

Background to TEOS-10

This is from section 1 of the TEOS-10 Manual (IOC *et al.* (2010))

1. Introduction

1.1 Oceanographic practice 1978 - 2009

The Practical Salinity Scale, PSS-78, and the International Equation of State of Seawater (Unesco (1981)) which expresses the density of seawater as a function of Practical Salinity, temperature and pressure, have served the oceanographic community very well for thirty years. The Joint Panel on Oceanographic Tables and Standards (JPOTS) (Unesco (1983)) also promulgated the Millero, Perron and Desnoyers (1973) algorithm for the specific heat capacity of seawater at constant pressure, the Chen and Millero (1977) expression for the sound speed of seawater and the Millero and Leung (1976) formula for the freezing point temperature of seawater. Three other algorithms supported under the auspices of JPOTS concerned the conversion between hydrostatic pressure and depth, the calculation of the adiabatic lapse rate, and the calculation of potential temperature. The expressions for the adiabatic lapse rate and for potential temperature could in principle have been derived from the other algorithms of the EOS-80 set, but in fact they were based on the formulas of Bryden (1973). We shall refer to all these algorithms jointly as 'EOS-80' for convenience because they represent oceanographic best practice from the early 1980s to 2009.

1.2 Motivation for an updated thermodynamic description of seawater

In recent years the following aspects of the thermodynamics of seawater, ice and moist air have become apparent and suggest that it is timely to redefine the thermodynamic properties of these substances.

- Several of the polynomial expressions of the International Equation of State of Seawater (EOS-80) are not totally consistent with each other as they do not exactly obey the thermodynamic Maxwell cross-differentiation relations. The new approach eliminates this problem.
- Since the late 1970s a more accurate and more broadly applicable thermodynamic description of pure water has been developed by the International Association for the Properties of Water and Steam, and has appeared as an IAPWS Release (IAPWS-95). Also since the late 1970s some measurements of higher accuracy have been made of several properties of seawater such as (i) heat capacity, (ii) sound speed and (iii) the temperature of maximum density. These can be incorporated into a new thermodynamic description of seawater.
- The impact on seawater density of the variation of the composition of seawater in the different ocean basins has become better understood. In order to further progress this aspect of seawater, a standard model of seawater composition is needed to serve as a generally recognised reference for theoretical and chemical investigations.
- The increasing emphasis on the ocean as being an integral part of the global heat engine points to the need for accurate expressions for the entropy, enthalpy and internal energy of seawater so that heat fluxes can be more accurately determined in the ocean and across the interfaces between the ocean and the atmosphere and ice (entropy, enthalpy and internal energy were not available from EOS-80).

- The need for a thermodynamically consistent description of the interactions between seawater, ice and moist air; in particular, the need for accurate expressions for the latent heats of evaporation and freezing, both at the sea surface and in the atmosphere.
- The temperature scale has been revised from IPTS-68 to ITS-90 and revised IUPAC (International Union of Pure and Applied Chemistry) values have been adopted for the atomic weights of the elements (Wieser (2006)).

1.3 SCOR/IAPSO WG127 and the approach taken

In 2005 SCOR (Scientific Committee on Oceanic Research) and IAPSO (International Association for the Physical Sciences of the Ocean) established Working Group 127 on the “Thermodynamics and Equation of State of Seawater” (henceforth referred to as WG127). This group has now developed a collection of algorithms that incorporate our best knowledge of seawater thermodynamics. The present document summarizes the work of SCOR/IAPSO Working Group 127.

To compute all thermodynamic properties of seawater it is sufficient to know one of its so-called thermodynamic potentials (Fofonoff 1962, Feistel 1993, Alberty 2001). It was J.W. Gibbs (1873) who discovered that *“an equation giving internal energy in terms of entropy and specific volume, or more generally any finite equation between internal energy, entropy and specific volume, for a definite quantity of any fluid, may be considered as the fundamental thermodynamic equation of that fluid, as from it... may be derived all the thermodynamic properties of the fluid (so far as reversible processes are concerned).”*

The approach taken by WG127 has been to develop a Gibbs function from which all the thermodynamic properties of seawater can be derived by purely mathematical manipulations (such as differentiation). This approach ensures that the various thermodynamic properties are self-consistent (in that they obey the Maxwell cross-differentiation relations) and complete (in that each of them can be derived from the given potential).

