ca}^{2+}$  from the dissolution of  $\text{CaCO}_3$ ) and the polynomial equation was adjusted for this effect. The relationship was referred

to as the new definition of salinity while, in fact, this polynomial merely expresses chlorinity in terms of the conductivity ratio at  $15^\circ\text{C}$  and is strictly valid only at  $S(\text{‰}) = 35$ , which is equivalent to the old definition of salinity.

Around 1969, in situ salinometers became commercially available. Because the new definition only went to  $10^\circ\text{C}$ , it became necessary to use either extrapolated values or equations based on the dilution of seawater with pure water. A number of samples of standard seawater bottled from 1962 to 1975 were examined for conductivity, salinity, and density (Poisson, 1976; Millero et al., 1976a). While all the conductivity results were in good agreement ( $\sigma = \pm 0.0012$ ), the differences ranged from  $-0.002$  to  $0.008$ , indicating the need to characterize the conductivity of seawater relative to a KCl standard. The densities measured on the same samples using conductivity- and chlorinity-derived salinities had small differences of  $\pm 0.002 \text{ kg m}^{-3}$  and showed no measurable differences in using  $S(\text{‰})$  or  $\text{Cl}(\text{‰})$  to calculate the density of seawater.

After considering a new equation of state of seawater, JPOTS suggested in 1975 that a background paper be prepared on the salinity method. This paper (Lewis, 1978) concluded that a revision was needed for the definition of salinity, and the committee then recommended the *Practical Salinity Scale* of 1978 (Lewis and Perkin, 1978; UNESCO, 1981, 1986). This new scale breaks the  $\text{Cl}(\text{‰})$ - $S(\text{‰})$  relationship in favor of a salinity-conductivity ratio relationship. All waters with the same conductivity ratio have the same salinity (even though the composition may differ). Because salinity is normally used to determine

a physical property like density, this method was thought to be the best for determining the effect of changes in ionic composition. This is not always the case because non-electrolytes like  $\text{Si}(\text{OH})_4$  are not detected by conductivity. There were quite a few committee discussions about how salinity should be defined. Physicists on the panel thought of salinity as  $3.5 \times 10^{-3}$  or  $0.035$ . Because most of the oceanographers considered average seawater as having a salinity of  $35.0\text{‰}$  or ppt, we fought to keep the average salinity as  $35.000$ . Because the salinity is a conductivity ratio or fraction, the compromise was to define practical salinity as  $S_p = 35.000$  without the  $\text{‰}$  symbol. This compromise was probably a mistake. We should have kept the symbol (or added  $\text{g kg}^{-1}$ ) and thus avoided the incorrect use of the practical salinity unit (PSU) to define salinity in terms of a unit (Millero, 1993).

In summary, a seawater sample with a conductivity ratio of 1.0 at  $15^\circ\text{C}$  with a KCl solution containing a mass of  $32.4356 \text{ g}$  of KCl in  $1 \text{ kg}$  of solution has a practical salinity ( $S_p$ ) of  $35.000$ . The KCl mass was determined as an average of three independent laboratory studies. The scale is limited to the salinity range of 2 to 42 and  $0$  to  $49^\circ\text{C}$ , but is frequently used outside of these ranges. It should be pointed out that all the conductivity measurements were made on a seawater sample of known chlorinity and the salinity was defined using Equation 4. This conductivity or practical salinity scale has been and continues to be used to characterize the salinity of ocean waters. Figure 1 is a photo of JPOTS from the committee's last meeting in Sidney, Canada. Only a few of the original group are still active in oceanography.



Figure 1. Those attending the Joint Panel for Oceanographic Tables and Standards Committee meeting in Sidney, British Columbia, in 1980 included from left to right: Jim Crease (now retired), Werner Kroebe (deceased), Tim M. Dauphinee (retired), Fred Culkin (retired but still active), Charlie Ross (retired), Edward Lyn Lewis (retired), Joris Gieskes (retired), Selim Morcos (active), Alain Poisson (active), Oleg I. Mamayev (deceased), Frank J. Millero (active), Nick P. Fofonoff (deceased), Ron G. Perkin (retired but still active), Fred Fisher (deceased), Maurice Ménaché (deceased).

## ABSOLUTE SALINITY OF SEAWATER

Millero et al. (1976c) first used the absolute ( $S_A$ ) or true ( $S_T$ ) salinity in  $\text{g kg}^{-1}$  of seawater (UNESCO, 1985), suggesting that the densities and other thermodynamic properties of most dilute natural waters were similar to seawater at the same absolute salinity. This was demonstrated to be the case for rivers, lakes, and most estuarine waters (Millero, 1975, 1984; Millero et al., 1976d). As discussed earlier, determination of salinity by drying and weighing presents some difficulties. At the temperature necessary to drive off the water, the bicarbonates and carbonates are decomposed, with the loss of  $\text{CO}_2$ ,  $\text{Br}_2$ ,  $\text{Cl}_2$ , and boric acid.