The Gibbs function (or Gibbs potential) is a function of Absolute Salinity S_A (rather than of Practical Salinity S_p), temperature and pressure. Absolute Salinity is traditionally defined as the mass fraction of dissolved material in seawater. The use of Absolute Salinity as the salinity argument for the Gibbs function and for all other thermodynamic functions (such as density) is a major departure from present practice (EOS-80). Absolute Salinity is preferred over Practical Salinity because the thermodynamic properties of seawater are directly influenced by the mass of dissolved constituents whereas Practical Salinity depends only on conductivity. Consider for example exchanging a small amount of pure water with the same mass of silicate in an otherwise isolated seawater sample at constant temperature and pressure. Since silicate is predominantly non-ionic, the conductivity (and therefore Practical Salinity S_p) is almost unchanged but the Absolute Salinity is increased, as is the density. Similarly, if a small mass of say NaCl is added and the same mass of silicate is taken out of a seawater sample, the mass fraction absolute salinity will not have changed (and so the density should be almost unchanged) but the Practical Salinity will have increased.

The variations in the relative concentrations of seawater constituents caused by biogeochemical processes actually cause complications in even defining what exactly is meant by “absolute salinity”. These issues have not been well studied to date, but what is known is summarized in section 2.5 and appendices A.4, A.5 and A.20. Here it is sufficient to point out that the Absolute Salinity S_A which is the salinity argument of the TEOS-10 Gibbs function is the version of absolute salinity that provides the best estimate of the density of seawater; another name for S_A is “Density Salinity”.

The Gibbs function of seawater, published as Feistel (2008), has been endorsed by the International Association for the Properties of Water and Steam as the Release IAPWS-08. This thermodynamic description of seawater properties, together with the Gibbs function of ice Ih, IAPWS-06, has been adopted by the Intergovernmental Oceanographic Commission at its 25th Assembly in June 2009 to replace EOS-80 as the official description of seawater and ice properties in marine science. The thermodynamic properties of moist air have also recently been described using a Helmholtz function (Feistel *et al.* (2010a), IAPWS (2010)) so allowing the equilibrium properties at the air-sea interface to be more accurately evaluated. The new approach to the thermodynamic properties of seawater, of ice Ih and of humid air is referred to collectively as the “International Thermodynamic Equation Of Seawater – 2010”, or “TEOS-10” for short. Appendix C lists the publications which lie behind TEOS-10.

A notable difference of TEOS-10 compared with EOS-80 is the adoption of Absolute Salinity to be used in journals to describe the salinity of seawater and to be used as the salinity argument in algorithms that give the various thermodynamic properties of seawater. This recommendation deviates from the current practice of working with Practical Salinity and typically treating it as the best estimate of Absolute Salinity. This practice is inaccurate and should be corrected. Note however that we strongly recommend that the salinity that is reported to national data bases remain Practical Salinity as determined on the Practical Salinity Scale of 1978 (suitably updated to ITS-90 temperatures as described in appendix E below).

There are three very good reasons for continuing to store Practical Salinity rather than Absolute Salinity in such data repositories. First, Practical Salinity is an (almost) directly measured quantity whereas Absolute Salinity is generally a derived quantity. That is, we calculate Practical Salinity directly from measurements of conductivity, temperature and pressure, whereas to date we derive Absolute Salinity from a combination of these measurements plus other measurements and correlations that are not yet well established. Practical Salinity is preferred over the actually measured *in situ* conductivity value because of its conservative nature with respect to changes of temperature or pressure, or dilution with pure water. Second, it is imperative that confusion is not created in national data bases where a change in the reporting of salinity may be mishandled at some stage and later be misinterpreted as a real increase in the ocean’s salinity. This second point argues strongly for no change in present practice in the reporting of Practical Salinity S_p in national data bases of oceanographic data. Thirdly, the algorithms for determining the “best” estimate of Absolute Salinity of seawater with non-standard composition are immature and will undoubtedly change in the future, so we cannot recommend storing Absolute Salinity in national data bases. Storage of a more robust intermediate value, the Reference Salinity, S_R (defined as discussed in appendix A.3 to give the best estimate of Absolute Salinity of Standard Seawater) would also introduce the possibility of confusion in the stored salinity values without providing any real advantage over storing Practical Salinity so we also avoid this possibility. Values of Reference Salinity obtained from suitable observational techniques (for example by direct measurement of the density of Standard Seawater) should be converted to corresponding numbers of Practical Salinity for storage, as described in sections 2.3 - 2.5.

Note that the practice of storing one type of salinity in national data bases (Practical Salinity) but using a different type of salinity in publications (Absolute Salinity) is exactly analogous to our present practice with temperature; *in situ* temperature t is stored in data bases (since it is the measured quantity) but the temperature variable that is used in publications is a calculated quantity, being either potential temperature θ or Conservative Temperature Θ .

In order to improve the determination of Absolute Salinity we need to begin collecting and storing values of the salinity anomaly $\delta S_A = S_A - S_R$ based on measured values of density (such as can be measured with a vibrating tube densimeter, Kremling (1971)). The 4-letter GF3 code (IOC (1987)) DENS is currently defined for *in situ* measurements or computed values from EOS-80. It is recommended that the density measurements made with a vibrating beam densimeter be reported with the GF3 code DENS along with the laboratory temperature (TLAB in °C) and laboratory pressure (PLAB, the sea pressure in the laboratory, usually 0 dbar). From this information and the Practical Salinity of the seawater sample, the absolute salinity anomaly $\delta S_A = S_A - S_R$ can be calculated using an inversion of the TEOS-10 equation for density to determine S_A . For completeness, it is advisable to also report δS_A under the new GF3 code DELS.

The thermodynamic description of seawater and of ice Ih as defined in IAPWS-08 and IAPWS-06 has been adopted as the official description of seawater and of ice Ih by the Intergovernmental Oceanographic Commission in June 2009. These new international standards were adopted while recognizing that the techniques for estimating Absolute Salinity will likely improve over the coming decades, and the algorithm for evaluating Absolute Salinity in terms of Practical Salinity, latitude, longitude and pressure will be updated from time to time, after relevant appropriately peer-reviewed publications have appeared, and that such an updated algorithm will appear on the www.TEOS-10.org web site. Users of this software should always state in their published work which version of the software was used to calculate Absolute Salinity.

The more prominent advantages of TEOS-10 compared with EOS-80 are

- The Gibbs function approach allows the calculation of internal energy, entropy, enthalpy, potential enthalpy and the chemical potentials of seawater as well as the freezing temperature, and the latent heats of freezing and of evaporation. These quantities were not available from the International Equation of State 1980 but are essential for the accurate accounting of “heat” in the ocean and for the consistent and accurate treatment of air-sea and ice-sea heat fluxes. For example, a new temperature variable, Conservative Temperature, can be defined as being proportional to potential enthalpy and is a valuable measure of the “heat” content per unit mass of seawater for use in physical oceanography and in climate studies, as it is approximately two orders of magnitude more conservative than potential temperature.
- For the first time the influence of the spatially varying composition of seawater can systematically be taken into account through the use of Absolute Salinity. In the open ocean, this has a non-trivial effect on the horizontal density gradient computed from the equation of state, and thereby on the ocean velocities and heat transports calculated via the “thermal wind” relation.
- The thermodynamic quantities available from the new approach are totally consistent with each other.
- The new salinity variable, Absolute Salinity, is measured in SI units. Moreover the treatment of freshwater fluxes in ocean models will be consistent with the use of Absolute Salinity, but is only approximately so for Practical Salinity.
- The Reference Composition of standard seawater supports marine physicochemical studies such as the solubility of sea salt constituents, the alkalinity, the pH and the ocean acidification by rising concentrations of atmospheric CO₂.