More reliable estimates of absolute salinity can be made from measurements of the major components of seawater. Forchhammer (1865) made

the first extensive investigations of the major inorganic components of surface seawater. He determined the major ionic concentrations of  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{K}^+$  directly by chemical precipitation techniques and  $\text{Na}^+$  by difference. Dittmar (1884) made measurements of major components of surface and deep seawater ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ ) relative to chlorinity. His results for the major components were in

reasonable agreement with the results of Forchhammer (1865), except for  $\text{Ca}^{2+}$  in deep waters. The higher concentrations of  $\text{Ca}^{2+}$  in deep waters are due to the dissolution of  $\text{CaCO}_3$  (Millero, 2006). Studies by Culkin and Cox (1966) and Riley and Tongudai (1967) also showed that the values of  $\text{Ca}^{2+}$  in deep waters are higher than surface waters. The results of Dittmar (1884) were recalculated by Lyman and Fleming (1940) using more modern atomic weights. Table 1 compares the estimate of  $S_A$  from various composition studies of the major components of seawater. It is interesting to note that the estimates of Lyman and Fleming (1940) based on the measurements of Dittmar (1884) are in good agreement with the values based on the more modern measurements (Millero, 2006; Millero et al., 2008a).

Most seawater density and other physical property definitions have been based on “standard seawater” collected in the North Atlantic, and all of the thermodynamic property measurements were made on this standard seawater with a known chlorinity (Millero, 1982, 1983). The conversion to salinity was made using Equation 4. As part of the development of the new thermodynamic equation of state for seawater, the

Table 1. The estimate of  $S_A$  in seawater from composition studies of the major components of seawater by various workers at  $\text{Cl}(\text{‰}) = 19.274$ .

Reference	Equation	$S_A$
Forchhammer (1865)	$S_A = 1.812 \text{ Cl}(\text{‰})$	35.11
Dittmar (1884)	$S_A = 1.806 \text{ Cl}(\text{‰})$	34.98
Lyman and Fleming (1940)	$S_A = 1.8148 \text{ Cl}(\text{‰})$	35.160
Millero (2006)	$S_A = 1.8154 \text{ Cl}(\text{‰})$	35.171
Millero et al. (2008a)	$S_A = 1.81505 \text{ Cl}(\text{‰})$	35.165 04



composition of seawater was reexamined (Millero et al., 2008a). The results were used to define reference salinity ( $S_R$ ) that is related to practical salinity by

$$S_R = (35.165\ 04/35) \text{ g kg}^{-1} \times S_p. \quad (5)$$

The value of  $S_R$  provides the best estimate of the absolute salinity of standard seawater that was used in physical property measurements. The values of  $S_R$  are used as the concentration variable for the thermodynamic functions of seawater, an SI-based extension of practical salinity that can be used to examine natural composition anomalies and as a theoretical model for the electrolyte mixture.

### EFFECT OF CHANGES IN THE COMPOSITION ON SALINITY

The composition of the dissolved material in seawater is not totally constant; rather, it varies a little from one ocean basin to another. Brewer and Bradshaw (1975) suggested that changes in the composition of deep seawater can affect the conductivity-density relationship. They pointed out that these small changes in density could affect the global circulation of world ocean waters along constant density surfaces. This observation led to a series of papers that examined the limitation of the density-conductivity relationship (Millero et al., 1976a,b,c,d, 1978, 2008b, 2009; Poisson et al., 1980b, 1981; Millero, 1984, 2000). Direct density measurements of seawater samples collected in all the major oceans were measured and compared to the international equation of state of seawater. The samples for deep waters were found to be higher than expected due to the addition of  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  from the dissolution of  $\text{CaCO}_3(\text{s})$ , silicic

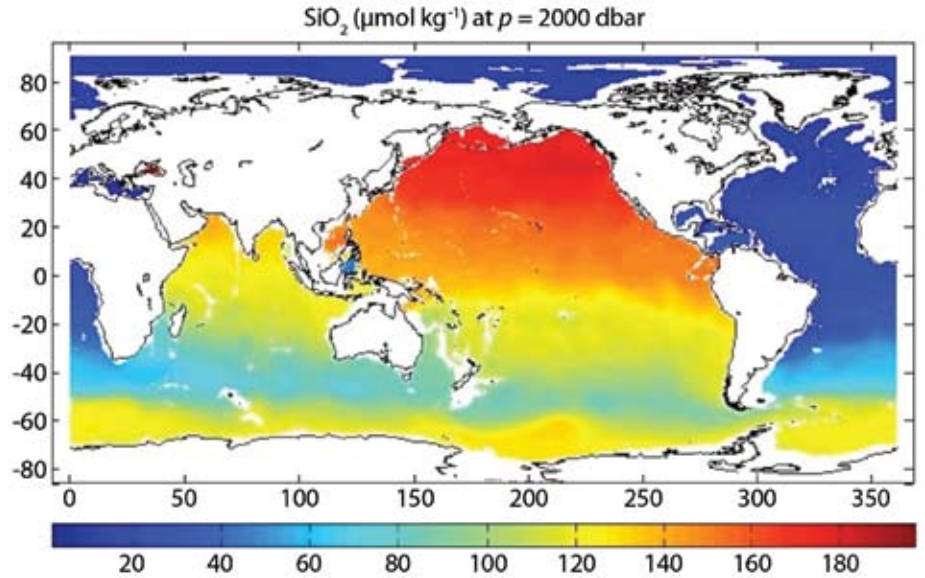


Figure 2. The changes in the concentrations of silicate ( $\mu\text{mol kg}^{-1}$ ) in the Pacific Ocean at a depth of 2000 dbar (McDougall et al., 2009).

acid ( $\text{Si}(\text{OH})_4$ ) from the dissolution of  $\text{SiO}_2(\text{s})$ ,  $\text{CO}_2$ ,  $\text{NO}_3^-$ , and  $\text{PO}_4^{3-}$  from the oxidation of plant material (as predicted by Brewer and Bradshaw, 1975).

Changes in the absolute salinity ( $\delta S_A$ ) of a seawater sample due to the addition of solutes is related to the differences between value with the added solutes ( $S_A$ ) and reference salinity,

$$\delta S_A = S_A - S_R. \quad (6)$$

The value of  $\delta S_A$  can be estimated from the difference,  $\Delta\rho/(\text{kg m}^{-3})$ , between the measured density and the value calculated from TEOS-10 at the  $S_R$  of the sample (Millero and Poisson, 1981a):

$$\delta S_A = \Delta\rho/0.75179 \text{ kg m}^{-3}/(\text{g kg}^{-1}). \quad (7)$$

The values of  $\delta S_A$  calculated in this manner can be fit to linear functions of the concentration of silicate ( $\Delta\text{Si}(\text{OH})_4$ ) (Brewer and Bradshaw, 1975; Millero et al., 1978, 2008b, 2009; Millero, 2000; McDougall et al., 2009). The fit of McDougall et al. (2009) applicable globally is

$$\delta S_A/(\text{g kg}^{-1}) = 98.24 \cdot 10^{-6} (\text{SiO}_2)/\mu\text{mol kg}^{-1}. \quad (8a)$$

The standard error in this fit is  $0.0054 \text{ g kg}^{-1}$  (McDougall et al., 2009). Figure 2 shows the values of  $\Delta\text{Si}(\text{OH})_4$  along 2000 db in the Pacific Ocean (from McDougall et al., 2009). A better fit to the data in each ocean basin was found by separating the data south of  $30^\circ\text{S}$  (the Southern Ocean fit) from separate basin-specific fits for data north of  $30^\circ\text{S}$ . The Southern Ocean fit is

$$\delta S_A/(\text{g kg}^{-1}) = 74.884 \cdot 10^{-6} (\text{SiO}_2)/\mu\text{mol kg}^{-1} \text{ Southern Ocean}, \quad (8b)$$

while the fits for the data north of  $30^\circ\text{S}$  in the Pacific, Indian, and Atlantic oceans are (for latitudes  $S$ )

$$\delta S_A/(\text{g kg}^{-1}) = 74.884 \cdot 10^{-6} (1 + 0.3622[\lambda/30^\circ + 1] (\text{SiO}_2)/\mu\text{mol kg}^{-1}) \text{ Pacific Ocean}, \quad (9)$$

$$\delta S_A/(\text{g kg}^{-1}) = 74.884 \cdot 10^{-6} (1 + 0.3861[\lambda/30^\circ + 1] (\text{SiO}_2)/\mu\text{mol kg}^{-1}) \text{ Indian Ocean}, \quad (10)$$

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 \cdot 10^{-6} (1 + 1.0028[\lambda/30^\circ + 1] (\text{SiO}_2) / \mu\text{mol kg}^{-1}) \text{ Atlantic Ocean.} \quad (11)$$

These three fits are intended to be used from 30°S through the equator and up to the northernmost extent of these ocean basins (McDougall et al., 2009). Figure 3 shows the resultant values of  $\delta S_A$  in a section along 180°E in the Pacific Ocean (McDougall et al., 2009). These values are some of the highest in the world ocean and range from 0.025 g kg<sup>-1</sup> in the north to 0.005 g kg<sup>-1</sup> in the South Pacific. Recent density measurements from the Arctic Ocean indicate that the surface values are much higher than expected due to high concentrations of dissolved organic carbon (DOC) and total alkalinity (TA) from river waters. The deep waters with few nutrients and normalized alkalinity (NTA = TA / 35/S) are similar to North Atlantic surface waters (2300 μmol kg<sup>-1</sup>) and show densities that are slightly lower than

expected (-0.005 kg m<sup>-3</sup>). This observation appears to be due to the DOC being lower in Arctic deep waters than in North Atlantic surface waters. Density measurement of samples collected at various locations will be continued in order to develop equations that can be used throughout the world ocean.

### EQUATION OF STATE FOR SEAWATER

The early equation of state for seawater was based on the density measurements of Forch et al. (1900) and expressed by Knudsen (1901). The high pressure (to 600 bars) measurements of Ekman (1908) were used for deep waters. These combined results were reformulated by Fofonoff and et al. (1958) and Sweers (1971) and were used for about 70 years, from approximately 1908 to 1980. A number of studies suggested that the one-atmosphere equations of Knudsen (1901) might be in error. Thompson and

Wirth (1931) found that their measured densities were higher by 0.020 kg m<sup>-3</sup>. Wirth (1940) also pointed out some problems with the Knudsen (1901) results. Cox et al. (1970) measurements of  $S_p = 35$  seawater found that the Knudsen (1901) results were too high by 0.013 kg m<sup>-3</sup>.

Ekman (1908) calculated the pressures of his measurements using the pure water results of Amagat (1893). Eckart (1958) questioned these results due to a possible error in the pressure gauge used by Amagat (1893). Li (1967), however, showed that Eckart (1958) made errors in his pressure calculations. Crease (1962) showed that the compressibilities calculated from the sound speed measurements of Wilson (1960) were in good agreement with the Ekman (1908) results at high pressures, but were different at low pressures. Newton and Kennedy (1965) and Wilson and Bradley (1968) measured the volumes as a function of pressure. Both studies had large errors at high pressures (0.200 m<sup>3</sup> kg<sup>-1</sup>). This was the equation-of-state situation when I entered the fray.

Before leaving New Jersey, I obtained copies of all the papers published on the PVT (pressure, volume, temperature) properties of aqueous electrolyte solutions. I later published a review article summarizing all the work done on the subject from 1700 to the 1970s (Millero, 1971). Shortly after arriving in Miami, I built a magnetic float densimeter that could be used to measure the densities of seawater and other solutions to a high precision (Millero, 1967). Figure 4 shows a sketch of the system, which was similar to the one I used during my summer work at the National Bureau of Standards (Millero, 1968). We made

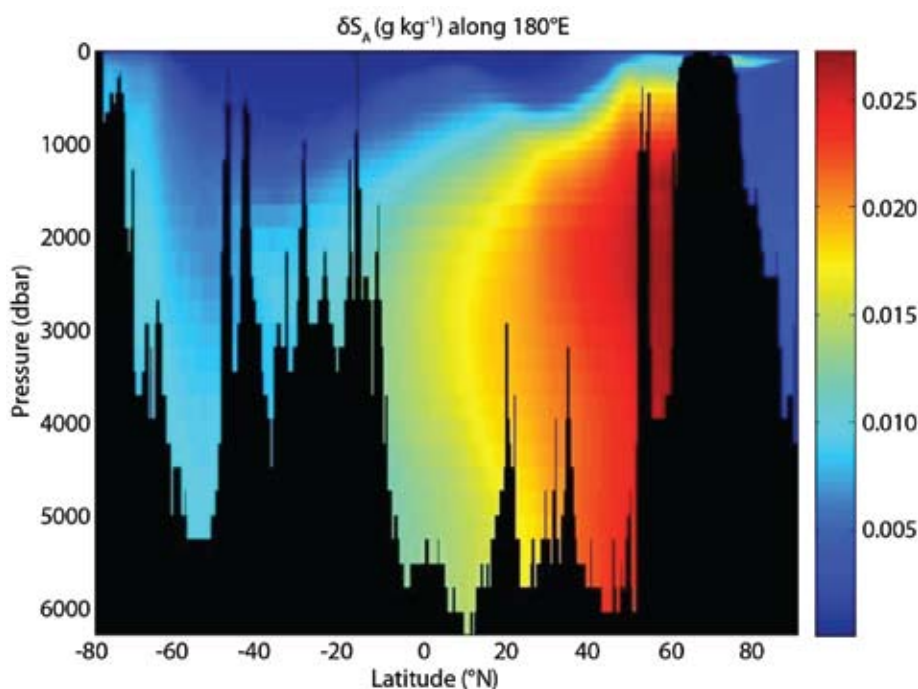


Figure 3. A Section of  $\delta S_A$  in the Pacific Ocean along 180°E (McDougall et al., 2009).

density measurements with the system on seawater (Millero and Lepple, 1973; Millero et al., 1976a) and a number of other major sea salts (Millero and Knox, 1973). Millero and Lepple (1973) made measurements on standard seawater ( $Cl(\%) = 19.374$ ) and artificial seawater from 0 to 40°C. These results were  $0.007 \pm 0.003 \text{ kg m}^{-3}$  lower than Knudsen (1901),  $0.019 \pm 0.004 \text{ kg m}^{-3}$  lower than Cox et al. (1970), and agreed to  $0.002 \pm 0.013 \text{ kg m}^{-3}$  with artificial seawater from 0 to 30°C. We attributed the offsets of earlier workers to the water used to calibrate the systems used by Knudsen (1901) and Cox et al. (1970). It should also be pointed out that the artificial seawater model used in this study (Kester et al., 1967) resulted in densities that agreed to  $\pm 0.020 \text{ kg m}^{-3}$  with the measurements on seawater. This result led us to believe that the composition assumed by Kester et al. (1967) for artificial seawater was close to the true composition of real seawater.

Millero et al. (1976c) made extensive measurements on the density of seawater from 0 to 40°C and  $Cl(\%)$  from 0.2 to 22.14. Poisson et al. (1980a) later made density measurements over a similar range of temperature and salinity using a vibrating tube densimeter similar to the one used in our laboratory (see Figure 5). Our measured densities were combined with the measurements of Poisson et al. (1980a) to formulate the one-atmosphere equation of state (Millero and Poisson, 1981a,b). It should be pointed out that all of these density measurements were made on seawater with a known chlorinity, and the salinities were estimated using Equation 4. More recent density measurements of seawater from 0.1 to 40 and 0 to 40°C and with

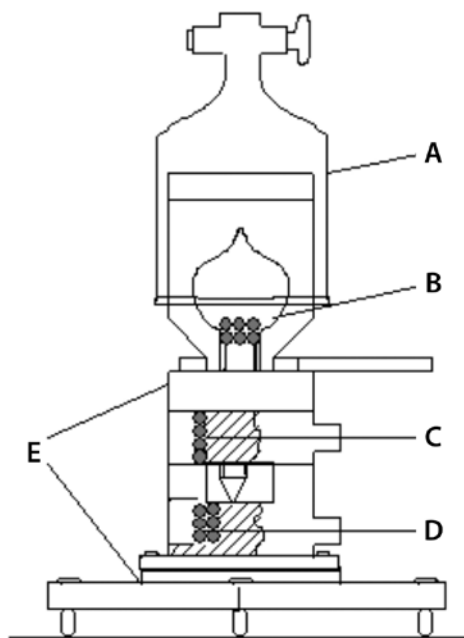


Figure 4. Magnetic float densimeter. (A) Glass solution container. (B) Magnetic glass float. (C) Pull-down solenoid coil. (D) Main solenoid coil. (E) Brass support and leveling platform. The force between the magnet and the induced field created by the coil is determined by measuring the current as a function of floats with added weight made of platinum.

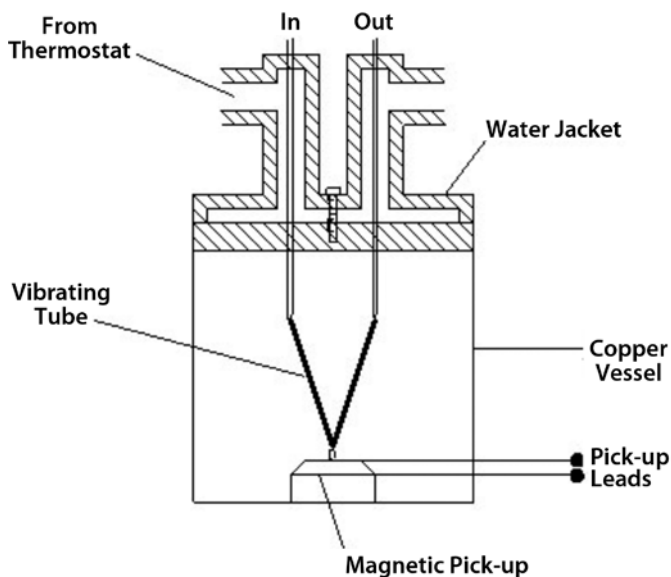


Figure 5. Sketch of the vibrating tube densimeter. The period of the vibrating tube is directly proportional to the density squared. Water and air or  $N_2$  of known density are used to calibrate the system.

a known practical salinity  $S_p$  (Millero and Huang, 2009) were in good agreement ( $0.003 \text{ kg m}^{-3}$ ) with the Millero and Poisson (1981a) one-atmosphere equation of state for seawater. This is important because it demonstrates that the earlier density measurements made at a known chlorinity are consistent with

the results from seawater with a known practical salinity.

To obtain the highest precision in our studies, all of our PVT measurements were made relative to pure water. The accuracies of these studies depended on reliable densities and compressibilities for water. At one atmosphere, getting



precise measurements was not a problem because reliable values were available for the densities of water from 0 to 150°C and the compressibilities from 0 to 100°C (Kell, 1975) based on the sound speed measurements of Del Grosso and Mader (1972a). This study led us to examine the PVT properties of water at high pressures. The most reliable high-pressure PVT properties for water

at the time were thought to be from the studies of Kell and Whalley (1965). They determined the specific volume of water from 0 to 150°C and 0 to 1000 bars of applied pressure. We had some doubt about the reliability of their compressibilities because their one-atmosphere values did not agree with our compressibility studies made at low pressures (Lepple and Millero, 1971) as well as the values determined from sound speeds (Kell, 1975). The compressibilities derived from sound speeds have been shown to be more accurate than direct measurements (Wang and Millero, 1973; Chen et al., 1977). At the time, the only high-pressure sound-speed measurements for water were carried out by Wilson (1959) and Barlow and Yazgan (1967). Unfortunately, Del Grosso and Mader (1972b) did not make any high-pressure measurements of sound speeds in water. Because the Wilson (1959) results at one atmosphere did not agree with the measurements of Del Grosso and Mader (1972b), we attempted to correct the Wilson (1959) measurements (Chen and Millero, 1976a). We used these adjusted sound speeds to derive an equation of state for water (Fine and Millero, 1973; Chen and Millero, 1981). Our high-pressure results for water did not agree with the measurements of Kell and Whalley (1965), who found that this offset was due to hysteresis of the stainless steel vessel they used to make their measurements. Later, Kell and Whalley (1975) used sound speed measurements to recalibrate the vessel and obtained volume at high pressure that agreed with those derived from sound speeds (Fine and Millero, 1973).

As part of our early pressure studies, we developed a system (Figure 6) that

could be used to measure the compressibility of seawater near one atmosphere (Millero et al., 1969). It was also used to measure the compressibility of water (Millero et al., 1969), seawater (Lepple and Millero, 1971), deuterium oxide (Millero and Lepple, 1971), and some major sea salts (Millero et al., 1974). The one-atmosphere results for water were found to be in good agreement with the values calculated from the sound speed measurements of Wilson (1959) and later studies by Del Grosso and Mader (1972a). Neither study agreed with the earlier work of Ekman (1908) due to the problems mentioned earlier with calibrating the pressure of his system.

We developed a high-pressure version of the magnetic float densimeter (Millero et al., 1972) to measure the density of seawater as a function of pressure (see Figure 7). The system was used to make high-pressure densities of seawater (Emmet and Millero, 1974; Chen and Millero, 1976b), deuterium oxide (Emmet and Millero, 1975), and a number of sea salts (Chen et al., 1980).

We used a sing-around sound velocimeter calibrated at one atmosphere using the water values of Del Grosso and Mader (1972a) to study sound speeds in seawater (Millero and Kubinski, 1975) as well as in a number of sea salts (Millero et al., 1977). The one-atmosphere seawater results were in good agreement with those of Del Grosso and Mader (1972a).

We developed a high-pressure vessel for measuring the speed of sound at high pressures (Chen and Millero, 1977) and calibrated it using Wilson's adjusted sound speeds in water (Chen and Millero, 1976a). We later found that the Wilson (1959) results at low temperature

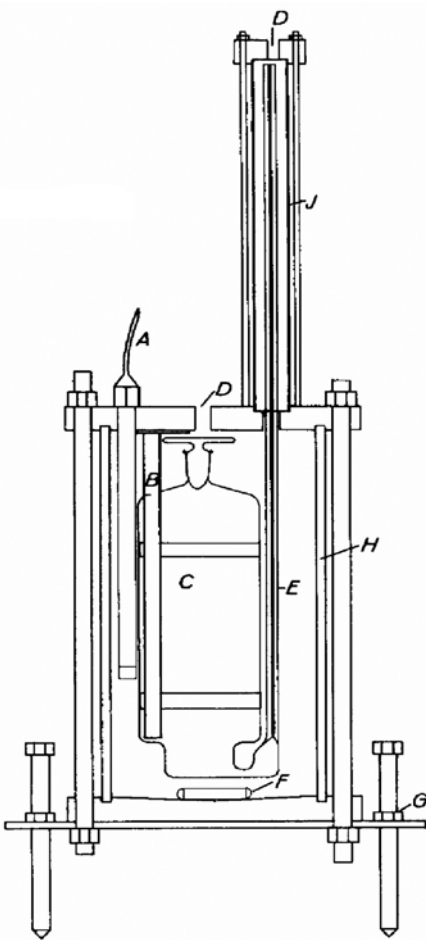


Figure 6. Dilatometer used to make low-pressure compressibility measurements. The cell (C) contains mercury and the solution. The metal pressure vessel contains pressurized water that is stirred (F). The system is leveled (G) and the mercury in the capillary (J) is measured with a cathetometer. The pressure is applied through the opening at the top (D). The pressure is measured with a pressure gauge and the temperature monitored with a temperature probe (A).

and high pressures adjusted by Chen and Millero (1977) were in error and led to errors in our high-pressure sound-speed equations for seawater in this range (Spiesberger and Metzger, 1991). Part of this problem was due to the lack of high-pressure water measurements with the system used by Del Grosso and Mader, and an attempt was made to correct this error (Millero and Li, 1994). Because we measured the difference between the sound speed of seawater and water, this limitation did not affect the precision of the measurements.

The equations of state for seawater derived from sound speeds (Chen and Millero, 1976a, 1978) and direct measurements (Chen and Millero, 1976b) were in good agreement (Fine et al., 1974, Millero et al., 1980, 1981). Around the same time, Bradshaw and Schleicher (1970, 1976) made very precise and accurate measurements of the thermal expansibility and compressibility of seawater as a function of pressure. They also made some measurements on the PVT properties of water (Bradshaw and Schleicher, 1986) over the oceanographic range of pressure and temperature that were in good agreement with our studies (Fine and Millero, 1973; Millero and Chen, 1975; Chen et al., 1977, 1981). Their expansion and compression measurements were made with a high-pressure dilatometer that was similar to the system we used near one atmosphere (Figure 6).

The studies of our group and of Bradshaw and Schleicher were used to formulate the high-pressure portion of the 1980 equation of state (UNESCO, 1981a; Millero et al., 1980, 1981). A thorough summary of the formulation of the equation of state is given elsewhere

(UNESCO, 1981). The form of the equation of state is a second-degree secant bulk modulus ( $K = P v^0 / (v^0 - v^P)$ , where  $v^0$  and  $v^P$  are the specific volume in  $\text{cm}^3$  at applied pressure 0 and  $P$  in bars). JPOTS approved the International Equation of State of Seawater (EOS-80) in 1980 (ICES et al., 1981).

The thermodynamic properties of seawater were also examined by my group (Millero, 1983). These measurements include enthalpy (Millero et al., 1973a) and heat capacity (Millero et al., 1973b). Millero and Leung (1976) used these measurements along with the osmotic coefficients of Robinson (1954) and those calculated from the freezing point of seawater (Doherty and Kester, 1974) to construct a free-energy equation for seawater. They used an extended Debye Hückel equation to represent the thermochemical properties of seawater. The results in the oceanographic range of temperature and salinity were in good agreement with the studies of Bromley (1968a,b) and co-workers (Bromley et al., 1967, 1970) over a wider range of temperature and salinity. This work is summarized in a review article (Millero, 1983).

In all our thermodynamic studies of seawater, we were interested in developing ionic interaction models for use in estimating the properties of seawater and other natural waters (Millero, 1974). In recent years, we have used the ionic interaction model of Pitzer (1991) to examine the PVT and thermochemical properties of seawater (Pierrot and Millero, 2000; Millero and Pierrot, 2005). These models allow reasonable estimates of the properties of seawater as well as other electrolyte mixtures over a wide range of pressure and temperature (Millero, 2009).

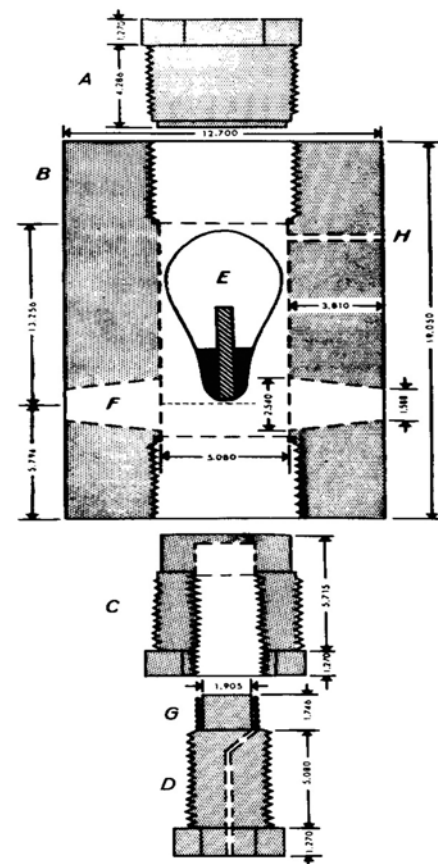


Figure 7. The high-pressure magnetic float densimeter used to measure densities at high pressure.

## A NEW THERMODYNAMIC EQUATION OF SEAWATER (TEOS-10)

The Practical Salinity Scale (PSS-78) and the International Equation of State of Seawater (EOS-80) have served the oceanographic community for over 30 years. JPOTS (Fofonoff and Millard, 1983) also “blessed” equations for the specific heat capacity (Millero et al., 1973b), sound speed in seawater (Chen and Millero, 1977), and the freezing point temperature derived from the free energy of seawater (Millero and Leung, 1976). JPOTS approved equations for the conversion between hydrostatic pressure and depth, the calculation of the adiabatic lapse rate, and the calculation of

potential temperature (Bryden, 1973). A number of problems articulated in recent years suggest that the thermodynamics of the EOS-80 equations are flawed and that it is time to redefine the thermodynamic properties of seawater (IOC et al., 2010). Some of the flaws include:

1. The equations expressing EOS-80 are not thermodynamically consistent with each other.
2. A more accurate thermodynamic description of pure water has appeared (IAPWS, 2009b).
3. More accurate thermodynamic properties of seawater over a wider range of temperature and salinity are available.
4. The densities of deep seawaters were found to be different from EOS-80

calculations due to changes in composition (Millero, 2000).

5. Modeling of the global heat engine needs accurate expressions for the entropy, enthalpy, and internal energy of seawater so that heat fluxes can be more accurately determined in the ocean (McDougall, 2003).
6. The EOS-80 equations were based on the International Temperature Scale of 1968 (ITS-68), while field measurements are now made on ITS-90 revised by the International Union of Pure and Applied Chemistry (IUPAC).
7. New values have been adopted for the atomic weights of elements (Weiser, 2006).

In 2005, SCOR and IAPSO established Working Group 127 on the Thermodynamics and Equation of State of Seawater (referred to as WG 127). The task of the group was to development recommendations on how the current EOS-80 should be updated, extended, and improved (see also the SCOR Web page <http://www.jhu.edu/scor/wg127.htm>). The first WG 127 meeting (Figure 8), chaired by Trevor McDougall, was in Warnemünde, Germany, from May 2–5, 2006, at the Leibniz Institute for Baltic Sea Research (IOW). The group agreed that future recommendations will rely on seven basic statements:

1. All thermodynamic formulas will be expressed using ITS-90.
2. The basis for the salinity definition is the Practical Salinity Scale of 1978, with extensions, in particular for the description of very low and very high salinities.
3. The physico-chemical properties of sea salt will be expressed using the atomic weights of IUPAC 2001.
4. The reference state of seawater at vanishing salinity is the international pure water standard IAPWS-95 (IAPWS, 2009b).
5. The properties of seawater will be expressed using a Gibbs function, which describes water property changes in the presence of sea salt.
6. Freezing points and properties of sea ice will be computed from the chemical potentials of ice and of water in seawater.
7. Vapor pressures and evaporation heats will be computed from the chemical potentials of vapor and of water in seawater.

WG 127 worked on the thermodynamic equation of seawater over the



Figure 8. Participants attending the first Scientific Committee on Oceanic Research/International Association of Physical Sciences of the Oceans (SCOR/IAPSO) Working Group 127 on the Thermodynamics and Equation of State of Seawater (WG 127) meeting held May 2–5, 2006, in Warnemünde, Germany, included, from left to right, Chen-Tung Arthur Chen (IMGC, Kaohsiung, Taiwan), Frank J. Millero (RSMAS, Miami, USA), Brian A. King (NOC, Southampton, UK), Rainer Feistel (IOW, Warnemünde, Germany), Dan Wright (BIO, Dartmouth, Canada), Trevor J. McDougall (CSIRO, Hobart, Australia), and Giles M. Marion (DRI, Reno, USA).



next three years. The second meeting of the group was in Italy (Figure 9), the third meeting was in Göttingen, Germany (Figure 10), and the final meeting was in Arnhem, Netherlands. All of the initial papers from WG 127 were presented in Berlin at the International Association for the Properties of Water and Steam (IAPWS) meeting in 2008.

WG 127 developed a collection of algorithms that incorporate our best knowledge of the thermodynamics of seawater (IOC et al., 2010). Unlike for EOS-80, all the thermodynamic properties were fitted to a free-energy equation (Alberty, 2001; Fofonoff, 1962; Feistel, 1993, 2003, 2008, 2010; Feistel and Hagan, 1995; Feistel and Wagner, 2005, 2006), based on the pioneering work of J.W. Gibbs (1873). TEOS-10 can be used to calculate all of the thermodynamic properties of water, ice, seawater, and sea air (Feistel et al., 2008). All the effects of changes in  $S_A$ ,  $T$ , and  $P$  can be derived from the appropriate differentiation of the equation, and the variables are self consistent. The Gibbs free-energy equation (Feistel, 1993, 2003, 2008, 2010) is a function of absolute salinity ( $S_A$ ), temperature, and pressure. The use of  $S_A$  rather than  $S_p$  is a major departure from EOS-80. TEOS-10 strongly recommends that practical salinity be retained in national databases and absolute salinity be used in publications.

Absolute salinity as used in the TEOS-10 Gibbs function is based on measurements of density and correlation functions that are derived from these direct-density measurements. In the presence of composition anomalies and the complications caused by biogeochemical cycling in the ocean, there are ongoing research questions concerning



Figure 9. Participants attending the second SCOR/IAPWS WG 127 meeting in Reggio Calabria, Italy, in 2007, included from left to right, Giles M. Marion (DRI, Reno, USA), Rainer Feistel (IOW, Warnemünde, Germany), Trevor J. McDougall (CSIRO, Hobart, Australia), Brian A. King (NOC, Southampton, UK), Chen-Tung Arthur Chen (IMGC, Kaohsiung, Taiwan), David R. Jackett (CSIRO, Hobart, Australia), Dan Wright (BIO, Dartmouth, Canada), Petra Spitzer (Physikalisch-Technische Bundesanstalt, Germany), and Frank J. Millero (RSMAS, Miami, USA).

the calculation and even the meaning of absolute salinity. Absolute salinity, as used above and as needed for the salinity argument of the TEOS-10 Gibbs function, may also be called “density salinity” in the sense that it is the salinity variable that gives the most accurate values of density when used in TEOS-10.

IOC et al. (2010) provides a seawater manual that gives details of TEOS-10 and describes the development and use of the equation of state. The manual’s appendices include:

- A. Background and theory underlying the use of the Gibbs function of seawater
- B. Derivation of the First Law of Thermodynamics
- C. Publications describing the TEOS-10 thermodynamic descriptions of

seawater, ice, and moist air

- D. Fundamental constants
- E. Algorithm for calculating practical salinity
- F. Coefficients of the IAPWS-95 Helmholtz function of fluid water (with extension down to 50 K)
- G. Coefficients of the pure liquid water Gibbs function of IAPWS-09 (IAPWS, 2009c)
- H. Coefficients of the saline Gibbs function for seawater of IAPWS-08 (IAPWS, 2008)
- I. Coefficients of the Gibbs function of ice Ih of IAPWS-06 (IAPWS, 2009a)
- J. Coefficients of the Helmholtz function of moist air of IAPWS-10 (a guideline is in preparation for the September 2010 meeting of IAPWS in Niagara Falls, Canada)





Figure 10. Participants attending the third SCOR/IAPSO WG 127 meeting in Götz, Germany, September 3–9, 2008, included, from left to right, Frank J. Millero (RSMAS, Miami, USA), Petra Spitzer (Physikalisch-Technische Bundesanstalt, Germany), Nigel Higgs (Ocean Scientific International Ltd), Trevor J. McDougall (CSIRO, Hobart, Australia), Chen-Tung Arthur Chen (IMGCC, Kaohsiung, Taiwan), Giles M. Marion (DRI, Reno, USA), David R Jackett (CSIRO, Hobart, Australia), Rainer Feistel (IOW, Warnemünde, Germany), Steffen Seitz (Physikalisch-Technische Bundesanstalt, Germany), Brian A. King (NOC, Southampton, UK), Dan Wright (BIO, Dartmouth, Canada).

- K. Coefficients of a 25-term expression for the density of seawater in terms of  $\theta$  and  $\Theta$
  - L. Recommended nomenclature, symbols, and units in oceanography
  - M. Seawater-Ice-Air library of computer software
  - N. Gibbs-Seawater library of computer software
  - O. Checking the Gibbs function of seawater against the original thermodynamic data
  - P. Thermodynamic properties based on  $g(S_A, t, p)$ ,  $\bar{h}(S_A, \eta, p)$ ,  $\tilde{h}(S_A, \theta, p)$ , and  $\dot{h}(S_A, \Theta, p)$
- The manual gives an excellent introduction to the thermodynamic equation of seawater and will be a useful text to oceanographic researchers and students.

The Intergovernmental Oceanographic Commission approved the following resolution at its 25<sup>th</sup> Assembly in June 2009:

*The TEOS-10 thermodynamic description of seawater, of ice and of moist air is recommended for use by oceanographers in place of the International Equation Of State–1980 (EOS-80). The software to implement this change is available at the web site [www.TEOS-10.org](http://www.TEOS-10.org).*


Extensions of the thermodynamic properties as a function of pressure and temperature are continuing. As mentioned earlier, density measurements of seawater have been made from 0 to 90°C and  $S_A$  to 70 g kg<sup>-1</sup> (Millero

and Huang, 2009). Safarov et al. (2009) extended the density measurements of standard seawater to 200°C and applied pressures up to 1400 bars. The free energy of seawater has been expanded from 0 to 250°C and  $S_A$  of 180 g kg<sup>-1</sup> (Millero and Pierrot, 2008). Feistel and Marion (2007) also developed a Pitzer (1991) model for seawater. Feistel (2008) extended the free-energy equation (Feistel, 2003) to higher temperatures (80°C) and absolute salinities ( $S_A = 120$  gm kg<sup>-1</sup>). More recently, Feistel (2010) also extended the free-energy equations for seawater to higher temperatures (90°C) and salinities (70 g kg<sup>-1</sup>).

In summary, TEOS-10 will be a useful tool for modeling the thermodynamic properties of seawater over a wide range of salinity, temperature, and pressure. It should be also useful in introducing the field to oceanography students studying the thermodynamics of seawater.

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and corrections on the first draft of this review. He was very instrumental in getting our working group (SCOR WG 127) to complete the new thermodynamic equation of state, TEOS-10. I also wish to note the recent sudden passing of Daniel Wright, a member of the SCOR/IAPSO working group. He was an important part of the TEOS-10 scientific team and will be greatly missed by all of us. 

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