1.4 A guide to this TEOS-10 manual

The remainder of this manual begins by listing (in section 2) the definitions of various thermodynamic quantities that follow directly from the Gibbs function of seawater by simple mathematical processes such as differentiation. These definitions are then followed in section 3 by the discussion of several derived quantities. The computer software to evaluate these quantities is available from two separate libraries, the Seawater-Ice-Air (SIA) library and the Gibbs-SeaWater (GSW) library, as described in appendices M and N. The functions in the SIA library are generally available in basic-SI units (kg kg^{-1} , kelvin and Pa), both for their input parameters and for the outputs of the algorithms. Some additional routines are included in the SIA library in terms of other commonly used units for the convenience of users. The SIA library takes significantly more computer time to evaluate most quantities (approximately a factor of 65 more computer time for many quantities, comparing optimized code in both cases) and provides significantly more properties than does the GSW library. The SIA library uses the world-wide standard for the thermodynamic description of pure water substance (IAPWS-95). Since this is defined over extended ranges of temperature and pressure, the algorithms are long and their evaluation time-consuming. The GSW library uses the Gibbs function of Feistel (2003) (IAPWS-09) to evaluate the properties of pure water, and since this is valid only over the restricted ranges of temperature and pressure appropriate for the ocean, the algorithms are shorter and their execution is faster. The GSW library is not as comprehensive as the SIA library; for example, the properties of moist air are only available in the SIA library. In addition, computationally efficient expressions for density ρ in terms of both Conservative Temperature and potential temperature (rather than in terms of *in situ* temperature) involving just 25 coefficients are also available and are described in appendix A.30 and appendix K.

The input and output parameters of the GSW library are in units which oceanographers will find more familiar than basic SI units. We expect that oceanographers will mostly use this GSW library because of its greater simplicity and computational efficiency, and because of the more familiar units compared with the SIA library. The library name GSW (Gibbs-SeaWater) has been chosen to be similar to, but different from the existing “sw” (Sea Water) library which is already in wide circulation. Both the SIA and GSW libraries, together with this TEOS-10 Manual are available from the website www.TEOS-10.org. Initially the SIA library is being made available in Visual Basic and FORTRAN while the GSW library is available mainly in MATLAB.

After these descriptions in sections 2 and 3 of how to determine the thermodynamic quantities and various derived quantities, we end with some conclusions (section 4). Additional information on Practical Salinity, the Gibbs function, Reference Salinity, composition anomalies, Absolute Salinity, and some fundamental thermodynamic properties such as the First Law of Thermodynamics, the non-conservative nature of many oceanographic variables, a list of recommended symbols, and succinct lists of thermodynamic formulae are given in the appendices. Much of this work has appeared elsewhere in the published literature but is collected here in a condensed form for the users' convenience.

1.5 A remark on units

The most convenient variables and units in which to conduct thermodynamic investigations are Absolute Salinity S_A in units of kg kg^{-1} , Absolute Temperature T (K), and Absolute Pressure P in Pa. These are the parameters and units used in the SIA software library. Oceanographic practice to date has used non-basic-SI units for many variables, in particular, temperature is usually measured on the Celsius ($^{\circ}\text{C}$) scale, pressure is sea pressure quoted in decibars relative to the pressure of a standard atmosphere (10.1325 dbar), while salinity has had its own oceanography-specific scale, the Practical Salinity Scale of 1978. In the GSW software library we adopt $^{\circ}\text{C}$ for the temperature unit, pressure is sea pressure in dbar and Absolute Salinity S_A is expressed in units of g kg^{-1} so that it takes numerical values close to those of Practical Salinity. Adopting these non-basic-SI units does not come without a penalty as there are many thermodynamic formulae that are more conveniently manipulated when expressed in SI units. As an example, the freshwater fraction of seawater is written correctly as $(1 - S_A)$, but it is clear that in this instance Absolute Salinity must be expressed in kg kg^{-1} not in g kg^{-1} . There are also cases within the GSW library in which SI units are required and this may occasionally cause some confusion. A common example of this issue arises when a variable is differentiated or integrated with respect to pressure. Nevertheless, for many applications it is deemed important to remain close to present oceanographic practice even though it means that one has to be vigilant to detect those expressions that need a variable to be expressed in the less-familiar SI units.

1.6 Recommendations

In accordance with resolution XXV-7 of the Intergovernmental Oceanographic Commission at its 25th Assembly in June 2009, and the several Releases and Guidelines of the International Association for the Properties of Water and Steam, 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.

Under TEOS-10 it is recognized that the composition of seawater varies around the world ocean and that the thermodynamic properties of seawater are more accurately represented as functions of Absolute Salinity S_A than of Practical Salinity S_p . It is useful to think of the transition from Practical Salinity to Absolute Salinity in two steps. In the first step a seawater sample is effectively treated as though it is Standard Seawater and its Reference Salinity S_R is calculated; Reference Salinity may be taken to be simply proportional to Practical Salinity. Reference Salinity has SI units (for example, g kg^{-1}) and is the natural starting point to consider the influence of any variation in composition. In the second step the Absolute Salinity Anomaly is evaluated using one of several techniques, the easiest of which is via a computer algorithm that effectively interpolates between a spatial atlas of these values. Then Absolute Salinity is estimated as the sum of Reference Salinity and Absolute Salinity Anomaly. Of the four possible versions of absolute salinity, the one that is used as the argument for the TEOS-10 Gibbs function is designed to provide accurate estimates of the density of seawater.

It is recognized that our knowledge of how to estimate seawater composition anomalies and their effect on thermodynamic properties is limited. Nevertheless, we should not continue to ignore the influence of these composition variations on seawater properties and on ocean dynamics. As more knowledge is gained in this area over the coming decade or so, and after such knowledge has been duly published in the scientific

literature, any updated algorithm to evaluate the Absolute Salinity Anomaly will be available (with its version number) from www.TEOS-10.org.

The storage of salinity in national data bases should continue to occur as Practical Salinity, as this will maintain continuity of this important time series. Oceanographic databases label stored, processed or exported parameters with the GF3 code PSAL for Practical Salinity and SSAL for salinity measured before 1978 (IOC, 1987). In order to avoid possible confusion in data bases between different types of salinity it is very strongly recommended that under no circumstances should either Reference Salinity or Absolute Salinity be stored in national data bases.

In order to accurately calculate the thermodynamic properties of seawater, Absolute Salinity must be calculated by first calculating Reference Salinity and then adding on the Absolute Salinity Anomaly. Because Absolute Salinity is the appropriate salinity variable for use with the equation of state, Absolute Salinity should be the salinity variable that is published in oceanographic journals. The version number of the software, or the exact formula, that was used to convert Reference Salinity into Absolute Salinity should always be stated in publications. Nevertheless, there may be some applications where the likely future changes in the algorithm that relates Reference Salinity to Absolute Salinity presents a concern, and for these applications it may be preferable to publish graphs and tables in Reference Salinity. For these studies or where it is clear that the effect of compositional variations are insignificant or not of interest, the Gibbs function may be called with S_R rather than S_A , thus avoiding the need to calculate the Absolute Salinity Anomaly. When this is done, it should be clearly stated that the salinity variable that is being graphed is Reference Salinity, not Absolute Salinity.

The TEOS-10 approach of using thermodynamic potentials to describe the properties of seawater, ice and moist air means that it is possible to derive many more thermodynamic properties than were available from EOS-80. The seawater properties entropy, internal energy, enthalpy and particularly potential enthalpy were not available from EOS-80 but are central to accurately calculating the transport of “heat” in the ocean and hence the air-sea heat flux in the coupled climate system.

Under EOS-80 the observed variables (S_p, t, p) were first used to calculate potential temperature θ and then water masses were analyzed on the $S_p - \theta$ diagram. Curved contours of potential density could also be drawn on this same $S_p - \theta$ diagram. Under TEOS-10, since density and potential density are now not functions of Practical Salinity S_p but rather are functions of Absolute Salinity S_A , it is now not possible to draw isolines of potential density on a $S_p - \theta$ diagram. Rather, because of the spatial variations of seawater composition, a given value of potential density defines an area on the $S_p - \theta$ diagram, not a curved line. Under TEOS-10, the observed variables (S_p, t, p), together with longitude and latitude, are used to first form Absolute Salinity S_A and Conservative Temperature Θ . Oceanographic water masses are then analyzed on the $S_A - \Theta$ diagram, and potential density contours can also be drawn on this $S_A - \Theta$ diagram, while preformed Salinity S_* is the natural salinity variable to be used in applications such as numerical modelling where it is important that the salinity variable be conservative.

When describing the use of TEOS-10, it is the present document (the TEOS-10 Manual) that should be referenced as IOC *et al.* (2010) [IOC, SCOR and IAPSO, 2010: *The international thermodynamic equation of seawater – 2010: Calculation and use of thermodynamic properties*. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp].