The international thermodynamic equation of seawater – 2010:
Calculation and use of thermodynamic properties

September 2010
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Foreword

This document describes the International Thermodynamic Equation Of Seawater – 2010 (TEOS-10 for short). TEOS-10 defines the thermodynamic properties of seawater and of ice Ih and has been adopted by the Intergovernmental Oceanographic Commission at its 25\textsuperscript{th} Assembly in June 2009, replacing EOS-80 as the official description of seawater and ice properties in marine science.

Fundamental to TEOS-10 are the concepts of Absolute Salinity and Reference Salinity. These variables are described in detail here, emphasising their relationship to Practical Salinity.

The science underpinning TEOS-10 has been described in a series of papers published in the refereed literature (see appendix C). The present document may be called the “TEOS-10 Manual” and acts as a guide to those published papers and concentrates on how the thermodynamic properties obtained from TEOS-10 are to be used in oceanography.

In addition to the thermodynamic properties of seawater, TEOS-10 also describes the thermodynamic properties of ice and of humid air, and these properties are summarised in this document. The TEOS-10 computer software, this TEOS-10 Manual and other documents may be obtained from www.TEOS-10.org. In particular, there are two introductory articles about TEOS-10 on this web site, namely “What every oceanographer needs to know about TEOS-10 (The TEOS-10 Primer)” (Pawlowicz, 2010b) and “Getting started with TEOS-10 and the Gibbs Seawater (GSW) Oceanographic Toolbox” (McDougall and Barker, 2011). An historical account of how TEOS-10 was developed has appeared in Pawlowicz et al. (2012).

When referring to the use of TEOS-10, it is the present document that should be referenced as IOC et al. (2010a) [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.].

This version of the TEOS-10 Manual includes corrections up to 14\textsuperscript{th} September 2010.
Abstract

This document outlines how the thermodynamic properties of seawater are evaluated using the International Thermodynamic Equation Of Seawater – 2010 (TEOS-10). This thermodynamic description of seawater is based on a Gibbs function formulation from which thermodynamic properties such as entropy, potential temperature, enthalpy and potential enthalpy are calculated directly. When determined from the Gibbs function, these quantities are fully consistent with each other. Entropy and enthalpy are required for an accurate description of the advection and diffusion of heat in the ocean interior and for quantifying the ocean’s role in exchanging heat with the atmosphere and with ice. The Gibbs function is a function of Absolute Salinity, temperature and pressure. In contrast to Practical Salinity, Absolute Salinity is expressed in SI units and it includes the influence of the small spatial variations of seawater composition in the global ocean. Absolute Salinity is the appropriate salinity variable for the accurate calculation of horizontal density gradients in the ocean. Absolute Salinity is also the appropriate salinity variable for the calculation of freshwater fluxes and for calculations involving the exchange of freshwater with the atmosphere and with ice. Potential functions are included for ice and for moist air, leading to accurate expressions for numerous thermodynamic properties of ice and air including freezing temperature and latent heats of melting and of evaporation. This TEOS-10 Manual describes how the thermodynamic properties of seawater, ice and moist air are used in order to accurately represent the transport of heat in the ocean and the exchange of heat with the atmosphere and with ice.
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”.

IOC Manuals and Guides No. 56
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 \( S_R \) 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; \( \text{in situ} \) 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 \( \theta \) or Conservative Temperature \( \Theta \).
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, Krembling (1971)). The 4-letter GF3 code (IOC (1987)) DENS is currently defined for \textit{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 DENS5 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 \( \delta S_A \) 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 website. 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 both potential temperature and entropy.

- 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 CO\textsubscript{2}.
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. 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 \(\rho\) in terms of both Conservative Temperature and potential temperature (rather than in terms of \textit{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 $S_{\Delta}$ 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 (°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 °C for the temperature unit, pressure is sea pressure in dbar and Absolute Salinity $S_{\Delta}$ 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 $(1−S_{\Delta})$, 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 than of Practical Salinity. 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 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 changes in the future 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. 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.

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]. The reader is also referred to the TEOS-10 User’s Guide [IOC, SCOR and IAPSO, 2010: User’s guide to the international thermodynamic equation of seawater – 2010. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56 (abridged edition), UNESCO], which is a succinct summary of the salient features of TEOS-10 and the associated computer software.
2. Basic Thermodynamic Properties

2.1 ITS-90 temperature

In 1990 the International Practical Temperature Scale 1968 (IPTS-68) was replaced by the International Temperature Scale 1990 (ITS-90). There are two main methods to convert between these two temperature scales; Rusby’s (1991) 8th order fit valid over a wide range of temperatures, and Saunders’ (1990) 1.00024 scaling widely used in the oceanographic community. The two methods are formally indistinguishable in the oceanographic temperature range because they differ by less than either the uncertainty in thermodynamic temperature (of order 1 mK), or the practical application of the IPTS-68 and ITS-90 scales. The differences between the Saunders (1990) and Rusby (1991) formulae are less than 1 mK throughout the temperature range -2 °C to 40 °C and less than 0.03 mK in the temperature range between -2 °C and 10 °C. Hence we recommend that the oceanographic community continues to use the Saunders formula

\[
(t_{68/\circ C}) = 1.00024 \left(t_{90/\circ C}\right). \tag{2.1.1}
\]

One application of this formula is in the updated computer algorithm for the calculation of Practical Salinity (PSS-78) in terms of conductivity ratio. The algorithms for PSS-78 require \(t_{68}\) as the temperature argument. In order to use these algorithms with \(t_{90}\) data, \(t_{68}\) may be calculated using (2.1.1).

An extended discussion of the different temperature scales, their inherent uncertainty and the reasoning for our recommendation of (2.1.1) can be found in appendix A.1.

2.2 Sea pressure

Sea pressure \(p\) is defined to be the Absolute Pressure \(P\) less the Absolute Pressure of one standard atmosphere, \(P_0 = 101325\) Pa; that is

\[
p \equiv P - P_0. \tag{2.2.1}
\]

It is common oceanographic practice to express sea pressure in decibars (dbar). Another common pressure variable that arises naturally in the calibration of sea-board instruments is gauge pressure \(p^{\text{gauge}}\) which is Absolute Pressure less the Absolute Pressure of the atmosphere at the time of the instrument’s calibration (perhaps in the laboratory, or perhaps at sea). Because atmospheric pressure changes in space and time, sea pressure \(p\) is preferred as a thermodynamic variable as it is unambiguously related to Absolute Pressure. The seawater Gibbs function in the GSW library is expressed as a function of sea pressure \(p\) (functionally equivalent to the use of Absolute Pressure \(P\) in the IAPWS Releases and in the SIA library); that is, \(g\) is a function of \(p\), it is not a function of \(p^{\text{gauge}}\).

2.3 Practical Salinity

Practical Salinity \(S_p\) is defined on the Practical Salinity Scale of 1978 (Unesco (1981, 1983)) in terms of the conductivity ratio \(K_{15}\) which is the electrical conductivity of the sample at temperature \(t_{68} = 15\) °C and pressure equal to one standard atmosphere (\(p = 0\) dbar and absolute pressure \(P\) equal to 101325 Pa), divided by the conductivity of a standard
potassium chloride (KCl) solution at the same temperature and pressure. The mass fraction of KCl (i.e., the mass of KCl per mass of solution) in the standard solution is \(32.4356 \times 10^{-3}\). When \(K_{IS} = 1\), the Practical Salinity \(S_p\) is by definition 35. Note that Practical Salinity is a unit-less quantity. Though sometimes convenient, it is technically incorrect to quote Practical Salinity in “psu”; rather it should be quoted as a certain Practical Salinity “on the Practical Salinity Scale PSS-78”. The formula for evaluating Practical Salinity can be found in appendix E along with the simple change that must be made to the Unesco (1983) formulae so that the algorithm for Practical Salinity can be called with ITS-90 temperature as an input parameter rather than the older \(t_{SG}\) temperature in which the PSS-78 algorithms were defined. The reader is also directed to the CDIAC chapter on “Method for salinity (conductivity ratio) measurement” which describes best practice in measuring the conductivity ratio of seawater samples (Kawano (2009)).

Practical Salinity is defined only in the range \(2 < S_p < 42\). Practical Salinities below 2 or above 42 computed from conductivity, as measured for example in coastal lagoons, should be evaluated by the PSS-78 extensions of Hill et al. (1986) and Poisson and Gadhoumi (1993). Samples exceeding a Practical Salinity of 50 must be diluted to the valid salinity range and the measured value should be adjusted based on the added water mass and the conservation of sea salt during the dilution process. This is discussed further in appendix E.

Data stored in national and international data bases should, as a matter of principle, be measured values rather than derived quantities. Consistent with this, we recommend continuing to store the measured (in situ) temperature rather than the derived quantity, potential temperature. Similarly we strongly recommend that Practical Salinity \(S_p\) continue to be the salinity variable that is stored in such data bases since \(S_p\) is closely related to the measured values of conductivity. This recommendation has the very important advantage that there is no change to the present practice and so there is less chance of transitional errors occurring in national and international data bases because of the adoption of Absolute Salinity in oceanography.

### 2.4 Reference Composition and the Reference-Composition Salinity Scale

The reference composition of seawater is defined by Millero et al. (2008a) as the exact mole fractions given in Table D.3 of appendix D below. This composition was introduced by Millero et al. (2008a) as their best estimate of the composition of Standard Seawater, being seawater from the surface waters of a certain region of the North Atlantic. The exact location for the collection of bulk material for the preparation of Standard Seawater is not specified. Ships gathering this bulk material are given guidance notes by the Standard Seawater Service, requesting that water be gathered between longitudes 50°W and 40°W, in deep water, during daylight hours. Reference-Composition Salinity \(S_R\) (or Reference Salinity for short) was designed by Millero et al. (2008b) to be the best estimate of the mass-fraction Absolute Salinity \(S_A\) of Standard Seawater. Independent of accuracy considerations, it provides a precise measure of dissolved material in Standard Seawater and is the correct salinity argument to be used in the TEOS-10 Gibbs function for Standard Seawater.

For the range of salinities where Practical Salinities are defined (that is, in the range \(2 < S_p < 42\) ) Millero et al. (2008a) show that

\[
S_R \approx u_{PS} S_p \quad \text{where} \quad u_{PS} = (35.165 \ 04/35) \ \text{g kg}^{-1}.
\]  

In the range \(2 < S_p < 42\), this equation expresses the Reference Salinity of a seawater sample on the Reference-Composition Salinity Scale (Millero et al. (2008a)). For practical
purposes, this relationship can be taken to be an equality since the approximate nature of this relation only reflects the extent to which Practical Salinity, as determined from measurements of conductivity ratio, temperature and pressure, varies when a seawater sample is heated, cooled or subjected to a change in pressure but without exchange of mass with its surroundings. The Practical Salinity Scale of 1978 was designed to satisfy this property as accurately as possible within the constraints of the polynomial approximations used to determine Chlorinity (and hence Practical Salinity) in terms of the measured conductivity ratio.

From (2.4.1), a seawater sample of Reference Composition whose Practical Salinity $S_p$ is 35 has a Reference Salinity $S_R$ of 35.165 04 g kg$^{-1}$. Millero et al. (2008a) estimate that the absolute uncertainty in this value is ±0.007 g kg$^{-1}$. The difference between the numerical values of Reference and Practical Salinities can be traced back to the original practice of determining salinity by evaporation of water from seawater and weighing the remaining solid material. This process also evaporated some volatile components and most of the 0.165 04 g kg$^{-1}$ salinity difference is due to this effect.

Measurements of the composition of Standard Seawater at a Practical Salinity $S_p$ of 35 using mass spectrometry and/or ion chromatography are underway and may provide updated estimates of both the value of the mass fraction of dissolved material in Standard Seawater and its uncertainty. Any update of this value will not change the Reference-Composition Salinity Scale and so will not affect the calculation of Reference Salinity nor of Absolute Salinity as calculated from Reference Salinity plus the Absolute Salinity Anomaly.

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.

Detailed information on Reference Composition and Reference Salinity can be found in Millero et al. (2008a). For the user’s convenience a brief summary of information from Millero et al. (2008a), including the precise definition of Reference Salinity is given in appendix A.3 and in Table D3 of appendix D.

### 2.5 Absolute Salinity

Absolute Salinity is traditionally defined as the mass fraction of dissolved material in seawater. For seawater of Reference Composition, Reference Salinity gives our current best estimate of Absolute Salinity. To deal with composition anomalies in seawater, we need an extension of the Reference-Composition Salinity $S_R$ that provides a useful measure of salinity over the full range of oceanographic conditions and agrees precisely with Reference Salinity when the dissolved material has Reference Composition. When composition anomalies are present, no single measure of dissolved material can fully represent the influences on seawater properties on all thermodynamic properties, so it is clear that either additional information will be required or compromises will have to be made. In addition, we would like to introduce a measure of salinity that is traceable to the SI (Seitz et al., 2010b) and maintains the high accuracy of PSS-78 necessary for oceanographic applications. The introduction of “Density Salinity” $S_{\lambda}^{\text{dens}}$ addresses both of these issues; it is this type of absolute salinity that in TEOS-10 parlance is labeled $S_{\lambda}$ and called Absolute Salinity. In this section we explain how $S_{\lambda}$ is defined and evaluated, but first we outline other choices that are available for the definition of absolute salinity in the presence of composition variations in seawater.
The most obvious definition of absolute salinity is “the mass fraction of dissolved non-H$_2$O material in a seawater sample at its temperature and pressure”. This seemingly simple definition is actually far more subtle than it first appears. Notably, there are questions about what constitutes water and what constitutes dissolved material. Perhaps the most obvious example of this issue occurs when CO$_2$ is dissolved in water to produce a mixture of CO$_2$, H$_2$CO$_3$, HCO$_3^-$, CO$_3^{2-}$, H$^+$, OH$^-$ and H$_2$O, with the relative proportions depending on dissociation constants that depend on temperature, pressure, and pH. Thus, the dissolution of a given mass of CO$_2$ in pure water essentially transforms some of the water into dissolved material. A change in the temperature and even an adiabatic change in pressure results in a change in absolute salinity defined in this way due to the dependence of chemical equilibria on temperature and pressure. Pawlowicz et al. (2010) and Wright et al. (2010b) address this second issue by defining “Solution Absolute Salinity” (usually shortened to “Solution Salinity”), $S_A^{\text{soln}}$, as the mass fraction of dissolved non-H$_2$O material after a seawater sample is brought to the constant temperature $t = 25^\circ$C and the fixed sea pressure 0 dbar (fixed Absolute Pressure of 101 325 Pa).

Another measure of absolute salinity is the “Added-Mass Salinity” $S_A^{\text{add}}$ which is $S_A$ plus the mass fraction of material that must be added to Standard Seawater to arrive at the concentrations of all the species in the given seawater sample, after chemical equilibrium has been reached, and after the sample is brought to the constant temperature $t = 25^\circ$C and the fixed sea pressure of 0 dbar. The estimation of absolute salinity $S_A^{\text{add}}$ is not straightforward for seawater with anomalous composition because while the final equilibrium state is known, one must iteratively determine the mass of anomalous solute prior to any chemical reactions with Reference-Composition seawater. Pawlowicz et al. (2010) provide an algorithm to achieve this, at least approximately. This definition of absolute salinity, $S_A^{\text{add}}$, is useful for laboratory studies of artificial seawater and it differs from $S_A^{\text{soln}}$ because of the chemical reactions that take place between the several species of the added material and the components of seawater that exist in Standard Seawater. Added-Mass Salinity may be the most appropriate form of salinity for accurately accounting for the mass of salt discharged by rivers and hydrothermal vents into the ocean.

“Preformed Absolute Salinity” (usually shortened to “Preformed Salinity”), $S_*$, is a different type of absolute salinity which is specifically designed to be as close as possible to being a conservative variable. That is, $S_*$ is designed to be insensitive to biogeochemical processes that affect the other types of salinity to varying degrees. Preformed Salinity $S_*$ is formed by first estimating the contribution of biogeochemical processes to one of the salinity measures $S_A$, $S_A^{\text{soln}}$, or $S_A^{\text{add}}$, and then subtracting this contribution from the appropriate salinity variable. In this way Preformed Salinity $S_*$ is designed to be a conservative salinity variable which is independent of the effects of the non-conservative biogeochemical processes. $S_*$ will find a prominent role in ocean modeling. The three types of absolute salinity $S_A^{\text{soln}}$, $S_A^{\text{add}}$ and $S_*$ are discussed in more detail in appendices A.4 and A.20, where approximate relationships between these variables and $S_A = S_A^{\text{den}}$ are presented, based on the work of Pawlowicz et al. (2010) and Wright et al. (2010b). Note that for a sample of Standard Seawater, all of the five salinity variables $S_R$, $S_A$, $S_A^{\text{soln}}$, $S_A^{\text{add}}$ and $S_*$ are equal.

There is no simple means to measure either $S_A^{\text{soln}}$ or $S_A^{\text{add}}$ for the general case of the arbitrary addition of many components to Standard Seawater. Hence a more precise and easily determined measure of the amount of dissolved material in seawater is required and TEOS-10 adopts “Density Salinity” for this purpose. “Density Salinity” $S_A^{\text{dens}}$ is defined as the value of the salinity argument of the TEOS-10 expression for density which gives the sample’s actual measured density at the temperature $t = 25^\circ$C and at the sea pressure $p = 0$ dbar. When there is no risk of confusion, “Density Salinity” is also called.
Absolute Salinity with the label $S_A$, that is $S_A = S_A^{\text{dens}}$. Usually we do not have accurate measurements of density but rather we have measurements of Practical Salinity, temperature and pressure, and in this case, Absolute Salinity may be calculated using Practical Salinity and the computer algorithm of McDougall, Jackett and Millero (2010a) which provides an estimate of $\delta S_A = S_A - S_R$. This computer program was formed as follows.

In a series of papers (Millero et al. (1976a, 1978, 2000, 2008b), McDougall et al. (2010a)), accurate measurements of the density of seawater samples, along with the Practical Salinity of those samples, gave estimates of $\delta S_A = S_A - S_R$ from most of the major basins of the world ocean. This was done by first calculating the "Reference Density" from the TEOS-10 equation of state using the sample’s Reference Salinity as the salinity argument (this calculation essentially assumes that the seawater sample has the composition of Standard Seawater). The difference between the measured density and the "Reference Density" was then used to estimate the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ (Millero et al. (2008a)). The McDougall et al. (2010a) algorithm is based on the observed correlation between $S_A - S_R$ data and the silicate concentration of the seawater samples (Millero et al., 2008a), with the silicate concentration being estimated by interpolation of a global atlas (Gouretski and Koltermann (2004)).

The algorithm for Absolute Salinity takes the form

$$S_A = S_R + \delta S_A = S_A (S_P, \phi, \lambda, p),$$

(2.5.1)

Where $\phi$ is latitude (degrees North), $\lambda$ is longitude (degrees east, ranging from 0°E to 360°E) while $p$ is sea pressure.

Heuristically the dependence of $\delta S_A = S_A - S_R$ on silicate can be thought of as reflecting the fact that silicate affects the density of a seawater sample without significantly affecting its conductivity or its Practical Salinity. In practice this explains about 60% of the effect and the remainder is due to the correlation of other composition anomalies (such as nitrate) with silicate. In the McDougall et al. (2010a) algorithm the Baltic Sea is treated separately, following the work of Millero and Kremling (1976) and Feistel et al. (2010c, 2010d), because some rivers flowing into the Baltic are unusually high in calcium carbonate.

---

**Figure 1.** A sketch indicating how thermodynamic quantities such as density are calculated as functions of Absolute Salinity. Absolute Salinity is found by adding an estimate of the Absolute Salinity Anomaly $\delta S_A$ to the Reference Salinity.
Since the density of seawater is rarely measured, we recommend the approach illustrated in Figure 1 as a practical method to include the effects of composition anomalies on estimates of Absolute Salinity and density. When composition anomalies are not known, the algorithm of McDougall et al. (2010a) may be used to estimate Absolute Salinity in terms of Practical Salinity and the spatial location of the measurement in the world oceans.

The difference between Absolute Salinity and Reference Salinity, as estimated by the McDougall et al. (2010a) algorithm, is illustrated in Figure 2(a) at a pressure of 2000 dbar, and in a vertical section through the Pacific Ocean in Figure 2(b).

Of the approximately 800 samples of seawater from the world ocean that have been examined to date for \( \delta S_A = S_A - S_R \) the standard error (square root of the mean squared value) of \( \delta S_A = S_A - S_R \) is 0.0107 g kg\(^{-1}\). That is, the “typical” value of \( \delta S_A = S_A - S_R \) of the 811 samples taken to date is 0.0107 g kg\(^{-1}\). The standard error of the difference between the measured values of \( \delta S_A = S_A - S_R \) and the values evaluated from the computer algorithm of McDougall et al. (2010a) is 0.0048 g kg\(^{-1}\). The maximum values of \( \delta S_A = S_A - S_R \) of approximately 0.025 g kg\(^{-1}\) occur in the North Pacific.

**Figure 2 (a).** Absolute Salinity Anomaly \( \delta S_A \) at \( p = 2000 \) dbar.

**Figure 2 (b).** A vertical section of Absolute Salinity Anomaly \( \delta S_A \) along 180\(^\circ\)E in the Pacific Ocean.

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 thermodynamic
descriptions of seawater and ice were endorsed recognizing that the techniques for estimating Absolute Salinity will likely improve over the coming decades. The algorithm for evaluating Absolute Salinity in terms of Practical Salinity, latitude, longitude and pressure, will likely be updated from time to time, after relevant appropriately peer-reviewed publications have appeared, and such an updated algorithm will appear on the www.TEOS-10.org web site. Users of this software should state in their published work which version of the software was used to calculate Absolute Salinity.

The present computer software which evaluates Absolute Salinity $S_\lambda$ given the input variables Practical Salinity $S_p$, longitude $\lambda$, latitude $\phi$ and pressure is available at www.TEOS-10.org. Absolute Salinity is also available as the inverse function of density $S_\lambda(T,P,\rho)$ in the SIA library of computer algorithms as the algorithm sea_sa_si (see appendix M) and in the GSW software library as the algorithm gsw_SA_from_density.

### 2.6 Gibbs function of seawater

The Gibbs function of seawater $g(S_\lambda,t,p)$ is related to the specific enthalpy $h$ and entropy $\eta$, by $g = h - (T_0 + t)\eta$ where $T_0 = 273.15K$ is the Celsius zero point. TEOS-10 defines the Gibbs function of seawater as the sum of a pure water part and the saline part (IAPWS-08)

$$g(S_\lambda,t,p) = g^w(t,p) + g^S(S_\lambda,t,p). \quad (2.6.1)$$

The saline part of the Gibbs function, $g^S$, is valid over the ranges $0 < S_\lambda < 42$ g kg$^{-1}$, $-6.0 \, ^{\circ}\!C < t < 40 \, ^{\circ}\!C$, and $0 < p < 10^9$ dbar, although its thermal and colligative properties are valid up to $t = 80 \, ^{\circ}\!C$ and $S_\lambda = 120$ g kg$^{-1}$ at $p = 0$.

The pure-water part of the Gibbs function, $g^w$, can be obtained from the IAPWS-95 Helmholtz function of pure-water substance which is valid from the freezing temperature or from the sublimation temperature to 1273 K. Alternatively, the pure-water part of the Gibbs function can be obtained from the IAPWS-09 Gibbs function which is valid in the oceanographic ranges of temperature and pressure, from less than the freezing temperature of seawater (at any pressure), up to 40$^\circ$C (specifically from $- (2.65 + (p + P_0) \times 0.0743 \, \text{MPa}^{-1}) \, ^{\circ}\!C$ to $40 \, ^{\circ}\!C$), and in the pressure range $0 < p < 10^9$ dbar. For practical purposes in oceanography it is expected that IAPWS-09 will be used because it executes approximately two orders of magnitude faster than the IAPWS-95 code for pure water. However if one is concerned with temperatures between $40^\circ$C and $80^\circ$C then one must use the IAPWS-95 version of $g^w$ (expressed in terms of absolute temperature (K) and absolute pressure (Pa)) rather than the IAPWS-09 version.

The thermodynamic properties derived from the IAPWS-95 (the Release providing the Helmholtz function formulation for pure water) and IAPWS-08 (the Release endorsing the Feistel (2008) Gibbs function) combination are available from the SIA software library, while that derived from the IAPWS-09 (the Release endorsing the pure water part of Feistel (2003)) and IAPWS-08 combination are available from the GSW software library. The GSW library is restricted to the oceanographic standard range in temperature and pressure, however the validity of results extends at $p = 0$ to Absolute Salinity up to mineral saturation concentrations (Marion et al. 2009). Specific volume (which is the pressure derivative of the Gibbs function) is presently an extrapolated quantity outside the Neptunian range (i.e. the oceanographic range) of temperature and Absolute Salinity at $p = 0$, and exhibits errors there of up to 3%. We emphasize that models of seawater properties that use a single salinity variable, $S_\lambda$, as input require approximately fixed chemical composition ratios (e.g., Na/Cl, Ca/Mg, Cl/HCO$_3$ etc.). As seawater evaporates or freezes, eventually minerals such as CaCO$_3$ will precipitate. Small anomalies are reasonably handled by using $S_\lambda$ as the input variable (see section 2.5) but precipitation
may cause large deviations from the nearly fixed ratios associated with standard seawater. Under extreme conditions of precipitation, models of seawater based on the Millero et al. (2008a) Reference Composition will no longer be applicable. Figure 3 illustrates $S_A - t$ boundaries of validity (determined by the onset of precipitation) for 2008 ($pCO_2 = 385 \text{ \mu atm}$) and 2100 ($pCO_2 = 550 \text{ \mu atm}$) (from Marion et al. (2009)).

![Figure 3. The boundaries of validity of the Millero et al. (2008a) composition at $p = 0$ in Year 2008 (solid lines) and potentially in Year 2100 (dashed lines). At high salinity, calcium carbonate saturates first and comes out of solution; thereafter the Reference Composition of Standard Seawater of Millero et al. (2008a) does not apply.](image)

The Gibbs function (2.6.1) contains four arbitrary constants that cannot be determined by any set of thermodynamic measurements. These arbitrary constants mean that the Gibbs function (2.6.1) is unknown and unknowable up to the arbitrary function of temperature and Absolute Salinity (where $T_0$ is the Celsius zero point, 273.15 K)

$$ \left[ a_1 + a_2 \left( T_0 + t \right) \right] + \left[ a_3 + a_4 \left( T_0 + t \right) \right] S_A $$

(2.6.2)

(see for example Fofonoff (1962) and Feistel and Hagen (1995)). The first two coefficients $a_1$ and $a_2$ are arbitrary constants of the pure water Gibbs function $g^W(t,p)$ while the second two coefficients $a_3$ and $a_4$ are arbitrary coefficients of the saline part of the Gibbs function $g^S(S_A, t, p)$. Following generally accepted convention, the first two coefficients are chosen to make the entropy and internal energy of liquid water zero at the triple point

$$ \eta^W(t_r, p_r) = 0 $$

(2.6.3)

and

$$ u^W(t_r, p_r) = 0 $$

(2.6.4)

as described in IAPWS-95 and in more detail in Feistel et al. (2008a) for the IAPWS-95 Helmholtz function description of pure water substance. When the pure-water Gibbs function $g^W(t,p)$ of (2.6.1) is taken from the fitted Gibbs function of Feistel (2003), the two arbitrary constants $a_1$ and $a_2$ are (in the appropriate non-dimensional form) $g_{00}$ and $g_{10}$ of the table in appendix G below. These values of $g_{00}$ and $g_{10}$ are not identical to the values in Feistel (2003) because the present values have been taken from IAPWS-09 and
have been chosen to most accurately achieve the triple-point conditions (2.6.3) and (2.6.4) as discussed in Feistel et al. (2008a).

The remaining two arbitrary constants $a_3$ and $a_4$ of (2.6.2) are determined by ensuring that the specific enthalpy $h$ and specific entropy $\eta$ of a sample of standard seawater with standard-ocean properties $(S_{SO}, t_{SO}, p_{SO}) = (35.165 \text{ mol kg}^{-1}, 0^\circ \text{C}, 0 \text{ bar})$ are both zero, that is that

$$h(S_{SO}, t_{SO}, p_{SO}) = 0$$

and

$$\eta(S_{SO}, t_{SO}, p_{SO}) = 0.$$  \hfill (2.6.6)

In more detail, these conditions are actually officially written as (Feistel 2008, IAPWS-08)

$$h^S(S_{SO}, t_{SO}, p_{SO}) = u^W(t, p) - h^W(t_{SO}, p_{SO})$$

and

$$\eta^S(S_{SO}, t_{SO}, p_{SO}) = \eta^W(t, p) - \eta^W(t_{SO}, p_{SO}).$$

Written in this way, (2.6.7) and (2.6.8) use properties of the pure water description (the right-hand sides) to constrain the arbitrary constants in the saline Gibbs function. While the first terms on the right-hand sides of these equations are zero (see (2.6.3) and (2.6.4)), these constraints on the saline Gibbs function are written this way so that they are independent of any subsequent change in the arbitrary constants involved in the thermodynamic description of pure water. While the two slightly different thermodynamic descriptions of pure water, namely IAPWS-95 and IAPWS-09, both achieve zero values of the internal energy and entropy at the triple point of pure water, the values assigned to the enthalpy and entropy of pure water at the temperature and pressure of the standard ocean, $h^W(t_{SO}, p_{SO})$ and $\eta^W(t_{SO}, p_{SO})$ on the right-hand sides of (2.6.7) and (2.6.8), are slightly different in the two cases. For example $h^W(t_{SO}, p_{SO})$ is $3.3\times 10^{-3}$ J kg$^{-1}$ from IAPWS-09 (as described in the table of appendix G) compared with the round-off error of $2\times 10^{-8}$ J kg$^{-1}$ when using IAPWS-95 with double-precision arithmetic. This issues is discussed in more detail in section 3.3.

The polynomial form and the coefficients for the pure water Gibbs function $g^W(t, p)$ from Feistel (2003) and IAPWS-09 are given in appendix G, while the combined polynomial and logarithmic form and the coefficients for the saline part of the Gibbs function $g^S(S_A, t, p)$ (from Feistel (2008) and IAPWS-08) are reproduced in appendix H.

SCOR/IAPSO Working Group 127 has independently checked that the Gibbs functions of Feistel (2003) and of Feistel (2008) do in fact fit the underlying data of various thermodynamic quantities to the accuracy quoted in those two fundamental papers. This checking was performed by Giles M. Marion, and is summarized in appendix O. Further checking of these Gibbs functions has occurred in the process leading up to IAPWS approving these Gibbs function formulations as the Releases IAPWS-08 and IAPWS-09.

Discussions of how well the Gibbs functions of Feistel (2003) and Feistel (2008) fit the underlying (laboratory) data of density, sound speed, specific heat capacity, temperature of maximum density etc may be found in those papers, along with comparisons with the corresponding algorithms of EOS-80. The IAPWS-09 release discusses the accuracy to which the Feistel (2003) Gibbs function fits the underlying thermodynamic potential of IAPWS-95; in summary, for the variables density, thermal expansion coefficient and specific heat capacity, the rms misfit between IAPWS-09 and IAPWS-95, in the region of validity of IAPWS-09, are a factor of between 20 and 100 less than the corresponding error in the laboratory data to which both thermodynamic potentials were fitted. Hence, in the oceanographic range of parameters, IAPWS-09 and IAPWS-95 may be regarded as equally accurate thermodynamic descriptions of pure liquid water.

The Gibbs function $g$ has units of J kg$^{-1}$ in both the SIA and GSW computer libraries.
2.7 Specific volume

The specific volume of seawater \( v \) is given by the pressure derivative of the Gibbs function at constant Absolute Salinity \( S_{\lambda} \) and in situ temperature \( t \), that is

\[
v = v(S_{\lambda},t,p) = g_p = \left. \frac{\partial g}{\partial P} \right|_{S_{\lambda},t}.
\] (2.7.1)

Notice that specific volume is a function of Absolute Salinity \( S_{\lambda} \) rather than of Reference Salinity \( S_R \) or Practical Salinity \( S_p \). The importance of this point is discussed in section 2.8. When derivatives are taken with respect to in situ temperature, or at constant in situ temperature, the symbol \( t \) is avoided as it can be confused with the same symbol for time. Rather, we use \( T \) in place of \( t \) in the expressions for these derivatives.

For many theoretical and modeling purposes in oceanography it is convenient to regard the independent temperature variable to be potential temperature \( \Theta \) or Conservative Temperature \( \Theta \) rather than in situ temperature \( t \). We note here that the specific volume is equal to the pressure derivative of specific enthalpy at fixed Absolute Salinity when any one of \( \eta, \Theta \) or \( \Theta \) is also held constant, as follows (from appendix A.11)

\[
\frac{\partial h}{\partial P} \bigg|_{S_{\lambda},\eta} = \frac{\partial h}{\partial P} \bigg|_{S_{\lambda},\Theta} = \frac{\partial h}{\partial P} \bigg|_{S_{\lambda},\Theta} = v.
\] (2.7.2)

The use of \( P \) in these equations emphasizes that it must be in Pa not dbar. Specific volume \( v \) has units of \( \text{m}^3 \text{kg}^{-1} \) in both the SIA and GSW computer libraries.

2.8 Density

The density of seawater \( \rho \) is the reciprocal of the specific volume. It is given by the reciprocal of the pressure derivative of the Gibbs function at constant Absolute Salinity \( S_{\lambda} \) and in situ temperature \( t \), that is

\[
\rho = \rho(S_{\lambda},t,p) = \left( g_p \right)^{-1} = \left( \left. \frac{\partial g}{\partial P} \right|_{S_{\lambda},t} \right)^{-1}.
\] (2.8.1)

Notice that density is a function of Absolute Salinity \( S_{\lambda} \) rather than of Reference Salinity \( S_R \) or Practical Salinity \( S_p \). This is an extremely important point because Absolute Salinity \( S_{\lambda} \) in units of \( \text{g kg}^{-1} \) is numerically greater than Practical Salinity by between 0.165 \( \text{g kg}^{-1} \) and 0.195 \( \text{g kg}^{-1} \) in the open ocean so that if Practical Salinity were inadvertently used as the salinity argument for the density algorithm, a significant density error of between 0.12 \( \text{kg m}^{-3} \) and 0.15 \( \text{kg m}^{-3} \) would result.

For many theoretical and modeling purposes in oceanography it is convenient to regard density to be a function of potential temperature \( \Theta \) or Conservative Temperature \( \Theta \) rather than of in situ temperature \( t \). That is, it is convenient to form the following two functional forms of density,

\[
\rho = \hat{\rho}(S_{\lambda},\Theta,p) = \hat{\rho}(S_{\lambda},\Theta,p),
\] (2.8.2)

where \( \Theta \) and \( \Theta \) are respectively potential temperature and Conservative Temperature, both referenced to \( p_r = 0 \text{ dbar} \). We will adopt the convention (see Table L.2 in appendix L) that when enthalpy \( h \), specific volume \( v \) or density \( \rho \) are taken to be functions of potential temperature they attract an over-tild as in \( \tilde{v} \) or \( \tilde{\rho} \), and when they are taken to be functions of Conservative Temperature they attract a caret as in \( \hat{v} \) and \( \hat{\rho} \). With this convention, expressions involving partial derivatives such as (2.7.2) can be written more compactly as (from appendix A.11)

\[
\hat{h}_p = \tilde{h}_p = \hat{h}_p = v = \rho^{-1}
\] (2.8.3)

since the other variables are taken to be constant during the partial differentiation. Appendix P lists expressions for many thermodynamic variables in terms of the thermodynamic potentials.
\[ h = \hat{h}(S_{\Lambda}, \eta, p), \quad h = \hat{h}(S_{\Lambda}, \Theta, p) \quad \text{and} \quad h = \hat{h}(S_{\Lambda}, \Theta, p). \]  

(2.8.4)

Density \( \rho \) has units of \( \text{kg m}^{-3} \) in both the SIA and GSW computer libraries.

Computationally efficient expressions for \( \hat{\rho}(S_{\Lambda}, \Theta, p) \) and \( \hat{\rho}(S_{\Lambda}, \theta, p) \) involving 25 coefficients are available (McDougall et al. (2010b)) and are described in appendix A.30 and appendix K. These expressions can be integrated with respect to pressure to provide closed expressions for \( \hat{h}(S_{\Lambda}, \Theta, p) \) and \( \hat{h}(S_{\Lambda}, \theta, p) \) (see Eqn. (A.30.6)).

### 2.9 Chemical potentials

As for any two-component thermodynamic system, the Gibbs energy, \( G \), of a seawater sample containing the mass of water \( m_w \) and the mass of salt \( m_s \) at temperature \( T \) and pressure \( p \) can be written in the form (Landau and Lifshitz (1959), Alberty (2001), Feistel (2008))

\[ G(m_w, m_s, T, p) = m_w \mu^w + m_s \mu^s \]  

(2.9.1)

where the chemical potentials of water in seawater \( \mu^w \) and of salt in seawater \( \mu^s \) are defined by the partial derivatives

\[ \mu^w = \frac{\partial G}{\partial m_w} \bigg|_{m_s, T, p}, \quad \text{and} \quad \mu^s = \frac{\partial G}{\partial m_s} \bigg|_{m_w, T, p}. \]  

(2.9.2)

Identifying absolute salinity with the mass fraction of salt dissolved in seawater, \( S_{\Lambda} = m_s / (m_w + m_s) \) (Millero et al. (2008a)), the specific Gibbs energy \( g \) is given by

\[ g(S_{\Lambda}, T, p) = \frac{G}{m_w + m_s} = (1 - S_{\Lambda}) \mu^w + S_{\Lambda} \mu^s = \mu^w + S_{\Lambda}(\mu^s - \mu^w) \]  

(2.9.3)

and is independent of the total mass of the sample. Note that this expression for \( g \) as the sum of a water part and a saline part is not the same as the pure water and the saline split in (2.6.1) (\( \mu^w \) is the chemical potential of water in seawater; it does not correspond to a pure water sample as \( g^w \) does). This Gibbs energy \( g \) is used as the thermodynamic potential function (Gibbs function) for seawater. The above three equations can be used to write expressions for \( \mu^w \) and \( \mu^s \) in terms of the Gibbs function \( g \) as

\[ \mu^w = \frac{\partial \left[ (m_w + m_s) g \right]}{\partial m_w} \bigg|_{m_s, T, p} = g + (m_w + m_s) \frac{\partial g}{\partial S_{\Lambda}} \bigg|_{T, p} \frac{\partial S_{\Lambda}}{\partial m_w} \bigg|_{m_s} = g - S_{\Lambda} \frac{\partial g}{\partial S_{\Lambda}} \bigg|_{T, p} \]  

(2.9.4)

and for the chemical potential of salt in seawater,

\[ \mu^s = \frac{\partial \left[ (m_w + m_s) g \right]}{\partial m_s} \bigg|_{m_w, T, p} = g + (m_w + m_s) \frac{\partial g}{\partial S_{\Lambda}} \bigg|_{T, p} \frac{\partial S_{\Lambda}}{\partial m_s} \bigg|_{m_w} = g + (1 - S_{\Lambda}) \frac{\partial g}{\partial S_{\Lambda}} \bigg|_{T, p} \]  

(2.9.5)

The relative chemical potential \( \mu \) (commonly called the “chemical potential of seawater”) follows from (2.9.4) and (2.9.5) as

\[ \mu = \mu^s - \mu^w = \frac{\partial g}{\partial S_{\Lambda}} \bigg|_{T, p}. \]  

(2.9.6)

and describes the change in the Gibbs energy of a parcel of seawater of fixed mass if a small amount of water is replaced by salt at constant temperature and pressure. Also, from the fundamental thermodynamic relation (Eqn. (A.7.1)) it follows that the chemical potential of seawater \( \mu \) describes the change of enthalpy \( dh \) if at constant pressure and entropy, a small mass fraction of water is replaced by salt, \( dS_{\Lambda} \). Equations (2.9.4) – (2.9.6) serve to define the three chemical potentials in terms of the
Gibbs function \( g \) of seawater. Note that the weights of the sums that appear in Eqns. (2.9.1) – (2.9.5) are strictly the mass fractions of salt and of pure water in seawater, so that for a seawater sample of anomalous composition these mass fractions would be more accurately given in terms of \( S^\text{soln}_A \) than by \( S_A = S^\text{m} \). In this regard, the Gibbs energy in Eqn. (2.9.1) should strictly be the weighted sum of the chemical potentials of all the constituents in seawater. However, practically speaking, the vapour pressure, the latent heat and the freezing temperature are all rather weakly dependent on salinity, and hence the use of \( S_A \) in this section is recommended.

The SIA computer software library (appendix M) predominantly uses basic SI units, so that \( S_A \) has units of \( \text{kg kg}^{-1} \) and \( g, \mu, \mu^S \) and \( \mu^W \) all have units of \( \text{J kg}^{-1} \). In the GSW library of computer code (appendix N) \( S_A \) has units of \( \text{g kg}^{-1} \) while \( \mu, \mu^S \) and \( \mu^W \) all have units of \( \text{J g}^{-1} \). This adoption of oceanographic (i.e. non-basic-SI) units for \( S_A \) means that special care is needed in evaluating equations such as (2.9.3) and (2.9.5) where in the term \( 1 - S_A \) it is clear that \( S_A \) must have units of \( \text{kg kg}^{-1} \). The adoption of non-basic-SI units is common in oceanography, but often causes some difficulties such as this.

### 2.10 Entropy

The specific entropy of seawater \( \eta \) is given by

\[
\eta = \eta(S_A,t,p) = -g_T = -\frac{\partial g}{\partial T} \bigg|_{S_A,p}.
\]

(2.10.1)

When taking derivatives with respect to in situ temperature, the symbol \( T \) will be used for temperature in order that these derivatives not be confused with time derivatives.

Entropy \( \eta \) has units of \( \text{J kg}^{-1} \text{K}^{-1} \) in both the SIA and GSW computer libraries.

### 2.11 Internal energy

The specific internal energy of seawater \( u \) is given by (where \( T_0 \) is the Celsius zero point, 273.15 K and \( P_0 = 101325 \text{Pa} \) is the standard atmosphere pressure)

\[
u = u(S_A,t,p) = g + (T_0 + t)\eta - (p + P_0)v = g - (T_0 + t)\frac{\partial g}{\partial T} \bigg|_{S_A,p} - (p + P_0)\frac{\partial g}{\partial P} \bigg|_{S_A,T}.
\]

(2.11.1)

This expression is an example where the use of non-basic SI units presents a problem, because in the product \( - (p + P_0)v \), \( (p + P_0) = P \) must be in Pa if specific volume has its regular units of \( \text{m}^3 \text{kg}^{-1} \); hence here sea pressure \( p \) must be expressed in Pa. Also, the pressure derivative in Eqn. (2.11.1) must be done with respect to pressure in Pa.

Specific internal energy \( u \) has units of \( \text{J kg}^{-1} \) in both the SIA and GSW computer libraries.

### 2.12 Enthalpy

The specific enthalpy of seawater \( h \) is given by

\[
h = h(S_A,t,p) = g + (T_0 + t)\eta = g - (T_0 + t)\frac{\partial g}{\partial T} \bigg|_{S_A,p}.
\]

(2.12.1)

Specific enthalpy \( h \) has units of \( \text{J kg}^{-1} \) in both the SIA and GSW computer libraries.
2.13 Helmholtz energy

The specific Helmholtz energy of seawater \( f \) is given by

\[
f = f(S_A, t, p) = g - (p + P_0)v = g - (p + P_0) \frac{\partial g}{\partial P} S_A, T .
\] (2.13.1)

This expression is another example where the use of non-basic SI units presents a problem, because in the product \(-(p + P_0)\), \( p \) must be in Pa if specific volume has its regular units of \( \text{m}^3 \text{kg}^{-1} \). The specific Helmholtz energy \( f \) has units of \( \text{J kg}^{-1} \) in both the SIA and GSW computer software libraries.

2.14 Osmotic coefficient

The osmotic coefficient of seawater \( \phi \) is given by

\[
\phi = \phi(S_A, t, p) = - \left( g - S_A \frac{\partial g}{\partial S_A} \right) (m_{SW} R (T_0 + t))^{-1} .
\] (2.14.1)

The osmotic coefficient of seawater describes the change of the chemical potential of water per mole of added salt, expressed as multiples of the thermal energy, \( R(T_0 + t) \) (Millero and Leung (1976), Feistel and Marion (2007), Feistel (2008)),

\[
\mu^W(0,t,p) = \mu^W(S_A,t,p) + m_{SW} R (T_0 + t) \phi .
\] (2.14.2)

Here, \( R = 8.314 \text{472 J mol}^{-1} \text{K}^{-1} \) is the universal molar gas constant. The molality \( m_{SW} \) is the number of dissolved moles of solutes (ions) of the Reference Composition as defined by Millero et al. (2008a), per kilogram of pure water. Note that the molality of seawater may take different values if neutral molecules of salt rather than ions are counted (see the discussion on page 519 of Feistel and Marion (2007)). The freezing-point lowering equations (3.33.1, 3.33.2) or the vapour-pressure lowering can be computed from the osmotic coefficient of seawater (see Millero and Leung (1976), Bromley et al. (1974)).

2.15 Isothermal compressibility

The thermodynamic quantities defined so far are all based on the Gibbs function itself and its first derivatives. The remaining quantities discussed in this section all involve higher order derivatives.

The isothermal and isohaline compressibility of seawater \( \kappa' \) is defined by

\[
\kappa' = \kappa' (S_A, t, p) = \rho^{-1} \frac{\partial \rho}{\partial P} S_A, T = - \nu^{-1} \frac{\partial \nu}{\partial P} S_A, T = - \frac{g_{PP}}{g_P} .
\] (2.15.1)

where the second derivative of \( g \) is taken with respect to pressure (in Pa) at constant \( S_A \) and \( t \). The use of \( P \) in the pressure derivatives in Eqn. (2.15.1) serves to emphasize that these derivatives must be taken with respect to pressure in Pa not in dbar. The isothermal compressibility of seawater \( \kappa' \) produced by both the SIA and GSW computer software libraries (appendices M and N) has units of \( \text{Pa}^{-1} \).
2.16 Isentropic and isohaline compressibility

When the entropy and Absolute Salinity are held constant while the pressure is changed, the isentropic and isohaline compressibility \( \kappa \) is obtained:

\[
\kappa = \kappa(S_A, t, p) = \rho^{-1} \frac{\partial \rho}{\partial P_{S_A, t}} = - \nu^{-1} \frac{\partial \nu}{\partial P_{S_A, t}} = \rho^{-1} \frac{\partial \rho}{\partial P_{S_A, \theta}} = \rho^{-1} \frac{\partial \rho}{\partial P_{S_A, \varphi}} \quad (2.16.1)
\]

The isentropic and isohaline compressibility \( \kappa \) is sometimes called simply the isentropic compressibility (or sometimes the “adiabatic compressibility”), on the unstated understanding that there is also no transfer of salt during the isentropic or adiabatic change in pressure. The isentropic and isohaline compressibility of seawater \( \kappa \) produced by both the SIA and GSW software libraries (appendices M and N) has units of Pa\(^{-1}\).

2.17 Sound speed

The speed of sound in seawater \( c \) is given by

\[
c = c(S_A, t, p) = \sqrt{\frac{\partial P}{\partial \rho}_{S_A, t}} = \sqrt{\left(\frac{\partial P}{\partial \rho}_{S_A, t}\right)^{-1}} = g_p \sqrt{g_s^2 - g_{ST}^2 g_{PP}^2} . \quad (2.17.1)
\]

Note that in these expressions in Eqn. (2.17.1), since sound speed is in m s\(^{-1}\) and density has units of kg m\(^{-3}\) it follows that the pressure of the partial derivatives must be in Pa and the isentropic compressibility \( \kappa \) must have units of Pa\(^{-1}\). The sound speed \( c \) produced by both the SIA and the GSW software libraries (appendices M and N) has units of m s\(^{-1}\).

2.18 Thermal expansion coefficients

The thermal expansion coefficient \( \alpha' \) with respect to \textit{in situ} temperature \( t \), is

\[
\alpha' = \alpha' (S_A, t, p) = - \frac{1}{\rho} \frac{\partial \rho}{\partial T_{S_A, t}} = \frac{1}{\nu} \frac{\partial \nu}{\partial T_{S_A, t}} = \frac{g_{ST}}{g_p} . \quad (2.18.1)
\]

The thermal expansion coefficient \( \alpha^\theta \) with respect to potential temperature \( \theta \), is (see appendix A.15)

\[
\alpha^\theta = \alpha^\theta (S_A, t, p, p_r) = - \frac{1}{\rho} \frac{\partial \rho}{\partial \theta_{S_A, p}} = \frac{1}{\nu} \frac{\partial \nu}{\partial \theta_{S_A, p}} = \frac{g_{ST}}{g_p} \frac{g_{ST} (S_A, \theta, p_r)}{g_{TT}} , \quad (2.18.2)
\]

where \( p_r \) is the reference pressure of the potential temperature. The \( g_{ST} \) derivative in the numerator is evaluated at \((S_A, \theta, p_r)\) whereas the other derivatives are all evaluated at \((S_A, t, p)\).

The thermal expansion coefficient \( \alpha^\Theta \) with respect to Conservative Temperature \( \Theta \), is (see appendix A.15)

\[
\alpha^\Theta = \alpha^\Theta (S_A, t, p) = - \frac{1}{\rho} \frac{\partial \rho}{\partial \Theta_{S_A, p}} = \frac{1}{\nu} \frac{\partial \nu}{\partial \Theta_{S_A, p}} = - \frac{g_{ST}}{g_p} \frac{c^\Theta}{(T_0 + \theta)} g_{TT} . \quad (2.18.3)
\]

Note that Conservative Temperature \( \Theta \) is defined only with respect to a reference pressure of 0 dbar so that the \( \theta \) in Eqn. (2.18.3) is the potential temperature with \( p_r = 0 \) dbar. All the derivatives on the right-hand side of Eqn. (2.18.3) are evaluated at \((S_A, t, p)\). The constant \( c^\Theta \) is defined in Eqn. (3.3.3) below.
2.19 Saline contraction coefficients

The saline contraction coefficient $\beta'$ (sometimes also called the haline contraction coefficient) at constant in situ temperature $t$, is

$$\beta' = \beta'\left(S_A, t, p \right) = \frac{1}{\rho} \frac{\partial \rho}{\partial S_A} \frac{\partial S_A}{\partial t, p} = -\frac{1}{\nu} \frac{\partial \nu}{\partial S_A} \frac{\partial S_A}{\partial t, p} = -\frac{g_{S_A,t}}{g_T}. \quad (2.19.1)$$

The saline contraction coefficient $\beta^\theta$ at constant potential temperature $\theta$, is (see appendix A.15)

$$\beta^\theta = \beta^\theta\left(S_A, t, p, p_r \right) = \frac{1}{\rho} \frac{\partial \rho}{\partial S_A} \frac{\partial S_A}{\partial \theta, p} = -\frac{1}{\nu} \frac{\partial \nu}{\partial S_A} \frac{\partial S_A}{\partial \theta, p}$$

$$= \frac{g_{T_P} \left[ g_{S_A,T} - g_{S_A T} \left(S_A, \theta, p \right) \right] - g_{T_P} g_{S_A, p}}{g_T g_{T_P}}, \quad (2.19.2)$$

where $p_r$ is the reference pressure of $\theta$. One of the $g_{S_A,T}$ derivatives in the numerator is evaluated at $(S_A, \theta, p_r)$ whereas all the other derivatives are evaluated at $(S_A, t, p)$.

The saline contraction coefficient $\beta^{\Theta}$ at constant Conservative Temperature $\Theta$, is (see appendix A.15)

$$\beta^{\Theta} = \beta^{\Theta}\left(S_A, t, p \right) = \frac{1}{\rho} \frac{\partial \rho}{\partial S_A} \frac{\partial S_A}{\partial \Theta, p} = -\frac{1}{\nu} \frac{\partial \nu}{\partial S_A} \frac{\partial S_A}{\partial \Theta, p}$$

$$= \frac{g_{T_P} \left[ g_{S_A,T} - \left(T_0 + \Theta \right)^{-1} g_{S_A} \left(S_A, \Theta, 0 \right) \right] - g_{T_P} g_{S_A, \Theta}}{g_T g_{T_P}}, \quad (2.19.3)$$

Note that Conservative Temperature $\Theta$ is defined only with respect to a reference pressure of 0 dbar as indicated in this equation. The $g_{S_A}$ derivative in the numerator is evaluated at $(S_A, \theta, 0)$ whereas all the other derivatives are evaluated at $(S_A, t, p)$.

In the SIA computer software (appendix M) all three saline contraction coefficients are produced in units of kg kg$^{-1}$ while in the GSW library (appendix N) all three saline contraction coefficients are produced in units of kg g$^{-1}$ consistent with the preferred oceanographic unit for $S_A$ in the GSW library being g kg$^{-1}$. 
2.20 Isobaric heat capacity

The specific isobaric heat capacity \( c_p \) is the rate of change of specific enthalpy with temperature at constant Absolute Salinity \( S_A \) and pressure \( p \), so that

\[
c_p = c_p (S_A, t, p) = \left. \frac{\partial h}{\partial T} \right|_{S_A, p} = - (T_0 + t) g_{TT}.
\] (2.20.1)

The isobaric heat capacity \( c_p \) varies over the \( S_A - \Theta \) plane at \( p = 0 \) by approximately 5%, as illustrated in Figure 4.

![Figure 4. Contours of isobaric specific heat capacity \( c_p \) of seawater (in J kg\(^{-1}\) K\(^{-1}\))](image)

The isobaric heat capacity \( c_p \) has units of J kg\(^{-1}\) K\(^{-1}\) in both the SIA and GSW computer libraries.

2.21 Isochoric heat capacity

The specific isochoric heat capacity \( c_v \) is the rate of change of specific internal energy \( u \) with temperature at constant Absolute Salinity \( S_A \) and specific volume, \( v \), so that

\[
c_v = c_v (S_A, t, p, v) = \left. \frac{\partial u}{\partial T} \right|_{S_A, v} = - (T_0 + t) \left( g_{TT} g_{PP} - g_{TP}^2 \right) g_{PP}.
\] (2.21.1)

Note that the isochoric and isobaric heat capacities are related by

\[
c_v = c_p - \left( \frac{T_0 + t}{\rho \kappa'} \right)^2, \quad \text{and by} \quad c_v = c_p \frac{\kappa}{\kappa'}.
\] (2.21.2)

The isochoric heat capacity \( c_v \) has units of J kg\(^{-1}\) K\(^{-1}\) in both the SIA and GSW computer libraries.
2.22 The adiabatic lapse rate

The adiabatic lapse rate $\Gamma$ is the change of in situ temperature with pressure at constant entropy and Absolute Salinity, so that (McDougall and Feistel (2003))

$$\Gamma = \Gamma(S_A, t, p) = \left. \frac{\partial t}{\partial P} \right|_{S_A, \eta} = \left. \frac{\partial t}{\partial P} \right|_{S_A, \theta} = -\frac{g_{pp}}{g_{TT}} = \left. \frac{\partial^2 h}{\partial \eta \partial P} \right|_{S_A} = \left. \frac{\partial \eta}{\partial P} \right|_{S_A, p} = \frac{(T_0 + t) \alpha^i}{\rho c_p}$$

(2.22.1)

The adiabatic (and isohaline) lapse rate is commonly (and incorrectly) explained as being proportional to the work done on a fluid parcel as its volume changes in response to an increase in pressure. According to this explanation the adiabatic lapse rate would increase with both pressure and the fluid’s compressibility, but this is not the case. Rather, the adiabatic lapse rate is proportional to the thermal expansion coefficient and is independent of the fluid’s compressibility. Indeed, the adiabatic lapse rate changes sign at the temperature of maximum density whereas the compressibility and the work done by compression is always positive. McDougall and Feistel (2003) show that the adiabatic lapse rate is independent of the increase in the internal energy that a parcel experiences when it is compressed. Rather, the adiabatic lapse rate represents that change in temperature that is required to keep the entropy (and also $\theta$ and $\Theta$) of a seawater parcel constant when its pressure is changed in an adiabatic and isohaline manner. The reference pressure of the potential temperature $\theta$ that appears in the last four expressions in Eqn. (2.22.1) is $p_r = 0$ dbar.

The adiabatic lapse rate $\Gamma$ output of both the SIA and the GSW software libraries is in units of K Pa$^{-1}$.  

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3. Derived Quantities

3.1 Potential temperature

The very useful concept of potential temperature was applied to the atmosphere originally by Helmholtz (1888), first under the name of ‘heat content’, and later renamed ‘potential temperature’ (Bezold (1888)). These concepts were transferred to oceanography by Helland-Hansen (1912). Potential temperature is the temperature that a fluid parcel would have if its pressure were changed to a fixed reference pressure \( p_r \) in an isentropic and isohaline manner. The phrase “isentropic and isohaline” is used repeatedly in this document. To these two qualifiers we should really also add “without dissipation of mechanical energy”. A process that obeys all three restrictions is a thermodynamically reversible process. Note that one often (falsely) reads that the requirement of a reversible process is that the process occurs at constant entropy. However this statement is misleading because it is possible for a fluid parcel to exchange some heat and some salt with its surroundings in just the right ratio so as to keep its entropy constant, but the processes is not reversible (see Eqn. (A.7.1)).

Potential temperature referred to reference pressure \( p_r \) is often written as the pressure integral of the adiabatic lapse rate (Fofonoff (1962), (1985))

\[
\theta = \theta(S_A,t,p,p_r) = t + \int_{p}^{p_r} \Gamma(S_A,\theta(S_A,t,p',p'),p') \, dP'.
\]  

(3.1.1)

Note that this pressure integral needs to be done with respect to pressure expressed in Pa not dbar.

The algorithm that is used with the TEOS-10 Gibbs function approach to seawater equates the specific entropies of two seawater parcels, one before and the other after the isentropic and isohaline pressure change. In this way, \( \theta \) is evaluated using a Newton-Raphson iterative solution technique to solve the following equation for \( \theta \)

\[
\eta(S_A,\theta,p_r) = \eta(S_A,t,p),
\]  

(3.1.2)

or, in terms of the Gibbs function, \( g \),

\[
- g'_T(S_A,\theta,p_r) = - g'_T(S_A,t,p).
\]  

(3.1.3)

This relation is formally equivalent to Eqn. (3.1.1). In the GSW computer software \( \theta \) is found to machine precision \((-10^{-14} \, ^\circ C)\) in two iterations of a modified Newton-Raphson method, using a suitable initial value as described by McDougall et al. (2010b).

Note that the difference between the potential and \emph{in situ} temperatures is not due to the work done in compressing a fluid parcel on going from one pressure to another:- the sign of this work is often in the wrong sense and the magnitude is often wrong by a few orders of magnitude (McDougall and Feistel (2003)). Rather, the difference between these temperatures is what is required to keep the entropy constant during the adiabatic and isohaline pressure change. The potential temperature \( \theta \) output of the SIA software is in units of K while the output from the GSW library is in \(^\circ C\).
3.2 Potential enthalpy

Potential enthalpy \( h^0 \) is the enthalpy that a fluid parcel would have if its pressure were changed to a fixed reference pressure \( p_r \) in an isentropic and isohaline manner. Because heat fluxes into and out of the ocean occur mostly near the sea surface, the reference pressure for potential enthalpy is always taken to be \( p_r = 0 \) dbar (that is, at zero sea pressure). Potential enthalpy can be expressed as the pressure integral of specific volume as (McDougall (2003) and see the discussion below Eqn. (2.8.2))

\[
\begin{align*}
    h^0(S_A, t, p) &= h(S_A, \Omega, 0) = \tilde{h}^0(S_A, \theta) = h(S_A, t, p) - \int_{p_h}^{p} v(S_A, \theta[p_r, p, p'], p') \, dp' \\
    &= h(S_A, t, p) - \int_{p_h}^{p} \tilde{v}(S_A, \eta, p') \, dp' \\
    &= h(S_A, t, p) - \int_{p_h}^{p} \tilde{v}(S_A, \theta, p') \, dp' \\
    &= h(S_A, t, p) - \int_{p_h}^{p} \tilde{v}(S_A, \Theta, p') \, dp',
\end{align*}
\]

(3.2.1)

and we emphasize that the pressure integrals here must be done with respect to pressure expressed in Pa rather than dbar. In terms of the Gibbs function, potential enthalpy \( h^0 \) is evaluated as

\[
    h^0(S_A, t, p) = h(S_A, \theta, 0) = g(S_A, \theta, 0) - (T_0 + \theta)g_r(S_A, \theta, 0).
\]

(3.2.2)

3.3 Conservative Temperature

Conservative Temperature \( \Theta \) is defined to be proportional to potential enthalpy according to

\[
    \Theta(S_A, t, p) = \tilde{\Theta}(S_A, \theta) = \frac{h^0(S_A, t, p)}{c_p^0} = \frac{\tilde{h}^0(S_A, \theta)}{c_p^0}
\]

(3.3.1)

where the value that is chosen for \( c_p^0 \) is motivated in terms of potential enthalpy evaluated at an Absolute Salinity of \( S_{SO} = 35 \, u_{PS} = 35.165 \, 04 \, \text{gkg}^{-1} \) and at \( \theta = 25 \, ^\circ\text{C} \) by

\[
    \left[ \frac{h(S_{SO}, 25 \, ^\circ\text{C}, 0) - h(S_{SO}, 0 \, ^\circ\text{C}, 0)}{25 \, \text{K}} \right] \approx 3991.867 \, 957 \, 119 \, 63 \, \text{Jkg}^{-1} \text{K}^{-1},
\]

(3.3.2)

noting that \( h(S_{SO}, 0 \, ^\circ\text{C}, 0 \text{dbar}) \) is zero according to the way the Gibbs function is defined in (2.6.5). In fact we adopt the exact definition for \( c_p^0 \) to be the 15-digit value in (3.3.2), so that

\[
    c_p^0 = 3991.867 \, 957 \, 119 \, 63 \, \text{Jkg}^{-1} \text{K}^{-1}.
\]

(3.3.3)

When IAPWS-95 is used for the pure water part of the Gibbs function, \( \Theta(S_{SO}, 0 \, ^\circ\text{C}, 0) \) and \( \Theta(S_{SO}, 25 \, ^\circ\text{C}, 0) \) differ from 0 \( ^\circ\text{C} \) and 25 \( ^\circ\text{C} \) respectively by the round-off amount of \( 5 \times 10^{-12} \, ^\circ\text{C} \). When IAPWS-09 (which is based on the paper of Feistel (2003), see appendix G) is used for the pure water part of the Gibbs function, \( \Theta(S_{SO}, 0 \, ^\circ\text{C}, 0) \) differs from 0 \( ^\circ\text{C} \) by \( -8.25 \times 10^{-8} \, ^\circ\text{C} \) and \( \Theta(S_{SO}, 25 \, ^\circ\text{C}, 0) \) differs from 25 \( ^\circ\text{C} \) by \( 9.3 \times 10^{-6} \, ^\circ\text{C} \). Over the temperature range from 0 \( ^\circ\text{C} \) to 40 \( ^\circ\text{C} \) the difference between Conservative Temperature using IAPWS-95 and IAPWS-09 as the pure water part is no more than \( \pm 1.5 \times 10^{-3} \, ^\circ\text{C} \), a temperature difference that will be ignored.

The value of \( c_p^0 \) in (3.3.3) is very close to the average value of the specific heat capacity \( c_p \) at the sea surface of today’s global ocean. This value of \( c_p^0 \) also causes the average value of \( \theta - \Theta \) at the sea surface to be very close to zero. Since \( c_p^0 \) is simply a constant of proportionality between potential enthalpy and Conservative Temperature, it is totally
arbitrary, and we see no reason why its value would need to change from (3.3.3) even when in future decades an improved Gibbs function of seawater is agreed upon.

Appendix A.18 outlines why Conservative Temperature gets its name; it is approximately two orders of magnitude more conservative compared with either potential temperature or entropy.

The SIA and GSW software libraries both include an algorithm for determining Conservative Temperature $\Theta$ from values of Absolute Salinity $S_A$ and potential temperature $\theta$ referenced to $p = 0$ dbar. These libraries also have an algorithm for evaluating potential temperature (referenced to 0 dbar) from $S_A$ and $\Theta$. This inverse algorithm, $\theta(S_A, \Theta)$, has an initial seed based on a rational function approximation and finds potential temperature to machine precision ($-10^{-14} \, ^\circ C$) in one and a half iterations of a modified Newton-Raphson technique (McDougall et al. (2010b)).

### 3.4 Potential density

Potential density $\rho^o$ is the density that a fluid parcel would have if its pressure were changed to a fixed reference pressure $p_r$ in an isentropic and isohaline manner. Potential density referred to reference pressure $p_r$ can be written as the pressure integral of the isentropic compressibility as

$$\rho^o(S_A, t, p, p_r) = \rho(S_A, t, p) + \int_{p_r}^p \rho(S_A, \theta(S_A, t, p, p'), p') \kappa(S_A, \theta(S_A, t, p, p'), p') \, dp'. \quad (3.4.1)$$

The simpler expression for potential density in terms of the Gibbs function is

$$\rho^o(S_A, t, p, p_r) = \rho(S_A, \theta(S_A, t, p, p_r), p_r) = g_P^{-1}(S_A, \theta(S_A, t, p, p_r), p_r). \quad (3.4.2)$$

Using either of the functional forms (2.8.2) for in situ density, that is, either $\rho = \tilde{\rho}(S_A, \theta, p)$ or $\rho = \tilde{\rho}(S_A, \Theta, p)$, potential density with respect to reference pressure $p_r$ (e. g. 1000 dbar) can be easily evaluated as

$$\rho^o(S_A, t, p, p_r) = \rho^o(S_A, t, p, p_r) = \tilde{\rho}(S_A, \eta, p_r) = \tilde{\rho}(S_A, \theta, p_r) = \tilde{\rho}(S_A, \Theta, p_r). \quad (3.4.3)$$

where we note that the potential temperature $\theta$ in the third expression is the potential temperature with respect to 0 dbar. Once the reference pressure is fixed, potential density is a function only of Absolute Salinity and Conservative Temperature (or equivalently, of Absolute Salinity and potential temperature). Note that it is equally correct to label potential density as $\rho^o$ or $\rho^o$ (or indeed as $\rho^o$) because $\eta$, $\theta$ and $\Theta$ are constant during the isentropic and isohaline pressure change from $p$ to $p_r$; that is, these variables possess the “potential” property of appendix A.9.

Following the discussion after Eqn. (2.8.2) above, potential density may also be expressed in terms of the pressure derivative of the expressions $h = \tilde{h}(S_A, \theta, p)$ and $h = \tilde{h}(S_A, \Theta, p)$ for enthalpy as (see also appendix P)

$$\rho^o(S_A, t, p, p_r) = \rho^o(S_A, t, p, p_r) = \left[\tilde{h}_P(S_A, \theta, p = p_r)\right]^{-1} = \left[\tilde{h}_P(S_A, \Theta, p = p_r)\right]^{-1}. \quad (3.4.4)$$

### 3.5 Density anomaly

Density anomaly $\sigma'$ is an old-fashioned density measure that is now seldom used. It is the density evaluated at the in situ temperature but at zero sea pressure, minus 1000 kg m$^{-3}$, that is,

$$\sigma'(S_A, t, p) = \rho(S_A, t, 0) - 1000 \, \text{kg m}^{-3} = g_P^{-1}(S_A, t, 0) - 1000 \, \text{kg m}^{-3}. \quad (3.5.1)$$

$\sigma'$ was used as an approximation to $\sigma^0$ which avoided the computational demand of evaluating $\theta$. Density anomaly $\sigma'$ is not provided in the TEOS-10 software libraries.
3.6 Potential density anomaly

Potential density anomaly, \( \sigma^\theta \) or \( \sigma^\theta \), is simply potential density minus 1000 kg m\(^{-3}\),
\[
\sigma^\theta(S_A, t, p, p_r) = \sigma^\theta(S_A, t, p, p_r) = \rho^\theta(S_A, t, p, p_r) - 1000 \text{ kg m}^{-3} \\
= \rho^\theta(S_A, t, p, p_r) - 1000 \text{ kg m}^{-3} \\
= g_p^{-1}(S_A, \theta[S_A, t, p, p_r], p_r) - 1000 \text{ kg m}^{-3} \quad (3.6.1)
\]

Note that it is equally correct to label potential density anomaly as \( \sigma^\theta \) or \( \sigma^\theta \) because both \( \theta \) and \( \Theta \) are constant during the isentropic and isohaline pressure change from \( p \) to \( p_r \).

3.7 Specific volume anomaly

The specific volume anomaly \( \delta \) is defined as the difference between the specific volume and a given function of pressure. Traditionally \( \delta \) has been defined as
\[
\delta(S_A, t, p) = v(S_A, t, p) - v(S_{SO}, 0^\circ C, p) \quad (3.7.1)
\]
(where the traditional value of Practical Salinity of 35 has been updated to an Absolute Salinity of \( S_{SO} = 35u_p = 35.16504 \text{ g kg}^{-1} \) in the present formulation). Note that the second term, \( v(S_{SO}, 0^\circ C, p) \), is a function only of pressure. In order to have a surface of constant specific volume anomaly more accurately approximate neutral tangent planes (see section 3.11), it is advisable to replace the arguments \( S_{SO} \) and \( 0^\circ C \) with more general values \( \tilde{S}_A \) and \( \tilde{t} \) that are carefully chosen (as say the median values of Absolute Salinity and temperature along the surface) so that the more general definition of specific volume anomaly is
\[
\tilde{\delta}(S_A, t, p) = v(S_A, t, p) - v(\tilde{S}_A, \tilde{t}, p) = g_p(S_A, t, p) - g_p(\tilde{S}_A, \tilde{t}, p) \quad (3.7.2)
\]

The last terms in Eqns. (3.7.1) and (3.7.2) are simply functions of pressure and one has the freedom to choose any other function of pressure in its place and still retain the dynamical properties of specific volume anomaly. In particular, one can construct specific volume and enthalpy to be functions of Conservative Temperature (rather than \( \text{in situ} \) temperature) as \( \tilde{v}(S_A, \Theta, p) \) and \( \tilde{h}(S_A, \Theta, p) \) and write a slightly different definition of specific volume anomaly as
\[
\tilde{\delta}(S_A, \Theta, p) = \tilde{v}(S_A, \Theta, p) - \tilde{v}(\tilde{S}_A, \tilde{\Theta}, p) = \tilde{h}_p(S_A, \Theta, p) - \tilde{h}_p(\tilde{S}_A, \tilde{\Theta}, p) \quad (3.7.3)
\]

The same can also be done with potential temperature so that in terms of the specific volume \( \tilde{v}(S_A, \Theta, p) \) and enthalpy \( \tilde{h}(S_A, \Theta, p) \) we can write another form of the specific volume anomaly as
\[
\tilde{\delta}(S_A, \Theta, p) = \tilde{v}(S_A, \Theta, p) - \tilde{v}(\tilde{S}_A, \tilde{\Theta}, p) = \tilde{h}_p(S_A, \Theta, p) - \tilde{h}_p(\tilde{S}_A, \tilde{\Theta}, p) \quad (3.7.4)
\]

These expressions exploit the fact that (see appendix A.11)
\[
\frac{\partial h}{\partial p} \bigg|_{S_A, \Theta} = \frac{\partial h}{\partial p} \bigg|_{S_A, \theta} = \frac{\partial h}{\partial p} \bigg|_{S_A, \theta} = v . \quad (3.7.5)
\]
3.8 Thermobaric coefficient

The thermobaric coefficient quantifies the rate of variation with pressure of the ratio of the thermal expansion coefficient and the saline contraction coefficient. With respect to potential temperature \( \Theta \) the thermobaric coefficient is (McDougall (1987b))

\[
T^\Theta_b = T^\Theta_b \left( S_{\alpha},t,p \right) = \beta^\Theta \frac{\partial \left( \alpha^\Theta / \beta^\Theta \right)}{\partial P} \bigg|_{S_{\alpha},\Theta} = \frac{\partial \alpha^\Theta}{\partial P} \bigg|_{S_{\alpha},\Theta} - \frac{\alpha^\Theta}{\beta^\Theta} \frac{\partial \beta^\Theta}{\partial P} \bigg|_{S_{\alpha},\Theta} \quad .
\]

(3.8.1)

This expression for the thermobaric coefficient is most readily evaluated by differentiating an expression for density expressed as a function of potential temperature rather than \textit{in situ} temperature, that is, with density expressed in the functional form \( \rho = \hat{\rho} \left( S_{\alpha},\Theta, p \right) \).

With respect to Conservative Temperature \( \Theta \) the thermobaric coefficient is

\[
T^\Theta_b = T^\Theta_b \left( S_{\alpha},t,p \right) = \hat{\beta}^\Theta \frac{\partial \left( \alpha^\Theta / \hat{\beta}^\Theta \right)}{\partial P} \bigg|_{S_{\alpha},\Theta} = \frac{\partial \alpha^\Theta}{\partial P} \bigg|_{S_{\alpha},\Theta} - \frac{\alpha^\Theta}{\hat{\beta}^\Theta} \frac{\partial \hat{\beta}^\Theta}{\partial P} \bigg|_{S_{\alpha},\Theta} \quad .
\]

(3.8.2)

This expression for the thermobaric coefficient is most readily evaluated by differentiating an expression for density expressed as a function of Conservative Temperature rather than \textit{in situ} temperature, that is, with density expressed in the functional form \( \rho = \hat{\rho} \left( S_{\alpha},\Theta, p \right) \).

The thermobaric coefficient enters various quantities to do with the path-dependent nature of neutral trajectories and the ill-defined nature of neutral surfaces (see (3.13.1) – (3.13.7)). The thermobaric dianeutral advection associated with the lateral mixing of heat and salt along neutral tangent planes is given by \( e^T_b = -gN^{-2}KT^\Theta_b \nabla_n \Theta \cdot \nabla_n P \) or \( e^T_b = -gN^{-2}KT^\hat{\Theta}_b \nabla_n \Theta \cdot \nabla_n P \) where \( \nabla_n \Theta \) and \( \nabla_n \Theta \) are the two-dimensional gradients of either potential temperature or Conservative Temperature along the neutral tangent plane, \( \nabla_n P \) is the corresponding epineutral gradient of absolute pressure and \( K \) is the epineutral diffusion coefficient. Note that the thermobaric dianeutral advection is proportional to the mesoscale eddy flux of “heat” along the neutral tangent plane, \( -c^\Theta_n K \nabla_n \Theta \), and is independent of the amount of small-scale (dineutral) turbulent mixing and hence is also independent of the dissipation of mechanical energy \( c \) (Klocker and McDougall (2010a)). It is shown in appendix A.14 below that while the epineutral diffusive fluxes \( -K \nabla_n \Theta \) and \( -K \nabla_n \Theta \) are different, the product of these fluxes with their respective thermobaric coefficients is the same, that is, \( T^\Theta_b \nabla_n \Theta = T^\hat{\Theta}_b \nabla_n \Theta \). Hence the thermobaric dianeutral advection \( e^T_b \) is the same whether it is calculated as \( -gN^{-2}KT^\Theta_b \nabla_n \Theta \cdot \nabla_n P \) or as \( -gN^{-2}KT^\hat{\Theta}_b \nabla_n \Theta \cdot \nabla_n P \). Expressions for \( T^\Theta_b \) and \( T^\hat{\Theta}_b \) in terms of enthalpy in the functional forms \( \tilde{h} \left( S_{\alpha},\Theta, p \right) \) and \( \tilde{h} \left( S_{\alpha},\Theta, p \right) \) can be found in appendix P.

Interestingly, for given magnitudes of the epineutral gradients of pressure and Conservative Temperature, the dianeutral advection, \( e^T_b = -gN^{-2}KT^\Theta_b \nabla_n \Theta \cdot \nabla_n P \), of thermobaricity is maximized when these gradients are parallel, while neutral helicity is maximized when these gradients are perpendicular, since neutral helicity is proportional to \( T^\Theta_b \left( \nabla_n P \times \nabla_n \Theta \right) \cdot \mathbf{k} \) (see Eqn. (3.13.2)).

This thermobaric vertical advection process, \( e^T_b \), is absent from standard layered ocean models in which the vertical coordinate is a function only of \( S_{\alpha} \) and \( \Theta \) (such as \( \sigma_z \), potential density referenced to 2000 dbar). As described in appendix A.27 below, the isopycnal diffusion of heat and salt in these layered models, caused by both parameterized diffusion along the coordinate and by eddy-resolved motions, does give rise to the cabling advection through the coordinate surfaces but does not allow the thermobaric velocity \( e^T \) through these surfaces (Klocker and McDougall (2010a)).

In both the SIA and GSW computer software, both versions of the thermobaric parameter \( T^\Theta_b \) and \( T^\hat{\Theta}_b \) are output in units of \( K^{-1} \text{Pa}^{-1} \).
3.9 Cabbeling coefficient

The cabbeling coefficient quantifies the rate at which dianeutral advection occurs as a result of mixing of heat and salt along the neutral tangent plane. With respect to potential temperature $\Theta$ the cabbeling coefficient is (McDougall (1987b))

$$
C_b^\Theta = C_b^\Theta (S_A,t,p) = \frac{\partial \alpha^\Theta}{\partial \Theta} |_{S_A,p} + 2 \frac{\alpha^\Theta}{\beta^\Theta} \frac{\partial \alpha^\Theta}{\partial S_A} \frac{\partial S_A}{\partial \Theta} |_{S_A,p} - \frac{\alpha^\Theta}{\beta^\Theta} \frac{\partial \beta^\Theta}{\partial S_A} \frac{\partial S_A}{\partial \Theta} |_{S_A,p} .
$$

This expression for the cabbeling coefficient is most readily evaluated by differentiating an expression for density expressed as a function of potential temperature rather than in situ temperature, that is, with density expressed in the functional form $\rho = \hat{\rho}(S_A,\Theta, p)$.

With respect to Conservative Temperature $\Theta$ the cabbeling coefficient is

$$
C_b^\Theta = C_b^\Theta (S_A,t,p) = \frac{\partial \alpha^\Theta}{\partial \Theta} |_{S_A,p} + 2 \frac{\alpha^\Theta}{\beta^\Theta} \frac{\partial \alpha^\Theta}{\partial S_A} \frac{\partial S_A}{\partial \Theta} |_{S_A,p} - \frac{\alpha^\Theta}{\beta^\Theta} \frac{\partial \beta^\Theta}{\partial S_A} \frac{\partial S_A}{\partial \Theta} |_{S_A,p} .
$$

This expression for the cabbeling coefficient is most readily evaluated by differentiating an expression for density expressed as a function of Conservative Temperature rather than in situ temperature, that is, with density expressed in the functional form $\rho = \hat{\rho}(S_A,\Theta, p)$.

The cabbeling dianeutral advection associated with the lateral mixing of heat and salt along neutral tangent planes is given by $e^{\text{cab}} = -gN^2K \frac{\partial \Theta}{\partial \Theta} \nabla \nabla \Theta$ (or less accurately by $e^{\text{cab}} = -gN^2K \frac{\partial \Theta}{\partial \Theta} \nabla \nabla \Theta$) where $\nabla \Theta$ and $\nabla \Theta$ are the two-dimensional gradients of either potential temperature or Conservative Temperature along the neutral tangent plane and $K$ is the epineutral diffusion coefficient. The cabbeling dianeutral advection is proportional to the mesoscale eddy flux of “heat” along the neutral tangent plane, $-K \nabla \Theta$, and is independent of the amount of small-scale (dianeutral) turbulent mixing and hence is also independent of the dissipation of mechanical energy (Klocker and McDougall (2010a)). It is shown in appendix A.14 that $C_b^{\Theta} \nabla \Theta \cdot \nabla \Theta$ is not $C_b^{\Theta} \nabla \Theta \cdot \nabla \Theta$ so that the estimate of the cabbeling dianeutral advection is different when calculated using potential temperature than when using Conservative Temperature. The estimate using potential temperature is slightly less accurate because of the non-conservative nature of potential temperature.

When the cabbeling and thermobaricity processes are analyzed by considering the mixing of two fluid parcels one finds that the density change is proportional to the square of the property ( $\Theta$ and/or $p$ ) contrasts between the two fluid parcels (for the cabbeling case, see Eqn. (A.19.4) in appendix A.19). This leads to the thought that if an ocean front is split up into a series of many smaller fronts then the effects of cabbeling and thermobaricity might be reduced by perhaps the square of the number of such fronts. This is not the case. Rather, the total dianeutral transport across a frontal region depends on the product of the lateral flux of heat passing through the front and the contrast in temperature and/or pressure across the front, but is independent of the sharpness of the front (Klocker and McDougall (2010a)). This can be understood by noting from above that the dianeutral velocity due to cabbeling, $e^{\text{cab}} = -gN^2K \frac{\partial \Theta}{\partial \Theta} \nabla \Theta$, is proportional to the scalar product of the epineutral flux of heat $-c^{\Theta} K \nabla \Theta$ and the epineutral temperature gradient $\nabla \Theta$. Spatially integrating this product over the area of the frontal region, one finds that the total dianeutral transport is proportional to the lateral heat flux times the difference in temperature across the frontal region (in the case of cabbeling) or the difference in pressure across the frontal region (in the case of thermobaricity).

In both the SIA and GSW software libraries, both versions of the cabbeling parameter $C_b^\Theta$ and $C_b^\Theta$ are output in units of $K^{-2}$. Expressions for $C_b^\Theta$ and $C_b^\Theta$ in terms of enthalpy in the functional forms $\tilde{h}(S_A,\Theta, p)$ and $\tilde{h}(S_A,\Theta, p)$ can be found in appendix P.
3.10 Buoyancy frequency

The square of the buoyancy frequency (sometimes called the Brunt-Väisälä frequency) $N^2$ is given in terms of the vertical gradients of density and pressure, or in terms of the vertical gradients of potential temperature and Absolute Salinity (or in terms of the vertical gradients of Conservative Temperature and Absolute Salinity) by (the $g$ on the left-hand side is the gravitational acceleration, and $x$, $y$ and $z$ are the spatial Cartesian coordinates)

$$g^{-1} N^2 = - \rho^{-1} \rho_z + \kappa P_z = - \rho^{-1} \left( \rho_z - P_z / c^2 \right)$$

$$= \alpha^\theta \Theta_z - \beta^\theta \Theta S_A / \partial z |_{x,y}$$

$$= \alpha^\Theta \Theta_z - \beta^\Theta \Theta S_A / \partial z |_{x,y}. \tag{3.10.1}$$

For two seawater parcels separated by a small distance $\Delta z$ in the vertical, an equally accurate method of calculating the buoyancy frequency is to bring both seawater parcels adiabatically and without exchange of matter to the average pressure and to calculate the difference in density of the two parcels after this change in pressure. In this way the potential density of the two seawater parcels are being compared at the same pressure. This common procedure calculates the buoyancy frequency $N$ according to

$$N^2 = \frac{g}{\rho} \frac{\Delta \rho^\theta}{\Delta z} = \frac{g^2 \Delta \rho^\theta}{\Delta P}, \tag{3.10.2}$$

where $\Delta \rho^\theta$ is the difference between the potential densities of the two seawater parcels with the reference pressure being the average of the two original pressures of the seawater parcels. The last part of Eqn. (3.10.2) has used the hydrostatic relation $P_z = - g \rho$.

3.11 Neutral tangent plane

The neutral plane is that plane in space in which the local parcel of seawater can be moved an infinitesimal distance without being subject to a vertical buoyant restoring force; it is the plane of neutral- or zero- buoyancy. The normal vector to the neutral tangent plane $n$ is given by

$$g^{-1} N^2 n = - \rho^{-1} \nabla \rho + \kappa \nabla P = - \rho^{-1} \left( \nabla \rho - \nabla P / c^2 \right)$$

$$= \alpha^\theta \nabla \Theta - \beta^\theta \nabla S_A$$

$$= \alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_A. \tag{3.11.1}$$

As defined, $n$ is not quite a unit normal vector, rather its vertical component is exactly $k$, that is, its vertical component is unity. It is clear that $\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_A$ is exactly equal to $\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_A$. Interestingly, both $\alpha^\Theta \nabla \Theta$ and $\beta^\Theta \nabla S_A$ are independent of the four arbitrary constants of the Gibbs function (see Eqn. (2.6.2)) while both $\alpha^\Theta \nabla \Theta$ and $\beta^\Theta \nabla S_A$ contain an identical additional arbitrary term proportional to $a_3 \nabla S_A$; terms that exactly cancel in their difference, $\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_A$, in Eqn. (3.11.1).

Expressing the two-dimensional gradient of properties in the neutral tangent plane by $\nabla_n$, the property gradients in a neutral tangent plane obey

$$- \rho^{-1} \nabla_n \rho + \kappa \nabla_n P = - \rho^{-1} \left( \nabla_n \rho - \nabla_n P / c^2 \right)$$

$$= \alpha^\theta \nabla_n \Theta - \beta^\theta \nabla_n S_A$$

$$= \alpha^\Theta \nabla_n \Theta - \beta^\Theta \nabla_n S_A$$

$$= 0. \tag{3.11.2}$$

Here $\nabla_n$ is an example of a projected non-orthogonal gradient.
\[ \nabla r = \frac{\partial r}{\partial x} \hat{i} + \frac{\partial r}{\partial y} \hat{j} + 0 \hat{k}, \quad (3.11.3) \]

that is widely used in oceanic and atmospheric theory and modelling. Horizontal distances are measured between the vertical planes of constant latitude \( x \) and longitude \( y \) while the values of the property \( r \) are evaluated on the \( r \) surface (e. g. an isopycnal surface, or in the case of \( \nabla r \), a neutral tangent plane). This coordinate system is described by Sutcliffe (1947), Bleck (1978), McDougall (1987b), McDougall (1995) and Griffies (2004). Note that \( \nabla r \) has no vertical component; it is not directed along the \( r \) surface, but rather it points in exactly the horizontal direction.

Finite difference versions of Eqn. (3.11.2) such as \( \bar{\alpha}' \Delta \Theta - \bar{b}' \Delta S_{\alpha} \approx 0 \) are also very accurate. Here \( \bar{\alpha}' \) and \( \bar{b}' \) are the values of these coefficients evaluated at the average values of \( \Theta \), \( S_{\alpha} \) and \( p \) of two parcels \( \left( S_{\alpha}^1, \Theta_1, p_1 \right) \) and \( \left( S_{\alpha}^2, \Theta_2, p_2 \right) \) on a “neutral surface” and \( \Delta \Theta \) and \( \Delta S_{\alpha} \) are the property differences between the two parcels. The error involved with this finite amplitude version of Eqn. (3.11.2), namely

\[ - \bar{r}' \int_1^2 \left( P - \bar{P} \right) d\Theta, \quad (3.11.4) \]

is described in section 2 and appendix A(c) of Jackett and McDougall (1997). An equally accurate finite amplitude version of Eqn. (3.11.2) is to equate the potential densities of the two fluid parcels, each referenced to the average pressure \( \bar{P} = 0.5 \left( p_1 + p_2 \right) \).

### 3.12 Geostrophic, hydrostatic and “thermal wind” equations

The geostrophic approximation to the horizontal momentum equations ((B9) below) equates the Coriolis term to the horizontal pressure gradient \( \nabla \cdot P \) so that the geostrophic equation is

\[ f \mathbf{k} \times \rho \mathbf{u} = -\nabla \cdot P \quad \text{or} \quad f \mathbf{v} = \frac{1}{\rho} \mathbf{k} \times \nabla \cdot P. \quad (3.12.1) \]

where \( \mathbf{u} \) is the three dimensional velocity and \( \mathbf{v} = -\mathbf{k} \times (\mathbf{k} \times \mathbf{u}) \) is the horizontal velocity where \( \mathbf{k} \) is the vertical unit vector (pointing upwards) and \( f \) is the Coriolis parameter.

The hydrostatic equation is an approximation to the vertical momentum equation (see Eqn. (B9)), namely

\[ P_z = -g \rho. \quad (3.12.2) \]

The use of \( P \) in these equations rather than \( p \) serves to remind us that in order to retain the usual units for height, density and the gravitational acceleration, pressure in these dynamical equations must be expressed in Pa not dbar.

The so called “thermal wind” equation is an equation for the vertical gradient of the horizontal velocity under the geostrophic approximation. Vertically differentiating Eqn. (3.12.1), using the hydrostatic equation Eqn. (3.12.2) and ignoring the tiny term in \( \rho_z \) (which is of Boussinesq magnitude), the thermal wind can be written as

\[ f \nabla_z = \frac{1}{\rho} \mathbf{k} \times \nabla_z \left( P_z \right) = -\frac{g}{\rho} \mathbf{k} \times \nabla \cdot \mathbf{\rho} = \frac{\nabla}{\rho} \mathbf{k} \times \nabla \cdot P, \quad (3.12.3) \]

where \( \nabla_z \) is the gradient operator in the exactly horizontal direction along geopotentials, and the last part of this equation relates the “thermal wind” to the pressure gradient in the neutral tangent plane, that is, effectively to the slope of the neutral tangent plane (see McDougall (1995)).
3.13 Neutral helicity

Neutral tangent planes (which do exist) do not link up in space to form a well-defined neutral surface unless the neutral helicity $H^n$ is everywhere zero on the surface. Neutral helicity is defined as the scalar product of the vector $(\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda)$ with its curl,

$$H^n = \left(\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda\right) \cdot \nabla \times \left(\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda\right)$$

(3.13.1)

and this is proportional to the thermobaric coefficient $T_b^\Theta$ of the equation of state according to

$$H^n = \beta^\Theta T_b^\Theta \nabla P \cdot \nabla S_\Lambda \times \nabla \Theta$$

$$= P_z \beta^\Theta T_b^\Theta \left(\nabla_p S_\Lambda \times \nabla_p \Theta\right) \cdot \mathbf{k}$$

$$= g^{-1} N^2 T_b^\Theta \left(\nabla_n P \times \nabla_n \Theta\right) \cdot \mathbf{k}$$

(3.13.2)

where $P_z$ is simply the vertical gradient of pressure (Pa m$^{-1}$) and $\nabla_n \Theta$ and $\nabla_n \Theta$ are the two-dimensional gradients of $\Theta$ in the neutral tangent plane and in the horizontal plane (actually the isobaric surface) respectively. The gradients $\nabla_n P$ and $\nabla_n \Theta$ are taken in an approximately neutral surface. Since $\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda$ and $\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda$ are exactly equal, neutral helicity can be defined in Eqn. (3.13.1) as the scalar product of this vector with its curl based on either formulation, so that (from the third line of Eqn. (3.13.2), and bearing in mind that $\nabla_n \Theta$ and $\nabla_n \Theta$ are parallel vectors) we see that $T_b^\Theta \nabla_n \Theta = T_b^\Theta \nabla_n \Theta$, a result that we use in section 3.8 and in appendix A.14. Neutral helicity has units of m$^{-3}$.

Because of the non-zero neutral helicity in the ocean, lateral motion following neutral tangent planes has the character of helical motion. That is, if we ignore the effects of diapycnal mixing processes (as well as ignoring cabling and thermobaricity), the mean flow around ocean gyres still passes through any well-defined “density” surface because of the helical nature of neutral trajectories, caused in turn by the non-zero neutral helicity. This dia-surface flow is expressed in Eqns. (A.25.4) and (A.25.6) in terms of the appropriate mean horizontal velocity and the difference between the slope of the neutral tangent plane and the slope of a well-defined “density” surface.

Neutral helicity is proportional to the component of the vertical shear of the geostrophic velocity ($v_z$, the “thermal wind”) in the direction of the temperature gradient along the neutral tangent plane $\nabla_n \Theta$, since, from Eqn. (3.12.3) and the third line of (3.13.2) we find that

$$H^n = \rho T_b^\Theta f v_z \cdot \nabla_n \Theta.$$  

(3.13.3)

In the evolution equation of potential vorticity defined with respect to potential density $\rho^\Theta$ there is the baroclinic production term $\rho^{-2} \nabla \rho^\Theta \cdot \nabla \rho \times \nabla P$ (Straub (1999)) and the first term in a Taylor series expansion for this baroclinic production term is proportional to neutral helicity and is given by (McDougall and Jackett (2007))

$$\rho^{-2} \nabla \rho^\Theta \cdot \nabla \rho \times \nabla P \approx \left(P_r - P\right) H^n$$

(3.13.4)

where $P_r$ is the reference pressure of the potential density. Similarly, the curl in a potential density surface of the horizontal pressure gradient term in the horizontal momentum equation, $\nabla \times \left(\frac{1}{\rho} \nabla_z P\right)$, is given by (McDougall and Klocker (2010))

$$\nabla \times \left(\frac{1}{\rho} \nabla_z P\right) \cdot \mathbf{k} = H^n \left(P_r - P\right) \left(-\frac{\partial \rho^\Theta}{\partial z}\right)^{-1}.$$  

(3.13.5)

The fact that this curl is nonzero proves that a geostrophic streamfunction does not exist in a potential density surface.

Neutral helicity $H^n$ also arises in the context of finding a closed expression for the mean velocity in the ocean. The component of the horizontal velocity in the direction
along a contour of \( \Theta \) in a neutral tangent plane, namely the velocity component 
\( \mathbf{v} \cdot \mathbf{k} \times \nabla_n \Theta / |\nabla_n \Theta| \), is given by (McDougall (1995), Zika et al. (2010a, 2010b))

\[
\mathbf{v} \cdot \mathbf{k} \times \frac{\nabla_n \Theta}{|\nabla_n \Theta|} = \frac{-H^n}{\phi_2 \rho f T^n_b |\nabla_n \Theta|} + \frac{v^z}{\phi_2}, \tag{3.13.6}
\]

so that the full expression for the horizontal velocity is

\[
\mathbf{v} = \left\{ \frac{-H^n}{\phi_2 \rho f T^n_b |\nabla_n \Theta|} + \frac{v^z}{\phi_2} \right\} \mathbf{k} \times \nabla_n \Theta \left/ |\nabla_n \Theta| \right. + \mathbf{v}^z \times \nabla_n \Theta. \tag{3.13.7}
\]

Here \( \phi_2 \) is the rate of spiraling (radians per meter) in the vertical of the \( \Theta \) contours on neutral tangent planes, and \( v^z \) is the velocity component across the \( \Theta \) contour on the neutral tangent plane (a velocity component that results from irreversible mixing processes). Neutral helicity arises in this context because it is proportional to the component of the thermal wind vector \( \mathbf{v}_z \) in the direction across the \( \Theta \) contour on the neutral tangent plane (see (3.13.3)). This equation (3.13.7) for the isopycnally-averaged velocity \( \mathbf{v} \) shows that in the absence of mixing processes (so that \( v^z = 0 \)) and so long as (i) the epineutral \( \Theta \) contours spiral in the vertical and (ii) \( |\nabla_n \Theta| \) is not zero, then neutral helicity \( H^n \) is required to be non-zero in the ocean whenever the ocean is not motionless.

Interestingly, for given magnitudes of the epineutral gradients of pressure and Conservative Temperature, neutral helicity is maximized when these gradients are perpendicular since neutral helicity is proportional to \( T^n_b (\nabla_n P \times \nabla_n \Theta) \cdot \mathbf{k} \) (see Eqn. (3.13.2)), while the dianeutral advection of thermobaricity, \( e^{T_b} = -gN^{-2}K T^n_b \nabla_n \Theta \cdot \nabla_n P \), is maximized when \( \nabla_n \Theta \) and \( \nabla_n P \) are parallel (see section 3.8).

### 3.14 Neutral Density

Neutral Density is the name given to a density variable that results from the computer software described in Jackett and McDougall (1997). Neutral Density is given the symbol \( \gamma^n \) but it is not a thermodynamic variable as it is a function not only of salinity, temperature and pressure, but also of latitude and longitude. Because of the non-zero neutral helicity \( H^n \) in the ocean it is not possible to form surfaces that are everywhere osculate with neutral tangent planes (McDougall and Jackett (1988)). Neutral Density surfaces minimize in some sense the global differences between the slopes of the neutral tangent plane and the Neutral Density surface. This slope difference is given by

\[
\mathbf{s} = \nabla_n z - \nabla_a z = gN^{-2} \left( \beta^n \nabla_a S_h - \alpha^n \nabla_a \Theta \right) \tag{3.14.1}
\]

where \( \nabla_n z \) is the slope of the neutral tangent plane, \( \nabla_a z \) is the slope of the approximately neutral surface and \( \nabla_a \) is the two-dimensional gradient operator in the approximately neutral surface (of which a Neutral Density surface is one example). The vertical velocity through an approximately neutral surface due to lateral motion along a neutral tangent plane is the scalar product \( \mathbf{v} \cdot \mathbf{s} \) where \( \mathbf{v} \) is the horizontal velocity (see Eqn. (A.25.4)). Since Neutral Density is not a thermodynamic variable, it will not be described more fully in this manual.
3.15 Stability ratio

The stability ratio $R_\rho$ is the ratio of the vertical contribution from Conservative Temperature to that from Absolute Salinity to the static stability $N^2$ of the water column. From (3.10.1) above we find

$$R_\rho = \frac{\alpha^\Theta \Theta_z}{\beta^\Theta (S_\lambda)_z} \approx \frac{\alpha^\Theta \Theta_z}{\beta^\Theta (S_\lambda)_z}. \quad (3.15.1)$$

3.16 Turner angle

The Turner angle $Tu$, named after J. Stewart Turner, is defined as the four-quadrant arctangent (Ruddick (1983) and McDougall et al. (1988), particularly their Figure 1)

$$Tu = \tan^{-1}\left(\alpha^\Theta \Theta_z + \beta^\Theta (S_\lambda)_z, \quad \alpha^\Theta \Theta_z - \beta^\Theta (S_\lambda)_z\right)$$

$$\approx \tan^{-1}\left(\alpha^\Theta \Theta_z + \beta^\Theta (S_\lambda)_z, \quad \alpha^\Theta \Theta_z - \beta^\Theta (S_\lambda)_z\right) \quad (3.16.1)$$

where the first of the two arguments of the arctangent function is the “$y$”-argument and the second one the “$x$”-argument, this being the common order of these arguments in Fortran and Matlab. The Turner angle $Tu$ is quoted in degrees of rotation. Turner angles between 45° and 90° represent the “salt-finger” regime of double-diffusive convection, with the strongest activity near 90°. Turner angles between −45° and −90° represent the “diffusive” regime of double-diffusive convection, with the strongest activity near −90°. Turner angles between −45° and 45° represent regions where the stratification is stably stratified in both $\Theta$ and $S_\lambda$. Turner angles greater than 90° or less than −90° characterize a statically unstable water column in which $N^2 < 0$. As a check on the calculation of the Turner angle, note that $R_\rho = -\tan(Tu + 45°)$.

3.17 Property gradients along potential density surfaces

The two-dimensional gradient of a scalar $\phi$ along a potential density surface $\nabla_\phi$ is related to the corresponding gradient in the neutral tangent plane $\nabla_\phi$ by (from McDougall (1987a))

$$\nabla_\phi = \nabla_\phi + \frac{\phi_z}{\Theta_z} \left[\frac{R_\rho - 1}{R_\rho - r}\right] \nabla_\phi \nabla_\Theta \quad (3.17.1)$$

where $r$ is defined by

$$r = \frac{\alpha^\Theta (S_\lambda, \Theta, p)}{\alpha^\Theta (S_\lambda, \Theta, p_t)} / \frac{\beta^\Theta (S_\lambda, \Theta, p)}{\beta^\Theta (S_\lambda, \Theta, p_t)} \quad (3.17.2)$$

being the ratio of the slope on the $S_\lambda - \Theta$ diagram of an isoline of potential density with reference pressure $p_t$ to the slope of a potential density surface with reference pressure $p$.

Substituting $\phi = \Theta$ into (3.17.1) gives the following relation between the (parallel) isopycnal and epineutral gradients of $\Theta$

$$\nabla_\phi \Theta = \frac{R_\rho - 1}{R_\rho - r} \nabla_\phi \Theta = G^\Theta \nabla_\phi \Theta \quad (3.17.3)$$

where the “isopycnal temperature gradient ratio”

$$G^\Theta = \left[\frac{R_\rho - 1}{R_\rho / r - 1}\right] \quad (3.17.4)$$
has been defined as a shorthand expression for future use. This ratio is available in the GSW software library as the algorithm gsw_isopyc_vs_ntp_CT_grad. Substituting $\phi = S_\lambda$ into Eqn. (3.17.1) gives the following relation between the (parallel) isopycnal and epineutral gradients of $S_\lambda$

$$\nabla_\phi S_\lambda = \left[ \frac{R_\rho - 1}{R_\rho - r} \right] \nabla_\rho S_\lambda. \quad (3.17.5)$$

### 3.18 Slopes of potential density surfaces and neutral tangent planes compared

The two-dimensional slope of a surface is defined as the two-dimensional gradient of height $z$ of that surface. The two-dimensional slope of a surface is an exactly horizontal gradient vector; it has no vertical component. The slope difference between the neutral tangent plane and a potential density surface with reference pressure $p_r$ is given by (McDougall (1988))

$$\nabla_\phi z - \nabla_\rho z = \frac{R_\rho [1 - r]}{R_\rho - r} \frac{\nabla_\phi \Theta}{\Theta} = \left( 1 - G^0 \right) \frac{\nabla_\phi \Theta}{\Theta} = \frac{\nabla_\phi \Theta - \nabla_\rho \Theta}{\Theta} = \frac{R_\rho [1 - r]}{R_\rho - 1} \frac{\nabla_\phi \Theta}{\Theta}. \quad (3.18.1)$$

While potential density surfaces have been the most commonly used surfaces with which to separate “isopycnal” mixing processes from vertical mixing processes, many other types of density surface have been used. The list includes specific volume anomaly surfaces, patched potential density surfaces (Reid and Lynn (1971)), Neutral Density surfaces (Jackett and McDougall (1997)), orthobaric density surfaces (de Szoeke et al. (2000)) and some polynomial fits of Neutral Density as function of only salinity and either $\theta$ or $\Theta$ (Eden and Willebrand (1999), McDougall and Jackett (2005b)). The most recent method for forming approximately neutral surfaces is that of Klocker et al. (2009a,b). This method is relatively computer intensive but has the benefit that the remnant mis-match between the final surface and the neutral tangent plane at each point is due only to the neutral helicity of the data through which the surface passes. The relative skill of all these surfaces at approximating the neutral tangent plane slope at each point has been summarized in the equations and histogram plots in the papers of McDougall (1989, 1995), McDougall and Jackett (2005a, 2005b), and Klocker et al. (2009a,b).

When lateral mixing with isopycnal diffusivity $K$ is imposed along potential density surfaces rather than along neutral tangent planes, a fictitious diapycnal diffusivity arises which is often labeled the “Veronis effect” after Veronis (1975) (who considered the ill effects of exactly horizontal versus isopycnal mixing). This fictitious diapycnal diffusivity of density is equal to $K$ times the square of the slope error, Eqn. (3.18.1) (Klocker et al. (2009a)).

### 3.19 Slopes of in situ density surfaces and specific volume anomaly surfaces

The vector slope of an in situ density surface, $\nabla_\rho z$, is defined to be the exactly horizontal vector

$$\nabla_\rho z = \frac{\partial z}{\partial \rho} \hat{i} + \frac{\partial z}{\partial \rho} \hat{j} + 0 \hat{k}, \quad (3.19.1)$$

representing the “dip” of the surface in both horizontal directions (note that height $z$ is defined positive upwards). This vector slope can be related to the (very small) slope of isobaric surface by ($g$ here is the gravitational acceleration) (McDougall (1989))
\[
\n\n
\n\]  

where \( c \) is the speed of sound and \( N \) is the buoyancy frequency. In the upper water column where the square of the buoyancy frequency is significantly larger than \( g^2/c^2 \approx 4.3 \times 10^3 \text{s}^{-2} \), the in situ density surface has a similar slope to the neutral tangent plane \( \nabla_p z \). In the deep ocean \( N^2 \) is only about 1% of \( g^2/c^2 \) and so the surfaces of constant in situ density have a slope of only 1% of the slope of the neutral tangent plane. At a pressure of about 1000 dbar where \( N^2 \approx 10^{-5} \text{s}^{-2} \), the slope of an in situ density surface is only about one fifth that of the neutral tangent plane. Neutrally buoyant floats in the ocean are usually metal cylinders that are much less compressible than seawater. These floats have a constant mass and an almost constant volume. Hence these floats have an almost constant in situ density and their motion approximately occurs on surfaces of constant in situ density which at mid depth in the ocean are much closer to being isobaric surfaces than being locally-referenced potential density surfaces. This is why these floats are sometimes described as “isobaric floats”.

The slope of a specific volume anomaly surface, \( \nabla_z \delta \), can be expressed as

\[
\n
\n\]

where \( \tilde{c} \) is the sound speed of the reference parcel \( \left( \tilde{S}_A, \tilde{\Theta} \right) \) at pressure \( p \). This expression confirms that where the local seawater properties are close to those of the reference parcel, the specific volume anomaly surface can closely approximate the neutral tangent plane. The square bracket in Eqn. (3.19.3) is equal to \( \rho g N^2 \partial \delta / \partial z \) (from section 7 of McDougall (1989) where \( \delta \) is specific volume anomaly).

### 3.20 Potential vorticity

Planetary potential vorticity is the Coriolis parameter \( f \) times the vertical gradient of a suitable variable. Potential density is sometimes used for that variable but using potential density (i) involves an inaccurate separation between lateral and diapycnal advection because potential density surfaces are not a good approximation to neutral tangent planes and (ii) incurs the non-conservative baroclinic production term of Eqn. (3.13.4). Using approximately neutral surfaces, “ans”, (such as Neutral Density surfaces) provides an optimal separation between the effects of lateral and diapycnal mixing in the potential vorticity equation. In this case the potential vorticity variable is proportional to the reciprocal of the thickness between a pair of closely spaced approximately neutral surfaces. This planetary potential vorticity variable is called Neutral-Surface-Potential-Vorticity (NSPV for short) and is related to \( fN^2 \) by

\[
\n
\n\]

The exponential expression was derived by McDougall (1988) (his equation (47)) and is approximate because the variation of the saline contraction coefficient \( \beta^a \) with pressure was neglected in comparison with the larger proportional change in the thermal expansion coefficient \( \alpha^o \) with pressure. The integral in Eqn. (3.20.1) is taken along an approximately neutral surface from a location where NSPV is equal to \( fN^2 \). Interestingly the combination \( \nabla_a \Theta \Theta - \Theta P \nabla_a \Theta \) is simply the isobaric gradient of Conservative Temperature, \( \nabla_p \Theta \), which is almost the same as the horizontal gradient, \( \nabla \Theta \). A more accurate version of this equation which does not ignore the variation of the saline contraction coefficient can be shown to be
\[ NSPV = -g \rho^{-1} f \gamma^\alpha \left\{ \int_a g^2 N^{-2} \left[ \langle \rho \beta^\alpha \rangle_p \nabla_r \Theta - \langle \rho \beta^\alpha \rangle_p \nabla_r \rho \nabla \right] \cdot dl \right\} = f N^2 \exp \left\{ \int_a g^2 N^{-2} \nabla_r (\rho \kappa) \cdot dl \right\}. \]  

(3.20.2)

The exponential factor in Eqn. (3.20.2) is approximately the integrating factor \( b \), defined as \( b = \nabla r^\alpha \cdot \nabla r^\beta \left( \nabla r^\beta \cdot \nabla r^\beta \right) \) where \( \nabla r^\beta = \rho (\beta^\alpha \nabla S - \alpha^\beta \nabla \Theta) \), which allows spatial integrals of \( \rho (\beta^\alpha \nabla S - \alpha^\beta \nabla \Theta) = b \nabla r^\alpha \approx \nabla r^\alpha \) to be approximately independent of path for “vertical paths”, that is, for paths in surfaces whose normal has zero vertical component.

The gradient \( \nabla^a \) of \( f N^2 \) is related to that of \( NSPV \) by (from Eqns. (3.20.2) and (3.20.1))

\[ \nabla^a (\ln f N^2) - \nabla^a (\ln NSPV) = -g^2 N^{-2} \nabla_r (\rho \kappa) \approx \rho g^2 N^{-2} T^\alpha \left( \nabla^a \Theta - \Theta^a \nabla \right). \]  

(3.20.3)

The deficiencies of \( f N^2 \) as a form of planetary potential vorticity have not been widely appreciated. Even in a lake, and also in the simple situation where temperature does not vary along a density surface (\( \nabla^a \Theta = 0 \)), the use of \( f N^2 \) as planetary potential vorticity is inaccurate since the right-hand side of (3.20.3) is then approximately

\[ -\rho g^2 N^{-2} T^\alpha \Theta^a \nabla^a = \frac{R_p}{\alpha^o \left( \frac{R_p}{R_p-1} \right)} T^\alpha \Theta^a \nabla^a, \]  

(3.20.4)

and the mere fact that the density surface has a slope (i.e., \( \nabla^a \Theta \neq 0 \)) means that the contours of \( f N^2 \) will not be parallel to contours of \( NSPV \) on the density surface. (In this situation (where \( \nabla^a \Theta = 0 \)) the contours of \( NSPV \) along approximately neutral surfaces coincide with those of isopycnal-potential-vorticity (\( IPV \)), the potential vorticity defined with respect to the vertical gradient of potential density by \( IPV = -fg \rho^{-1} \beta^\alpha \).

\( IPV \) is related to \( f N^2 \) by (McDougall 1988)

\[ \frac{IPV}{f N^2} = -g \rho^{-1} \frac{\beta^\alpha}{\beta^\alpha} \left( \frac{R_p}{R_p-1} \right) = \frac{\beta^\alpha (p_1)}{\beta^\alpha (p)} \frac{1}{G^\alpha} \approx \frac{1}{G^\alpha}, \]  

(3.20.5)

so that the ratio of \( NSPV \) to \( IPV \) plotted on an approximately neutral surface is given by

\[ \frac{NSPV}{IPV} = \frac{\beta^\alpha (p)}{\beta^\alpha (p_1)} \left( \frac{R_p}{R_p-1} \right) \exp \left\{ \int_a g^2 N^{-2} \nabla_r (\rho \kappa) \cdot dl \right\}. \]  

(3.20.6)

You and McDougall (1991) show that because of the highly differentiated nature of potential vorticity, isolines of \( IPV \) do not coincide with those of \( NSPV \) even at the reference pressure \( p_1 \) of the potential density variable (see equations (14) – (16) and Figure 14 of that paper). \( NSPV, f N^2 \) and \( IPV \) have the units \( s^{-3} \). The ratio \( IPV/f N^2 \) is available in the GSW computer software library as the function gsw_IPV_fNN.

### 3.21 Vertical velocity through the sea surface

There has been confusion regarding the expression that relates the net evaporation at the sea surface to the vertical velocity in the ocean through the sea surface. Since these expressions have often involved the salinity (through the factor \( 1-S_a \)) and so appear to be thermodynamic expressions, here we present the correct equation which we will see is merely kinematics, not thermodynamics. Let \( \rho^w (E-P) \) be the vertical mass flux through the air-sea interface on the atmospheric side of the interface (where \( E-P \) is the notional vertical velocity of freshwater through the air-sea interface with density \( \rho^w \); this density being that of pure water at the sea surface temperature and at atmospheric pressure). The same mass flux \( \rho^w (E-P) \) must flow through the air-sea interface on the ocean side of the interface where the density is \( \rho = \rho(S_a,t,0) \). The vertical velocity through an arbitrary surface whose height is \( z = \eta(x,y,t) \) can be expressed as \( w - \nabla_r \cdot \nabla \eta - \partial \eta / \partial t \) (where \( w \) is the vertical velocity through the geopotential surface, see section 3.24, and...
note that $t$ is time in this context) and the mass flux associated with this dia-surface vertical velocity component is this vertical velocity times the density of the seawater, $\rho$. By equating the two mass fluxes on either side of the air-sea interface we arrive at the vertical ocean velocity through the air-sea interface as (Griffies (2004), Warren (2009))

$$w = \nabla_h \cdot \nabla - \eta / \partial t = \rho^{-1} \rho^W (E - P).$$

(3.21.1)

### 3.22 Freshwater content and freshwater flux

Oceanographers traditionally call the pure water fraction of seawater the “freshwater fraction” or the “freshwater content”. This can cause confusion because in some science circles “freshwater” is used to describe water of low but non-zero salinity. Nevertheless, here we retain the oceanographic use of “freshwater” as being synonymous with pure water (with $S_A = 0$, this pure water being in liquid, gaseous or solid ice forms). The freshwater content of seawater is $(1 - S_A) = \left(1 - 0.001S_p / (g \text{ kg}^{-1})\right)$. The first expression here clearly requires that Absolute Salinity is expressed in kg of sea salt per kg of solution. Note that the freshwater content is not based on Practical Salinity, that is, it is not $(1 - 0.001S_p)$.

The advective flux of mass per unit area is $\rho u$ where $u$ is the fluid velocity through the chosen area element while the advective flux of sea salt is $\rho S_A u$. The advective flux of freshwater per unit area is the difference of these two mass fluxes, namely $\rho (1 - S_A) u$. As outlined in section 2.5 and appendices A.4 and A.20, for water of anomalous composition there are four types of absolute salinity that might be relevant to this discussion of freshwater fluxes; Density Salinity $S^\text{dens}_A = S_A$, Solution Salinity $S^\text{soln}_A$, Added-Mass Salinity $S^\text{add}_A$, and Preformed Salinity $S_0$. Since Preformed Salinity is designed to be a conservative variable with a zero flux air-sea boundary condition, probably the most relevant form of freshwater content, at least in the context of an ocean model, is $(1 - S_p) = \left(1 - 0.001S_p / (g \text{ kg}^{-1})\right)$.

### 3.23 Heat transport

A flux of heat across the sea surface at a sea pressure of 0 dbar is identical to the flux of potential enthalpy which in turn is exactly equal to $c^0_p$ times the flux of Conservative Temperature $\Theta$, where $c^0_p$ is given by (3.3.3). By contrast, the same heat flux across the sea surface changes potential temperature $\Theta$ in inverse proportion to $c_p(S_A, \Theta, 0)$ and this heat capacity varies by 5% at the sea surface, depending mainly on salinity.

The First Law of Thermodynamics, namely Eqn. (A.13.1) of appendix A.13, can be approximated as

$$\rho c^0_p \frac{d\Theta}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho e + h_{sA} \rho \mathcal{S} S_A,$$

(3.23.1)

with an error in $\Theta$ that is approximately one percent of the error incurred by treating either $c^0_p \Theta$ or $c_p(S_A, \Theta, 0) \Theta$ as the “heat content” of seawater (see McDougall (2003) and appendices A.13 and A.18). Equation (3.23.1) is exact at 0 dbar while at great depth in the ocean the error with the approximation (3.23.1) is no larger than the neglect of the dissipation of mechanical energy term $\rho e$ in this equation (see appendix A.21).

Because the left-hand side of the First Law of Thermodynamics, Eqn. (3.23.1), can be written as density times the material derivative of $c^0_p \Theta$ it follows that $\Theta$ can be treated as a conservative variable in the ocean and that $c^0_p \Theta$ is transported by advection and mixed by turbulent epineutral and dianeutral diffusion as though it is the “heat content” of seawater. For example, the advective meridional flux of “heat” is the area integral of
\[ \rho v h^0 = \rho v c^0_p \Theta \] (here \( v \) is the northward velocity). The error in comparing this advective meridional “heat flux” with the air-sea heat flux is approximately 1% of the error in so interpreting the area integral of either \( \rho v c^0_p \Theta \) or \( \rho v c_p(S_\lambda, \theta, 0) \). Similarly, turbulent diffusive fluxes of “heat” are accurately given by a turbulent diffusivity times the spatial gradient of \( c^0_p \Theta \) but are less accurately approximated by the same turbulent diffusivity times the spatial gradient of \( c_p \Theta \) (see appendix A.14 for a discussion of this point).

Warren (1999, 2006) has argued that because enthalpy is unknown up to a linear function of salinity, it is only possible to talk of a flux of “heat” through an ocean section if the fluxes of mass and salt through the ocean section are both zero. This opinion seems to be widely held, but it is incorrect. Because enthalpy is unknown and unknowable up to a linear function of \( S_\lambda \) (i.e. up to the arbitrary function \( a_1 + a_2 S_\lambda \) in terms of the constants defined in Eqn. (2.6.2)), the left-hand side of Eqn. (3.23.1) is unknowable to the extent \( a_1 \rho dS_\lambda / dr \). It is shown in appendix B that the terms \( -\nabla \cdot F^0 + h_{vi} \rho S^0 \) on the right-hand side of Eqn. (3.23.1) are also unknowable to the same extent so that the effect of \( a_1 \) cancels from Eqn. (3.23.1). Hence the fact that \( c^0_p \Theta \) is unknowable up to a linear function of \( S_\lambda \) does not affect the usefulness of \( h^0 \) or \( c^0_p \Theta \) as measures of “heat content”. Similarly, the difference between the meridional fluxes of \( c^0_p \Theta \) across two latitudes is equal to the area-integrated air-sea and geothermal heat fluxes between these latitudes (after allowing for any unsteady accumulation of \( c^0_p \Theta \) in the volume), irrespective of whether there are non-zero fluxes of mass or salt across the sections. This powerful result follows directly from the fact that \( c^0_p \Theta \) is a conservative variable, obeying the simple conservation statement Eqn. (3.23.1). This issue is discussed at greater length in section 6 of McDougall (2003).

### 3.24 Geopotential

The geopotential \( \Phi \) is the gravitational potential energy per unit mass with respect to the height \( z = 0 \). Allowing the gravitational acceleration to be a function of \( z \), \( \Phi \) is given by

\[ \Phi = \int_{0}^{z} g(z') \, dz'. \tag{3.24.1} \]

If the gravitational acceleration is taken to be constant \( \Phi \) is simply \( gz \). Note that height and \( \Phi \) are negative quantities in the ocean since the sea surface (or the geoid) is taken as the reference height and \( z \) is measured upward from this surface. In SI units \( \Phi \) is measured in J kg\(^{-1}\) m\(^2\) s\(^{-2}\). If the ocean is assumed to be in hydrostatic balance so that \( P_0 = -g \rho \) (or \( -g dz' = v dP' \)) then the geopotential Eqn. (3.24.1) may be expressed as the vertical pressure integral of the specific volume in the water column,

\[ \Phi = \Phi^0 - \int_{h_0}^{h} v(p') \, dP', \tag{3.24.2} \]

where \( \Phi^0 \) is the value of the geopotential at zero sea pressure, that is, the gravitational acceleration times the height of the free surface above the geoid. Note that the gravitational acceleration has not been assumed to be constant in Eqn. (3.24.2).

### 3.25 Total energy

The total energy \( \mathcal{E} \) is the sum of specific internal energy \( u \), kinetic energy per unit mass \( 0.5 \mathbf{u} \cdot \mathbf{u} \) (where \( \mathbf{u} \) is the three-dimensional velocity vector) and the geopotential \( \Phi \),

\[ \mathcal{E} = u + \Phi + \frac{1}{2} \mathbf{u} \cdot \mathbf{u}. \tag{3.25.1} \]

Total energy \( \mathcal{E} \) is not a function of only \( (S_\lambda, t, p) \) and so is not a thermodynamic quantity.
3.26 Bernoulli function

The Bernoulli function is the sum of specific enthalpy $h$, kinetic energy per unit mass $0.5 \mathbf{u} \cdot \mathbf{u}$, and the geopotential $\Phi$,

$$\mathcal{B} = h + \Phi + \frac{1}{2} \mathbf{u} \cdot \mathbf{u}. \quad (3.26.1)$$

Using the expression (3.2.1) that relates enthalpy and potential enthalpy, together with Eqn. (3.26.2) for $\mathcal{B}$, the Bernoulli function (3.26.1) may be written as

$$\mathcal{B} = h^0 + \Phi^0 + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} - \int_{h_0}^P \hat{v}(S_{SO,0^\circ C}, P') - \hat{v}(S_A, \Theta, P') \, dP'. \quad (3.26.2)$$

The pressure integral term here is a version of the dynamic height anomaly (3.27.1), this time for a specific volume anomaly defined with respect to the Absolute Salinity and Conservative Temperature (or equivalently, with respect to the Absolute Salinity and potential temperature) of the seawater parcel in question at pressure $P$. This pressure integral is equal to the Cunningham geostrophic streamfunction, Eqn. (3.29.2).

The Bernoulli function $\mathcal{B}$ is not a function of only $(S_A, t, p)$ and so is not a thermodynamic quantity.

The Bernoulli function is dominated by the contribution of enthalpy $h$ to (3.26.1) and by the contribution of potential enthalpy $h^0$ to (3.26.2). The variation of kinetic energy or the geopotential following a fluid parcel is typically several thousand times less than the variation of enthalpy or potential enthalpy following the fluid motion.

The definition of specific volume anomaly given in Eqn. (3.7.3) has been used by Saunders (1995) to write (3.26.2) as (with the dynamic height anomaly $\Psi$ defined in (3.27.1))

$$\mathcal{B} = h^0 + \Phi^0 + \Psi + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} - \int_{h_0}^P \hat{v}(S_{SO,0^\circ C}, P') - \hat{v}(S_A, \Theta, P') \, dP'$$

$$= h^0 + \Phi^0 + \Psi + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} - \hat{h}(S_{SO,0^\circ C}, P) + \hat{h}(S_{SO,0^\circ C}, 0) + \hat{h}(S_A, \Theta, P) - \hat{h}(S_A, \Theta, 0). \quad (3.26.3)$$

Note that $\hat{h}(S_A, \Theta, 0) = c_p^0 \Theta$ and $\hat{h}(S_{SO,0^\circ C, 0}) = 0$.

3.27 Dynamic height anomaly

The dynamic height anomaly $\Psi$, given by the vertical integral

$$\Psi = - \int_{h_0}^P \delta(S_A, t', h''), \, dP' \quad (3.27.1)$$

is the geostrophic streamfunction for the flow at pressure $P$ with respect to the flow at the sea surface and $\delta$ is the specific volume anomaly. Thus the two-dimensional gradient of $\Psi$ in the $P$ pressure surface is simply related to the difference between the horizontal geostrophic velocity $\mathbf{v}$ at $P$ and at the sea surface $\mathbf{v}_0$ according to

$$\mathbf{k} \times \nabla_P \Psi = \mathbf{f} \mathbf{v} - \mathbf{f} \mathbf{v}_0. \quad (3.27.2)$$

The definition Eqn. (3.27.1) of dynamic height anomaly applies to all choices of the reference values $S_A$ and $t$, $\Theta$ or $\tilde{\Theta}$ in the definition Eqns. (3.7.1 – 3.7.4) of the specific volume anomaly $\delta$. Also, $\delta$ in Eqn. (3.27.1) can be replaced with specific volume $v$ without affecting the isobaric gradient of the resulting streamfunction. That is, this substitution does not affect Eqn. (3.27.2) because the additional term is a function only of pressure. Traditionally it was important to use specific volume anomaly in preference to specific volume as it was more accurate with computer code which worked with single-precision variables. Since computers now regularly employ double-precision, this issue has been overcome and consequently either $\delta$ or $v$ can be used in the integrand of Eqn. (3.27.1), so making it either the “dynamic height anomaly” or the “dynamic height”. As in
the case of Eqn. (3.24.2), so also the dynamic height anomaly Eqn. (3.27.1) has not assumed that the gravitational acceleration is constant and so Eqn. (3.27.2) applies even when the gravitational acceleration is taken to vary in the vertical.

The dynamic height anomaly $\Psi$ should be quoted in units of $m^2 s^{-2}$. These are the units in which the GSW library (appendix N) outputs dynamic height anomaly. Note that the integration in Eqn. (3.27.1) of specific volume anomaly with pressure in dbar would yield dynamic height anomaly in units of $m^2 kg^{-1}dbar$, and the use of these units in Eqn. (3.27.2) would not give the resultant horizontal gradient in the usual units, being the product of the Coriolis parameter (units of $s^{-1}$) and the velocity (units of $m s^{-1}$). This is the reason why the pressure integration is done with pressure in Pa and dynamic height anomaly is output in $m^2 s^{-2}$.

### 3.28 Montgomery geostrophic streamfunction

The Montgomery “acceleration potential” $\pi$ defined by

$$\pi = (P - P_0)\delta - \frac{\rho}{h_0} \delta (S_{\lambda} [\rho'], t [\rho'], \rho') dP'$$  \quad (3.28.1)

is the geostrophic streamfunction for the flow in the specific volume anomaly surface $\delta (S_{\lambda}, t, P) = \delta_{\lambda}$ relative to the flow at $P = P_0$ (that is, at $P = 0$ dbar). Thus the two-dimensional gradient of $\pi$ in the $\delta_{\lambda}$ specific volume anomaly surface is simply related to the difference between the horizontal geostrophic velocity $v$ in the $\delta = \delta_{\lambda}$ surface and at the sea surface $v_0$ according to

$$k \times \nabla_{\delta_{\lambda}} \pi = f v - f v_0 \quad \text{or} \quad \nabla_{\delta_{\lambda}} \pi = -k \times (f v - f v_0).$$  \quad (3.28.2)

The definition, Eqn. (3.28.1), of the Montgomery geostrophic streamfunction applies to all choices of the reference values $\tilde{S}_{\lambda}$ and $t$ in the definition, Eqn. (3.7.2), of the specific volume anomaly $\delta$. By carefully choosing these reference values the specific volume anomaly surface can be made to closely approximate the neutral tangent plane (McDougall and Jackett (2007)).

It is not uncommon to read of authors using the Montgomery geostrophic streamfunction, Eqn (3.28.1), as a geostrophic streamfunction in surfaces other than specific volume anomaly surfaces. This incurs errors that should be recognized. For example, the gradient of the Montgomery geostrophic streamfunction, Eqn. (3.28.1), in a neutral tangent plane becomes (instead of Eqn. (3.28.2) in the $\delta = \delta_{\lambda}$ surface)

$$\nabla_{\delta} \pi = -k \times (f v - f v_0) + (P - P_0) \nabla_{\delta} \delta,$$  \quad (3.28.3)

where the last term represents an error arising from using the Montgomery streamfunction in a surface other than the surface for which it was derived.

Zhang and Hogg (1992) subtracted an arbitrary pressure offset, $(\overline{P} - P_0)$, from $(P - P_0)$ in the first term in Eqn. (3.28.1), so defining the modified Montgomery streamfunction

$$\pi^{ZH} = (P - \overline{P})\delta - \frac{\rho}{h_0} \delta (S_{\lambda} [\rho'], t [\rho'], \rho') dP'. $$  \quad (3.28.4)

The gradient of $\pi^{ZH}$ in a neutral tangent plane becomes

$$\nabla_{\delta} \pi^{ZH} = -k \times (f v - f v_0) + (P - \overline{P}) \nabla_{\delta} \delta,$$  \quad (3.28.5)

where the last term can be made significantly smaller than the corresponding term in Eqn. (3.28.3) by choosing the constant pressure $\overline{P}$ to be close to the average pressure on the surface.

This term can be further minimized by suitably choosing the constant reference values $\tilde{S}_{\lambda}$ and $\tilde{\Theta}$ in the definition, Eqn. (3.7.3), of specific volume anomaly $\tilde{\delta}$ so that this surface
more closely approximates the neutral tangent plane \( \text{(McDougall (1989))}. \) This improvement is available because it can be shown that
\[
\rho \dot{\nabla}_a \tilde{S} = - \left[ \kappa (S_A, \Theta, p) - \kappa (\tilde{S}_A, \tilde{\Theta}, p) \right] \nabla_a P \approx T_b \left( \Theta - \tilde{\Theta} \right) \nabla_a P. \tag{3.28.6}
\]
The last term in Eqn. (3.28.5) is then approximately
\[
(P - \bar{P}) \nabla_a \tilde{S}_A \tilde{\Theta} \approx \frac{1}{\rho} \rho^{-1} T_b \left( \Theta - \tilde{\Theta} \right) \nabla_a \left( P - \bar{P} \right) \tag{3.28.7}
\]
and hence suitable choices of \( \bar{P}, \tilde{S}_A \) and \( \tilde{\Theta} \) can reduce the last term in Eqn. (3.28.5) that represents the error in interpreting the Montgomery geostrophic streamfunction, Eqn. (3.28.4), as the geostrophic streamfunction in a surface that is more neutral than a specific volume anomaly surface.

The Montgomery geostrophic streamfunction should be quoted in units of \( \text{m}^2 \text{s}^{-2} \). These are the units in which the GSW library (appendix N) outputs dynamic height anomaly.

### 3.29 Cunningham geostrophic streamfunction

Cunningham (2000) and Alderson and Killworth (2005), following Saunders (1995) and Killworth (1986), suggested that a suitable streamfunction on a density surface in a compressible ocean would be the difference between the Bernoulli function \( B \) and potential enthalpy \( h^0 \). Since the kinetic energy per unit mass, \( 0.5 \mathbf{u} \cdot \mathbf{u} \), is a tiny component of the Bernoulli function, it was ignored and Cunningham (2000) essentially proposed the streamfunction \( \Pi + \Phi^0 \) (see his equation (12)), where
\[
\Pi = B - h^0 - \frac{1}{\rho} \mathbf{u} \cdot \mathbf{u} - \Phi^0 \\
= h - h^0 + \Phi - \Phi^0 \tag{3.29.1}
\]
The last line of this equation has used the hydrostatic equation \( P_z = -g \rho \) to express \( \Phi \approx \Phi_0 \) in terms of the vertical pressure integral of specific volume and the height of the sea surface where the geopotential is \( \Phi^0 \).

The definition of potential enthalpy, Eqn. (3.2.1), is used to rewrite the last line of Eqn. (3.29.1), showing that Cunningham’s \( \Pi \) is also equal to
\[
\Pi = - \int_{h_0}^P \bar{\nabla} (S_A(p'), \Theta(p'), p') - \bar{\nabla} (S_A, \Theta, p') dP'. \tag{3.29.2}
\]
In this form it appears very similar to the expression, Eqn. (3.27.1), for dynamic height anomaly, the only difference being that in Eqn. (3.27.1) the pressure-independent values of Absolute Salinity and Conservative Temperature were \( S_{SA} \) and \( ^\circ \text{C} \) whereas here they are the local values on the surface, \( S_A \) and \( \Theta \). While these local values of Absolute Salinity and Conservative Temperature are constant during the pressure integral in Eqn. (3.29.2), they do vary with latitude and longitude along any “density” surface.

The gradient of \( \Pi \) along the neutral tangent plane is (from McDougall and Klocker (2010))
\[
\nabla_a \Pi \approx \left[ \frac{1}{\rho} \nabla_a P - \nabla \Phi_0 \right] - \frac{1}{2} \rho^{-1} T_b \left( P - P_0 \right)^2 \nabla_a \Theta, \tag{3.29.3}
\]
so that the error in \( \nabla_a \Pi \) in using \( \Pi \) as the geostrophic streamfunction is approximately
\[- \frac{1}{2} \rho^{-1} T_b \left( P - P_0 \right)^2 \nabla_a \Theta. \] When using the Cunningham streamfunction \( \Pi \) in a potential density surface, the error in \( \nabla_a \Pi \) is approximately
\[- \frac{1}{2} \rho^{-1} T_b \left( 2P - P_0 \right) \nabla_a \Theta \] (McDougall and Klocker (2010)).
3.30 Geostrophic streamfunction in an approximately neutral surface

In order to evaluate a relatively accurate expression for the geostrophic streamfunction in an approximately neutral surface (such as an \( \omega \)-surface of Klocker et al. (2009a,b) or a Neutral Density surface of Jackett and McDougall (1997)) a suitable reference seawater parcel \( \left( \tilde{S}_\Lambda, \tilde{\Theta}, \tilde{P} \right) \) is selected from the approximately neutral surface that one is considering, and the specific volume anomaly \( \tilde{\delta} \) is defined as in (3.7.3) above. The approximate geostrophic streamfunction is given by (from McDougall and Klocker (2010))

\[
\varphi^\theta(S_\Lambda, \Theta, p) = \frac{1}{\rho} \left(P - \tilde{P}\right) \tilde{\delta}(S_\Lambda, \Theta, p) - \frac{1}{\rho} P^{-1} T_0^\theta \left( \Theta - \tilde{\Theta} \right) \left(P - \tilde{P} \right)^2 - \frac{p}{\tilde{h}} \tilde{\delta} dP'. \tag{3.30.1}
\]

This expression is very accurate when the variation of conservative temperature with pressure along the approximately neutral surface is either linear or quadratic. That is, in these situations \( \nabla \varphi^\theta \approx \frac{1}{\rho} \nabla P - \nabla \Phi_0 = -k \times \left( \tilde{\nabla} - \tilde{\nabla}_0 \right) \) to a very good approximation. In Eqn. (3.30.1) \( \rho^{-1} T_0^\theta \) is taken to be the constant value \( 2.7 \times 10^{-15} \text{K}^{-1} \left( \text{Pa} \right)^{2/3} \).

3.31 Pressure-integrated steric height

The depth-integrated mass flux of the geostrophic Eulerian flow between two fixed pressure levels can also be represented by a streamfunction. Using the hydrostatic relation \( P_z = -g \rho \), and assuming the gravitational acceleration to be independent of height, the depth-integrated mass flux \( \int \rho v \, dz \) is given by \( -g^{-1} \int \nabla P \) and this motivates taking the pressure integral of the Dynamic Height Anomaly \( \Psi \) (from Eqn. (3.27.1)) to form the Pressure-Integrated-Steric-Height \( \text{PISH} \) (also called Depth-Integrated Steric Height \( \text{DISH} \) by Godfrey (1989)),

\[
\text{PISH} = \Psi' = -g^{-1} \int_0^P \left[ \delta(S_\Lambda[p'], t[p'], p') \right] dP' dP. \tag{3.31.1}
\]

The two-dimensional gradient of \( \Psi' \) is related to the depth-integrated mass flux of the velocity difference with respect to the velocity at zero sea pressure, \( v_0 \), according to

\[
k \times \nabla_x \Psi' = f \int_{z(p')} \left[ \rho \left( v - v_0 \right) \right] \, dz'. \tag{3.31.2}
\]

The definition, Eqn. (3.31.1), of \( \text{PISH} \) applies to all choices of the reference values \( \tilde{S}_\Lambda, \tilde{S}_\Lambda \) and \( \tilde{t}, \tilde{\Theta} \) or \( \tilde{\Theta} \) in the definitions, Eqns. (3.7.2–3.7.4), of the specific volume anomaly.

Since the velocity at depth in the ocean is generally much smaller than at the sea surface, it is customary to take the reference pressure to be some constant (deep) pressure \( P_i \) so that Eqn. (3.27.1) becomes

\[
\Psi = \int_{p_i}^P \left[ \delta(S_\Lambda[p'], t[p'], p') \right] dP'. \tag{3.31.3}
\]

and \( \text{PISH} \), reflecting the depth-integrated horizontal mass transport from the sea surface to pressure \( P_i \), relative to the flow at \( P_i \), is

\[
\text{PISH} = \Psi' = -g^{-1} \int_0^P \left[ \delta(S_\Lambda[p'], t[p'], p') \right] dP' dP. \tag{3.31.4}
\]
The two-dimensional gradient of $\Psi'$ is now related to the depth-integrated mass flux of the velocity difference with respect to the velocity at $P_i$, $v_i$, according to

$$k \nabla_p \Psi' = \int z(h_i) \rho \left[ v(z') - v_i \right] dz' = g^{-1} \int \frac{h_i}{h_i} \left[ v(p') - v_i \right] dP'.$$  \hspace{1cm} (3.31.5)

The specific volume anomaly $\delta$ in Eqns. (3.31.1), (3.31.3) and (3.31.4) can be replaced with specific volume $v$ without affecting the isobaric gradient of the resulting streamfunction. That is, this substitution in $\Psi'$ does not affect Eqn. (3.31.2) or Eqn. (3.31.5), as the additional term is a function only of pressure. With specific volume in place of specific volume anomaly, Eqn. (3.31.4) becomes the depth-integrated gravitational potential energy of the water column (plus a very small term that is present because the atmospheric pressure is not zero, McDougall et al. (2003)).

PSH should be quoted in units of kg s$^{-2}$ so that its two-dimensional gradient has the same units as the depth-integrated flux of $\rho [v(z') - v_i]$ times the Coriolis frequency.

### 3.32 Pressure to height conversion

When vertically integrating the hydrostatic equation $P_z = -g \rho$ in the context of an ocean model where Absolute Salinity $S_A$ and Conservative Temperature $\Theta$ (or potential temperature $\theta$) are piecewise constant in the vertical, the geopotential (Eqn. (3.24.2))

$$\Phi = \Phi^0 - \int \frac{P}{h_i} v(p') dP',$$  \hspace{1cm} (3.32.1)

can be evaluated as a series of exact differences. If there are a series of layers of index $i$ separated by pressures $p'$ and $p^{i+1}$ (with $p^{i+1} > p^i$) then the integral can be expressed (making use of (3.7.5), namely $h_p|_{S_A, \Theta} = h_p = v$) as a sum over $n$ layers of the differences in specific enthalpy so that

$$\Phi = \Phi^0 - \int \frac{P}{h_i} v(p') dP' = \Phi^0 - \sum_{i=1}^{n} \left[ h_S(S_A^i, \Theta', p^{i+1}) - h_S(S_A^i, \Theta', p^i) \right].$$  \hspace{1cm} (3.32.2)

### 3.33 Freezing temperature

Freezing occurs at the temperature $t_f$ at which the chemical potential of water in seawater $\mu^W$ equals the chemical potential of ice $\mu^{ih}$. Thus, $t_f$ is found by solving the implicit equation

$$\mu^W(S_A, t_f, p) = \mu^{ih}(t_f, p)$$  \hspace{1cm} (3.33.1)

or equivalently, in terms of the two Gibbs functions,

$$g(S_A, t_f, p) - S_A g(S_A, t_f, p) = g^{ih}(t_f, p).$$  \hspace{1cm} (3.33.2)

The Gibbs function for ice Ih, $g^{ih}(t, p)$, is defined by IAPWS-06 (IAPWS (2009a)) and Feistel and Wagner (2006) and is summarized in appendix I below. In the special case of zero salinity, the chemical potential of water in seawater reduces to the Gibbs function of pure water, $\mu^W(0, t, p) = g^W(t, p)$. A simple correlation function for the melting pressure as a function of temperature is available from IAPWS (2008b) and has been implemented in the SIA library.

At the ocean surface, $p = 0$ dbar, from Eqn. (3.31.1) the TEOS-10 freezing point of pure water is $t_f(0 \text{kg} m^{-3}, 0 \text{dbar}) = 0.002519 ^\circ C$ with an uncertainty of only 2 $\mu K$, noting that the triple point temperature of water is exactly 273.16 K by definition of the ITS-90 temperature scale. The freezing temperature of the standard ocean is $t_f(S_{SG}, 0 \text{dbar}) = -1.919 ^\circ C$ with an uncertainty of 2 mK. Note that Eqn. (3.31.1) is valid for air-free
water/seawater. Dissolution of air in water lowers the freezing point slightly; saturation with air lowers the freezing temperatures by about 2 mK.

To estimate the effects of small changes in the pressure or salinity on the freezing temperature, it is convenient to consider a power series expansion of (3.33.1). The result in the limit of an infinitesimal pressure change at fixed salinity gives the pressure coefficient of freezing point lowering, as (Clausius-Clapeyron equation, Feistel et al. (2010a)),

$$\frac{\partial t_f}{\partial p} = \chi_p(S_A, p) = -\frac{g_p - S_A g_{S_A p} - g_{p}^{\text{m}}}{g_r - S_A g_{S_A r} - g_{r}^{\text{m}}}.$$  

(3.33.3)

Its values, evaluated from TEOS-10, vary only weakly with salinity between $\chi_p(0 \text{ g kg}^{-1}, 0 \text{ dbar}) = -0.7429$ mK/dbar for pure water and $\chi_p(S_{SO}, 0 \text{ dbar}) = -0.7483$ mK/dbar for the standard ocean. TEOS-10 is consistent with the most accurate measurement of $\chi_p$ and its experimental uncertainty of 0.0015 mK/dbar (Feistel and Wagner (2005), (2006)). Since the value of $|\chi_p|$ always exceeds that of the adiabatic lapse rate $|\Gamma|$, cold seawater may freeze and decompose into ice and brine during adiabatic uplift but this can never happen to a sinking parcel.

In the limit of infinitesimal changes in Absolute Salinity at fixed pressure, we obtain the saline coefficient of freezing point lowering, as (Raoults law),

$$\frac{\partial t_f}{\partial S_A_{p}} = \chi_S(S_A, p) = \frac{S_A g_{S_A S_A} - g_{S_A r}^{\text{m}}}{g_r - S_A g_{S_A r} - g_{r}^{\text{m}}}.$$  

(3.34.4)

Typical numerical values are $\chi_S(0 \text{ g kg}^{-1}, 0 \text{ dbar}) = -59.2$ mK/(g kg$^{-1}$) for pure water and $\chi_S(S_{SO}, 0 \text{ dbar}) = -56.9$ mK/(g kg$^{-1}$) for seawater.

As a raw practical estimate, Eqn. (3.34.4) can be expanded into powers of salinity, using only the leading term of the TEOS-10 saline Gibbs function, $g^S \approx R_S T_S \ln S_A$, which stems from Planck’s ideal-solution theory (Planck (1888)). Here, $R_S = R/M_S = 264.7599$ J kg$^{-1}$ K$^{-1}$ is the specific gas constant of sea salt, $R$ is the universal molar gas constant, and $M_S = 31.403$ 82 g mol$^{-1}$ is the molar mass of sea salt with Reference Composition. The denominator of Eqn. (3.34.4) is proportional to the melting heat $t_f^{\text{m}}$, Eqn. (3.34.7). The convenient result obtained with these simplifications is

$$\frac{\partial t_f}{\partial S_A_{p}} \approx -\frac{R_S}{t_f^{\text{m}}} \left( T_0 + t_f \right)^2 \approx -59 \text{ mK/(g kg}^{-1} \right).$$  

(3.35.5)

where we have used $t_f = -2^\circ \text{C}$ and $t_f^{\text{m}} = 330$ J kg$^{-1}$ as approximations that are appropriate for the standard ocean. This simple result is only weakly dependent on these choices and is in reasonable agreement with the exact values from Eqn. (3.34.4) and with Millero and Leung (1976). The freezing temperature of seawater is always lower than that of pure water.

When sea-ice is formed, it often contains remnants of seawater included in brine pockets. At equilibrium, the salinity in these pockets depends only on temperature and pressure, rather than, for example, on the pocket volume, and can be computed in the functional form $S_A(t, p)$ as an implicit solution of Eqn. (3.33.1). Measured values for the brine salinity of Antarctic sea ice agree very well with those computed of Eqn. (3.33.1) up to the saturation concentration of about 110 g kg$^{-1}$ at surface pressure (Feistel et al. (2010b)). At high pressures, the validity of the Gibbs function of seawater, and therefore of the computed freezing point or brine salinity, too, is limited to only 50 g kg$^{-1}$.

We note that in the first approximation, as inferred from Planck’s theory of ideal solutions, the above properties depend on the number of dissolved particles regardless of the particle sizes, masses or charges. In other words, they depend mainly on the molar rather than on the mass density of the solute, in contrast to properties such as the density of seawater and properties derived from it. The properties considered in the remainder of
this section (3.33-3.42) which share this attribute are referred to as the colligative properties of seawater.

3.34 Latent heat of melting

The melting process of ice in pure water can be conducted by supplying heat at constant pressure. If this is done slowly enough that equilibrium is maintained, then the temperature will also remain constant. The heat required per mass of molten ice is the latent heat, or enthalpy, of melting, \( L_p^{WI} \). It is found as the difference between the specific enthalpy of water, \( h^w \), and the specific enthalpy of ice, \( h^{li} \), (Kirchhoff’s law, Curry and Webster (1999)):

\[
L_p^{WI} (p) = h^w (t, p) - h^{li} (t, p). 
\]

(3.34.1)

Here, \( t_f (p) \) is the freezing temperature of water, section 3.33. The enthalpies \( h^w \) and \( h^{li} \) are available from IAPWS-95 (IAPWS (2009b)) and IAPWS-06 (IAPWS (2009a)), respectively.

In the case of seawater, the melt water will additionally mix with the ambient brine, thus changing the salinity and the freezing temperature of the seawater. Consequently, the enthalpy related to this phase transition will depend on the particular conditions under which the melting occurs.

Here, we define the latent heat of melting as the enthalpy increase per infinitesimal mass of molten ice of a composite system consisting of ice and seawater, when the temperature is increased at constant pressure and at constant total masses of water and salt, in excess to the heat needed to warm up the seawater and ice phases individually (Feistel and Hagen (1998), Feistel et al. (2010b)). Mass conservation of both water and salt during this thermodynamic process is essential to ensure the independence of the latent heat formula from the unknown absolute enthalpies of salt and water that otherwise would accompany any mass exchange.

The enthalpy of sea ice, \( h^{SI} \), is additive with respect to its constituents ice, \( h^{li} \), with the mass fraction \( w^{li} \), and seawater, \( h \), with the liquid mass fraction \( (1 - w^{li}) \):

\[
h^{SI} = (1 - w^{li}) h(S_A, t, p) + w^{li} h^{li} (t, p). \]

(3.34.2)

Upon warming, the mass of melt water changes the ice fraction \( w^{li} \) and the brine salinity \( S_A \). The related temperature derivative of Eqn. (3.34.2) is

\[
\frac{\partial h^{SI}}{\partial T} \bigg|_{p} = (1 - w^{li}) \frac{\partial h}{\partial T} \bigg|_{S_A, p} + w^{li} \frac{\partial h^{li}}{\partial T} \bigg|_{p} + \frac{\partial S_A}{\partial T} \bigg|_{p} + \frac{\partial h}{\partial T} \bigg|_{p}. \]

(3.34.3)

The rate of brine salinity change with temperature is given by the reciprocal of Eqn. (3.33.4) and is related to the isobaric melting rate, \(-\frac{\partial w^{li}}{\partial T} \bigg|_{p}\), by the conservation of the total salt, \((1 - w^{li}) S_A = \text{const.}\), in the form

\[
\frac{\partial S_A}{\partial T} \bigg|_{p} = \frac{S_A}{1 - w^{li}} \frac{\partial w^{li}}{\partial T} \bigg|_{p}. \]

(3.34.4)

Using this relation, Eqn. (3.34.3) takes the simplified form

\[
\frac{\partial h^{SI}}{\partial T} \bigg|_{p} = (1 - w^{li}) c_p + w^{li} c^{li}_p - \frac{L_p^{SI} \partial w^{li}}{\partial T} \bigg|_{p}. \]

(3.34.5)

The coefficient in front of the melting rate,

\[
L_p^{SI} (S_A, p) = h - S_A \frac{\partial h}{\partial S_A} \bigg|_{T, p} - h^{li}, \]

(3.34.6)
provides the desired expression for isobaric melting enthalpy, namely the difference between the partial specific enthalpies of water in seawater and of ice. As is physically required for any measurable thermodynamic quantity, the arbitrary absolute enthalpies of ice, water and salt cancel in the formula (3.34.6), provided that the reference state conditions for the ice and seawater formulations are chosen consistently (Feistel et al. (2008a)). Note that because of \( h = g + (T_0 + \eta) \) and Eqn. (3.33.2), the latent heat can also be written in terms of entropies \( \eta \) rather than enthalpies \( h \), in the form

\[
L_p^\text{SI}(S_A, P) = (T_0 + t_i) \times \left( \eta - S_A \frac{\partial \eta}{\partial S_A} - \eta^\text{liq} \right). \tag{34.7}
\]

Again the result is independent of unknown (and unknowable) constants.

The latent heat of melting depends only weakly on salinity and on pressure. At the surface pressure, the computed value is \( L_p^\text{SI}(0, 0) = L_p^\text{WI}(0) = 333 426.5 \text{ J kg}^{-1} \) for pure water, and \( L_p^\text{SI}(S_{\text{SO}}, 0) = 329 928.5 \text{ J kg}^{-1} \) for the standard ocean, with a difference of about 1% due to the dissolved salt. At a pressure of 1000 dbar, these values reduce by 0.6% to \( L_p^\text{SI}(0, 1000 \text{ dbar}) = L_p^\text{WI}(1000 \text{ dbar}) = 331 528 \text{ J kg}^{-1} \) and \( L_p^\text{SI}(S_{\text{SO}}, 1000 \text{ dbar}) = 328 \, 034 \text{ J kg}^{-1} \). TEOS-10 is consistent with the most accurate measurements of \( L_p^\text{WI} \) and their experimental uncertainties of 200 J kg\(^{-1}\), or 0.06% (Feistel and Wagner (2005), (2006)).

### 3.35 Sublimation pressure

The sublimation pressure of ice \( P^\text{subl} \) is defined as the absolute pressure \( P \) of water vapour in equilibrium with ice at a given temperature \( t \), at or below the freezing temperature. It is found by equating the chemical potential of water vapour \( \mu^V \) with the chemical potential of ice \( \mu^\text{liq} \), so it is found by solving the implicit equation

\[
\mu^V(t, P^\text{subl}) = \mu^\text{liq}(t, P^\text{subl}), \tag{35.1}
\]

or equivalently, in terms of the two Gibbs functions,

\[
g^V(t, P^\text{subl}) = g^\text{liq}(t, P^\text{subl}). \tag{35.2}
\]

The Gibbs function for ice \( g^\text{liq}(t, P) \) is defined by IAPWS-06 and Feistel and Wagner (2006) and is summarized in appendix I below. Note that here the absolute pressure \( P \) rather than the sea pressure \( p \) is used because the sublimation pressure of ice at ambient conditions is much lower than the atmospheric pressure.

The Gibbs function of vapour, \( g^V(t, P) \), is available from the Helmoltz function of fluid water, as defined by IAPWS-95; for details see for example Feistel et al. (2008a), (2010a), (2010b). The highest possible sublimation pressure is found at the triple point of water. The TEOS-10 value of the maximum sublimation pressure (i.e., the triple point pressure) computed from Eqn. (3.35.1) is \( P^\text{subl} = P^t = 611.655 \text{ Pa} \) and has an uncertainty of 0.01 Pa (IAPWS-06, Feistel et al. (2008a)).

Reliable theoretical values for the sublimation pressure are available down to 20 K (Feistel and Wagner (2007)); a simple correlation function for the sublimation pressure down to 50 K is provided by IAPWS (2008b) and is included as a function in the SIA library. The IAPWS-95 function \( \mu^V \) required for Eqn. (3.35.1) is only valid above 130 K. An extension to 50 K was developed for TEOS-10 (Feistel et al. (2010a)) and is available as the default option in the SIA library. In nature, vapour cannot reasonably be expected to exist below 50 K since it has extremely low density, even in the interstellar vacuum. For this reason, the ice of comets does not evaporate far from the sun. The lowest temperatures estimated for the terrestrial polar atmosphere do not go below 130 K.

In the presence of air, ice is under higher total pressure than just its own sublimation pressure. The partial pressure of vapour in humid air, \( P^\text{vap} = x_v P \), is computed from the
total absolute pressure \( P \) and the mole fraction of vapour, \( x_V \). Similar to the absolute salinity \( S_\lambda \) of seawater, the variable \( A \) describes the mass fraction of dry air present in humid air. Given \( A \), the mole fraction of vapour is computed from

\[
x_V = \frac{1 - A}{1 - A(1 - M_A / M_w)}
\]  
(3.35.3)

where \( M_A \) is the molar mass of dry air and \( M_w \) is the molar mass of water.

The sublimation pressure, \( P_{\text{subl}}(t, P) = x_{V,sat}P \), of ice in equilibrium with humid air is the partial pressure of vapour in saturated air. To compute \( x_{V,sat} \) from Eqn. (3.35.3), the required air fraction at saturation, \( A = A_{\text{sat}}(t, P) \), is found by equating the chemical potential of water vapour in humid air \( \mu_{w,V}^A \) with the chemical potential of ice \( \mu^h \), so that it is found by solving the implicit equation

\[
\mu_{w,V}^A(A_{\text{sat}}(t, P), P) = \mu^h(t, P),
\]  
(3.35.4)

or equivalently, in terms of the two Gibbs functions,

\[
g^A(A_{\text{sat}}(t, P) - A_{\text{sat}}^V g^A(A_{\text{sat}}(t, P), P) = g^h(t, P).
\]  
(3.35.5)

The Gibbs function of humid air, \( g^A(A, t, P) \), is defined by Feistel et al. (2010a).

At \( t = 0 \) °C and atmospheric pressure, the sublimation pressure of ice has the value \( P_{\text{subl}}(0 \, ^\circ\text{C}, 101325 \, \text{Pa}) = 613.745 \, \text{Pa} \), computed by solving Eqn. (3.35.4) for \( A_{\text{sat}} \), then using (3.35.3) to determine the corresponding mole fraction and multiplying the atmospheric pressure by this quantity. Similarly, at the freezing point of the standard ocean the sublimation pressure is \( P_{\text{subl}}(-1.919 \, ^\circ\text{C}, 101325 \, \text{Pa}) = 523.436 \, \text{Pa} \).

The difference between observed or modelled partial vapour pressures and the sublimation pressure computed from TEOS-10 is an appropriate quantity for use in parameterizations of the mass flux between ice and the atmosphere.

### 3.36 Sublimation enthalpy

The sublimation process that occurs when ice is in contact with pure water vapour can be conducted by supplying heat at constant \( t \) and \( P \), with \( t \) at or below the freezing temperature. The heat required per mass evaporated from the ice is the latent heat, or enthalpy, of sublimation, \( L_p^{VI} \). It is found as the difference between the specific enthalpy of water vapour, \( h^V \), and the specific enthalpy of ice, \( h^h \):

\[
L_p^{VI}(t) = h^V(t, P_{\text{subl}}) - h^h(t, P_{\text{subl}}).
\]  
(3.36.1)

Here, \( P_{\text{subl}}(t) \) is the sublimation pressure of ice at the temperature \( t \), section 3.35. The enthalpies \( h^V \) and \( h^h \) are available from IAPWS-95 and IAPWS-06, respectively. Reliable values for the sublimation enthalpy are theoretically available down to 20 K from a simple correlation function (Feistel and Wagner (2007)). At the triple point of water, the TEOS-10 sublimation enthalpy is \( L_p^{VI}(0.01 \, ^\circ\text{C}) = 2834.359 \, \text{J kg}^{-1} \) with an uncertainty of 1000 J kg\(^{-1}\), or 0.03%.

In the case when air is present, the vapour resulting from the sublimation will add to the gas phase, thus increasing the mole fraction of vapour \( x_{V,sat} \). If for example the total pressure \( P \) is held constant, the partial pressure \( x_{V,sat}P \) will rise, and the ice must get warmer to maintain equilibrium at the modified sublimation pressure \( P_{\text{subl}} = x_{V,sat}P \). Consequently, the enthalpy related to this phase transition will depend on the particular conditions under which the sublimation process occurs. These effects are small under ambient conditions but may be relevant at higher air densities.

Here, we define the latent heat of sublimation as the enthalpy increase per infinitesimal mass of sublimated ice of a composite system consisting of ice and humid air,
when the temperature is increased at constant pressure and at constant total masses of water and dry air, in excess of the enthalpy increase needed to warm up the ice and humid air phases individually (Feistel et al. (2010a)). Mass conservation of both total water and air during this thermodynamic process is essential to ensure the independence of the latent heat formula from the unknown absolute enthalpies of air and water that otherwise would accompany any mass exchange.

The enthalpy of ice air, $h_{\text{AI}}$, is additive with respect to its constituents ice, $h_{\text{Ih}}$, with the mass fraction $w_{\text{Ih}}$, and humid air, $h_{\text{AV}}$, with the gas fraction $(1 - w_{\text{Ih}})$:

$$h_{\text{AI}} = (1 - w_{\text{Ih}})h_{\text{AV}}(A, t, p) + w_{\text{Ih}}h_{\text{Ih}}(t, p). \quad (3.36.2)$$

Upon warming, the mass of vapour produced by sublimation reduces the ice fraction $w_{\text{Ih}}$ and increases the humidity, that is, decreases the relative dry-air fraction $A$ of the gas phase. The related temperature derivative of Eqn. (3.36.2) is

$$\frac{\partial h_{\text{AI}}}{\partial T} \bigg|_p = (1 - w_{\text{Ih}})\frac{\partial h_{\text{AV}}}{\partial T} \bigg|_{A, p} + \left(1 - w_{\text{Ih}}\right)\frac{\partial h_{\text{AV}}}{\partial A} \bigg|_{r, p} \frac{\partial A}{\partial T} \bigg|_p + w_{\text{Ih}}\frac{\partial h_{\text{Ih}}}{\partial T} \bigg|_p + \left(h_{\text{Ih}} - h_{\text{AV}}\right)\frac{\partial w_{\text{Ih}}}{\partial T} \bigg|_p. \quad (3.36.3)$$

The air-fraction change is related to the isobaric sublimation rate, $-\frac{\partial w_{\text{Ih}}}{\partial T} \bigg|_p$, by the conservation of the dry air, $(1 - w_{\text{Ih}})A = \text{const}$, in the form

$$\frac{\partial A}{\partial T} \bigg|_p = \frac{A}{1 - w_{\text{Ih}}} \frac{\partial w_{\text{Ih}}}{\partial T} \bigg|_p. \quad (3.36.4)$$

Using this relation, Eqn. (3.36.3) takes the simple form

$$\frac{\partial h_{\text{AI}}}{\partial T} \bigg|_p = \left(1 - w_{\text{Ih}}\right)\frac{\partial h_{\text{AV}}}{\partial T} \bigg|_{A, p} + w_{\text{Ih}}\frac{\partial h_{\text{Ih}}}{\partial T} \bigg|_p - L_p^\text{AI} \frac{\partial w_{\text{Ih}}}{\partial T} \bigg|_p. \quad (3.36.5)$$

The coefficient in front of the sublimation rate,

$$L_p^\text{AI}(A, p) = h_{\text{AV}} - A\frac{\partial h_{\text{AV}}}{\partial A} \bigg|_{r, p} - h_{\text{Ih}}, \quad (3.36.6)$$

provides the desired expression for isobaric sublimation enthalpy, namely the difference between the partial specific enthalpies of vapour in humid air and of ice. In the ideal-gas approximations for air and for vapour, the partial specific enthalpy of vapour in humid air, $h_{\text{AV}} - Ah_{\text{Ih}}$, equals the specific enthalpy of vapour, $h_{\text{Ih}}$, as a function of only the temperature, independent of the pressure and of the presence of air (Feistel et al. (2010a)). In this case, Eqn. (3.36.6) coincides formally with Eqn. (3.36.1), except that the two are evaluated at the different pressures $P$ and $P^\text{subl}$, respectively. As is physically required for any measurable thermodynamic quantity, the arbitrary absolute enthalpies of ice, vapour and air cancel in the formula (3.36.6), provided that the reference state conditions for the ice and humid air formulations are chosen consistently (Feistel et al. (2008a), (2010a)). The latent heat of sublimation depends only weakly on the air fraction and on the pressure.

For saturated air over sea ice, the air fraction $A = A^\text{sat}$ can be computed from the brine salinity, or from the sea surface salinity in the case of floating ice, section 3.38. At the absolute surface pressure $P_S = 101325$ Pa and the freezing point $t_f = -1.919$ °C of the standard ocean, the TEOS-10 value for saturated air with $A_S = A^\text{sat}(t_f, P_S) = 0.99678$ is $L_p^\text{AI}(A_S, P_S) = 2,833,006$ J kg$^{-1}$. The related sublimation pressure is $P^\text{subl}(t_f, P_S) = 523,436$ Pa, see section 3.35.

Observational data show that the ambient air over the ocean surface is sub-saturated in the climatological mean. Rather than being saturated, values for $A$ that correspond to a relative humidity of 75% – 82% (see section 3.40) may be a more realistic estimate for the
3.37 Vapour pressure

The vapour pressure of seawater \( P_{\text{vap}}(S_A, t) \) is defined as the absolute pressure \( P \) of water vapour in equilibrium with seawater at a given temperature \( t \) and salinity \( S_A \). It is found by equating the chemical potential of vapour \( \mu^V \) with the chemical potential of water in seawater \( \mu^W \) so that it is found by solving the implicit equation

\[
\mu^V(t, P_{\text{vap}}) = \mu^W(S_A, t, P_{\text{vap}}),
\]

or equivalently, in terms of the two Gibbs functions,

\[
g^V(t, P_{\text{vap}}) = g(S_A, t, P_{\text{vap}}) - S_A g_{S_A}(S_A, t, P_{\text{vap}}).
\]

Note that here we use the absolute pressure \( P \) rather than the sea pressure \( p \); since the vapour pressure of water at ambient conditions is much lower than the atmospheric pressure, the corresponding sea pressure \( (P_{\text{vap}} - 101325 \text{ Pa}) \) would be negative and near \(-10^5 \text{ Pa}\). The Gibbs functions of vapour and seawater, \( g^V(t, P) \) and \( g(S_A, t, P) \), are available from the Helmholtz function of fluid water, as defined by IAPWS-95, and the Gibbs function of seawater, IAPWS-08 or IAPWS-09 (IAPWS (2009c)).

In the case of pure water, \( S_A = 0 \), the solution of Eqn. (3.37.1) is the so-called saturation curve in the \( t – P \) diagram of water, which connects the triple point with the critical point. The lowest possible vapour pressure of pure liquid water is found at the triple point of water. The TEOS-10 value of this minimum vapour pressure, computed from Eqn. (3.37.1), is \( P_{\text{vap}}(0, 0.01 \text{ °C}) = P_t = 611.655 \text{ Pa} \) with an uncertainty of 0.01 Pa (IAPWS-95, Feistel et al. (2008a)). For comparison, the vapour pressure of the standard ocean is \( P_{\text{vap}}(S_{SO}, 0 \text{ °C}) = 599.907 \text{ Pa} \). At laboratory temperature the related values are \( P_{\text{vap}}(0, 25 \text{ °C}) = 3169.93 \text{ Pa} \) and \( P_{\text{vap}}(S_{SO}, 25 \text{ °C}) = 3110.57 \text{ Pa} \).

The relatively small vapour pressure lowering caused by the presence of dissolved salt can be computed from the ideal salinity derivative of Eqn. (3.37.1) in the form (Raoult’s law)

\[
\frac{\partial P_{\text{vap}}}{\partial S_A} \bigg|_T = \frac{S_A g_{S_A,S_A}}{g_p} - \frac{S_A}{g_{S_A,S_A}} \frac{\partial g^V}{\partial P}.
\]

As a raw practical estimate, this equation can be expanded into powers of salinity, using only the leading term of the TEOS-10 saline Gibbs function, \( g^V \approx R_g TS_A \ln S_A \), which stems from Planck’s ideal-solution theory. Here, \( R_g = R/M_S = 264.7399 \text{ J kg}^{-1} \text{ K}^{-1} \) is the specific gas constant of sea salt, \( R \) is the universal molar gas constant, and \( M_S = 31.40382 \text{ g mol}^{-1} \) is the molar mass of sea salt with Reference Composition. The specific volume of seawater, \( g_p \), is neglected in comparison to that of vapour. The latter is approximately considered as an ideal gas, \( g^V \approx RT/(M_W P_{\text{vap}}) \), where \( M_W = 18.015 268 \text{ g mol}^{-1} \) is the molar mass of water. The convenient result obtained with these simplifications is

\[
\frac{\partial P_{\text{vap}}}{\partial S_A} \bigg|_T \approx -\frac{M_W}{M_S} P_{\text{vap}} \approx -0.57 \times P_{\text{vap}}.
\]

The vapour pressure of seawater is always lower than that of pure water.

In the presence of air, seawater is under a higher pressure \( P \) than under its vapour pressure \( P_{\text{vap}} \). In this case, the vapour pressure of seawater \( P_{\text{vap}}(S_A, t, P) \) is defined as the partial pressure of water vapour in humid air that is in equilibrium with seawater at a given pressure \( P \), temperature \( t \) and salinity \( S_A \). It is found by equating the chemical
potential of vapour in humid air $\mu^V$ with the chemical potential of water in seawater $\mu^W$ so that it is found by solving the implicit equation

$$\mu^V(A^{\text{cond}}, t, P) = \mu^W(S_A, t, P)$$

(3.37.5)

for $A^{\text{cond}}(S_A, t, P)$, or equivalently, in terms of the two Gibbs functions,

$$g^V(A^{\text{cond}}, t, P) - A^{\text{cond}}g^W(A^{\text{cond}}, t, P) = g(S_A, t, P) - S_A g_{S_A}(S_A, t, P).$$

(3.37.6)

Since the vapour pressure is lowered in the presence of sea salt (Eqn. (3.37.4)), at vapour pressures above the condensation point vapour condenses out of the air at the sea surface, even before the saturation point (that is, relative humidity of 100%) is reached, to maintain local equilibrium with the seawater. The larger scale equilibration process may involve downward diffusion of water vapour to the sea surface rather than precipitation of dew or fog. From the calculated sub-saturated air fraction of the condensation point, $A^{\text{cond}}$, the mole fraction of vapour $x^{\text{cond}}_V$ (3.35.2), and in turn the vapour pressure $P^{\text{vap}}(S_A, t, P) = x^{\text{cond}}_V P$ are available from straightforward calculations. The Gibbs function of humid air $g^V$ is available from Feistel et al. (2010a) and is also planned to be made available as the document IAPWS (2010).

The TEOS-10 value computed from Eqn. (3.37.5) is $P^{\text{vap}}(0, 0 \degree C, P_{SO}) = 613.760$ Pa for pure water at surface air pressure; the vapour pressure of the standard ocean is $P^{\text{vap}}(S_{SO}, 0 \degree C, P_{SO}) = 602.403$ Pa. At laboratory temperature the related values are $P^{\text{vap}}(0, 25 \degree C, P_{SO}) = 3183.73$ Pa and $P^{\text{vap}}(S_{SO}, 25 \degree C, P_{SO}) = 3124.03$ Pa.

### 3.38 Boiling temperature

The boiling temperature of water or seawater is defined as the temperature $t^{\text{boil}}(S_A, P)$ at which the vapour pressure (of section 3.37) equals a given pressure $P$. It is found by equating the chemical potential of vapour $\mu^V$ with the chemical potential of water in seawater $\mu^W$ so that it is found by solving the implicit equation

$$\mu^V(t^{\text{boil}}, P) = \mu^W(S_A, t^{\text{boil}}, P),$$

(3.38.1)

for $t^{\text{boil}}(S_A, P)$, or equivalently in terms of the two Gibbs functions,

$$g^V(t^{\text{boil}}, P) = g(S_A, t^{\text{boil}}, P) - S_A g_{S_A}(S_A, t^{\text{boil}}, P).$$

(3.38.2)

The TEOS-10 boiling temperature of pure water at atmospheric pressure is $t^{\text{boil}}(0, P_{SO}) = 99.974 \degree C$. This temperature is outside the validity range of up to 80 °C of the TEOS-10 Gibbs function for seawater.

### 3.39 Latent heat of evaporation

The evaporation process of pure liquid water in contact with pure water vapour can be conducted by supplying heat at constant $t$ and $P$. The heat required per mass evaporated from the liquid is the latent heat, or enthalpy, of evaporation, $L^{\text{vap}}_{p}$. It is found as the difference between the specific enthalpy of water vapour, $h^{V}$, and the specific enthalpy of liquid water, $h^{W}$:

$$L^{\text{vap}}_{p}(t) = h^{V}(t, P^{\text{vap}}) - h^{W}(t, P^{\text{vap}}).$$

(3.39.1)

Here, $P^{\text{vap}}(t)$ is the vapour pressure of water at the temperature $t$ (section 3.37). The enthalpies $h^{V}$ and $h^{W}$ are available from IAPWS-95. At the triple point of water, the TEOS-10 evaporation enthalpy is $L^{\text{vap}}_{p}(0.01\degree C) = 2500.915$ J kg$^{-1}$.

In the case of seawater in contact with air, the vapour resulting from the evaporation will add to the gas phase, thus increasing the mole fraction of vapour, while the liquid
water loss will increase the brine salinity, and cause a change to the seawater enthalpy. Consequently, the enthalpy related to this phase transition will depend on the particular conditions under which the evaporation process occurs.

Here, we define the latent heat of evaporation as the enthalpy increase per infinitesimal mass of evaporated water of a composite system consisting of seawater and humid air, when the temperature is increased at constant pressure and at constant total masses of water, salt and dry air, in excess of the enthalpy increase needed to warm up the seawater and humid air phases individually (Feistel et al. (2010a)). Mass conservation during this thermodynamic process is essential to ensure the independence of the latent heat formula from the unknown absolute enthalpies of air, salt and water that otherwise would accompany any mass exchange.

The enthalpy of sea air, $h^{SA}$, is additive with respect to its constituents, seawater, $h$, with the mass fraction $w^{SW}$, and humid air, $h^{AV}$, with the gas fraction $(1-w^{SW})$:

$$h^{SA} = (1-w^{SW})h^{AV}(A, t, p) + w^{SW}h(S_A, t, p). \quad (3.39.2)$$

Upon warming, the mass of water transferred from the liquid to the gas phase by evaporation reduces the seawater mass fraction $w^{SW}$, increases the brine salinity $S_A$ and increases the humidity, with a corresponding decrease in the dry-air fraction $A$ of the gas phase. The related temperature derivative of Eqn. (3.39.2) is

$$\left. \frac{\partial h^{SA}}{\partial T} \right|_p = \left. \left(1-w^{SW}\right) \frac{\partial h^{AV}}{\partial T} \right|_{A,p} + \left. \left(1-w^{SW}\right) \frac{\partial h^{AV}}{\partial A} \right|_{T,p} \left. \frac{\partial A}{\partial T} \right|_p + \left. w^{SW} \frac{\partial h}{\partial T} \right|_{S_A,p} + \left. \left(w^{SW} \frac{\partial h}{\partial T} \right|_{S_A,p} + \left. \left(1-h^{AV}\right) \frac{\partial w^{SW}}{\partial T} \right|_p \right). \quad (3.39.3)$$

The isobaric evaporation rate $-\partial w^{SW}/\partial T$ is related to the air-fraction change by the conservation of the dry air, $(1-w^{SW})A = \text{const}$, in the form

$$\left. \frac{\partial A}{\partial T} \right|_p = \frac{A}{1-w^{SW}} \left. \frac{\partial w^{SW}}{\partial T} \right|_p, \quad (3.39.4)$$

and to the change of salinity by the conservation of the salt, $w^{SW}S_A = \text{const}$, in the form

$$\left. \frac{\partial S_A}{\partial T} \right|_p = - \frac{S_A}{w^{SW}} \left. \frac{\partial w^{SW}}{\partial T} \right|_p. \quad (3.39.5)$$

Using these relations, Eqn. (3.39.3) takes the simplified form

$$\left. \frac{\partial h^{SA}}{\partial T} \right|_p = \left. \left(1-w^{SW}\right)c_p^{AV} + w^{SW}c_p - L^A_p \frac{\partial w^{SW}}{\partial T} \right|_p. \quad (3.39.6)$$

The coefficient in front of the evaporation rate,

$$L^A_p (A, S_A, t, p) = h^{AV} - A \left. \frac{\partial h^{AV}}{\partial A} \right|_{T,p} - h + S_A \left. \frac{\partial h}{\partial S_A} \right|_{T,p}, \quad (3.39.7)$$

provides the desired expression for isobaric evaporation enthalpy, namely the difference between the partial specific enthalpies of vapour in humid air (the first two terms) and of water in seawater (the last two terms). In the ideal-gas approximations for air and for vapour, the partial specific enthalpy of vapour in humid air, $h^{AV} - Ah^{AV}$, equals the specific enthalpy of vapour, $h^V(t)$, as a function of only the temperature, independent of the pressure and of the presence of air (Feistel et al. (2010a)). As is physically required for any measurable thermodynamic quantity, the arbitrary absolute enthalpies of water, salt and air cancel in the formula (3.39.7), provided that the reference state conditions for both the seawater and the humid-air formulation are chosen consistently (Feistel et al. (2008a),
The latent heat of evaporation depends only weakly on salinity and on air fraction, and is an almost linear function of the temperature and of the pressure.

Selected representative values for the air fraction at condensation, \( A^{\text{cond}} \), and the latent heat of evaporation, \( L_p^{SA} \), are given in Table 3.39.1.

**Table 3.39.1:** Selected values for the equilibrium air fraction, \( A^{\text{cond}} \), computed from Eqn. (3.37.6), and the latent heat of evaporation, \( L_p^{SA} \), computed from Eqn. (3.39.7), for different sea-surface conditions. Note that the TEOS-10 formulation for humid-air is valid up to 5 MPa, i.e., almost 500 dbar sea pressure.

<table>
<thead>
<tr>
<th>Condition</th>
<th>( S_A ) g kg(^{-1})</th>
<th>( t ) °C</th>
<th>( p ) dbar</th>
<th>( A^{\text{cond}} ) %</th>
<th>( L_p^{SA} ) J kg(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>99.622 31</td>
<td>2 499 032</td>
</tr>
<tr>
<td>Brackish water</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>99.624 27</td>
<td>2 499 009</td>
</tr>
<tr>
<td>Standard ocean</td>
<td>35.165 04</td>
<td>0</td>
<td>0</td>
<td>99.629 31</td>
<td>2 498 510</td>
</tr>
<tr>
<td>Tropical ocean</td>
<td>35.165 04</td>
<td>25</td>
<td>0</td>
<td>98.059 33</td>
<td>2 438 971</td>
</tr>
<tr>
<td>High pressure</td>
<td>35.165 04</td>
<td>0</td>
<td>400</td>
<td>99.989 43</td>
<td>2 443 759</td>
</tr>
</tbody>
</table>

In the derivation of Eqn. (3.39.7), the value of \( A \) is indirectly assumed to be computed from the equilibrium condition (3.37.6) between humid air and seawater, \( A = A^{\text{cond}} \). At this humidity the air is still sub-saturated, \( A^{\text{cond}} > A^{\text{sat}} \), but its vapour starts condensing at the sea surface. The values of \( A^{\text{cond}} \) and \( A^{\text{sat}} \) coincide only below the freezing point of seawater, or at vanishing salinity, see also the following section 3.40.

The evaporation rate, \(-\dot{c}_w^{SW} / \dot{c}_T^{p}\), can be computed from Eqn. (3.37.6), the equilibrium condition between humid air and seawater, at changing temperature and constant pressure (Feistel et al. (2010a)). In contrast, the derivation of \( L_p^{SA} \) using Eqns. (3.39.2) - (3.39.7) is a mere consideration of mass and enthalpy balances; no equilibrium condition is actually involved. Hence, it is physically evident that Eqn. (3.39.7) can also be applied to situations in which \( A \) takes any given value different from \( A^{\text{cond}} \), that is, it can be applied regardless of whether or not the humid air is actually at equilibrium with the sea surface.

### 3.40 Relative humidity and fugacity

Parameterised formulas for the flux of water and heat through the ocean surface are usually expressed in terms of a given relative humidity of the air in contact with seawater. In this section we provide the formulas for the relative humidity and the fugacity from the TEOS-10 potential functions for seawater and humid air, and we explain why the relative fugacity with respect to condensation rather than with respect to saturation should be used for oceanographic flux estimates (Feistel et al. (2010a)). Near the saturation point, the two flux formulas may even exhibit different signs (different flux directions) since condensation occurs at the sea surface at sub-saturated values of relative humidity.

Relative humidity is not uniquely defined in the literature, but the common definitions give the same results in the ideal-gas limit of humid air. Also in this approximation, relative humidity is only a property of fluid water at given temperature and pressure of the vapour phase, independent of the presence of air.
The CCT\(^1\) definition of relative humidity is in terms of mole fraction: “At given pressure and temperature, [the relative humidity is defined as] the ratio, expressed as a percent, of the mole fraction of water vapour to the vapour mole fraction which the moist gas would have if it were saturated with respect to either water or ice at the same pressure and temperature.” Consistent with CCT, IUPAC\(^2\) defines relative humidity “as the ratio, often expressed as a percentage, of the partial pressure of water in the atmosphere at some observed temperature, to the saturation vapour pressure of pure water at this temperature” (Calvert (1990), IUPAC (1997)). This definition of the relative humidity takes the form

\[
RH_{\text{CCT}} = \frac{x_v}{x_v^{\text{sat}}} \tag{3.40.1}
\]

with regard to the mole fraction of vapour \(x_v(A)\), Eqn. (3.35.3), and the saturated air fraction \(A = A^{\text{sat}}(t, P) = A^{\text{cond}}(0, t, P)\) either from Eqn. (3.37.6) with respect to liquid water, at \(t\) above the freezing point of pure water, or from Eqn. (3.35.5) with respect to ice, at \(t\) below the freezing point of pure water. Here, \(A^{\text{cond}}(S_A, t, P)\) is the air fraction of humid air at equilibrium with seawater, Eqn. (3.37.5), which is subsaturated for \(S_A > 0\).

The WMO\(^3\) definition of the relative humidity is (Pruppacher and Klett (1997), Jacobson (2005)),

\[
RH_{\text{WMO}} = \frac{r}{r^{\text{sat}}} = \frac{1}{A^{\text{sat}}} - \frac{1}{A^{\text{sat}} - 1} \tag{3.40.2}
\]

where \(r = (1 - A) / A\) is the humidity ratio. If \(r\) is small, we can estimate \(x_v \approx rM_A / M_w\) (from Eqn. (3.35.3)) and therefore \(RH_{\text{WMO}} \approx RH_{\text{CCT}}\), that is, we find approximate consistency between Eqns. (3.40.1) and (3.40.2).

Sometimes, especially when considering phase or chemical equilibria, it is more convenient to use the fugacity (or activity) rather than partial pressure ratio (IUPAC (1997)). The fugacity of vapour in humid air is defined as

\[
f_v(A, T, P) = x_v P \exp \left( \frac{\mu_v^V - \mu_v^{\text{id}}}{R_W T} \right). \tag{3.40.3}
\]

Here, \(R_W = R / M_w\) is the specific gas constant of water, \(\mu_v^V(A, T, P) = g_v^V - A g_A^V\) is the chemical potential of vapour in humid air, and \(\mu_v^{\text{id}}(A, T, P)\) is its ideal-gas limit which is equal to the true chemical potential in the limit of very low pressure,

\[
\mu_v^{\text{id}}(A, T, P) = g_v^V + \int_0^T \left( 1 - \frac{T}{T'} \right) c_p^{\text{vd}}(T') \, dT' + R_W T \ln \frac{x_v P}{P_0}. \tag{3.40.4}
\]

The values of \(g_v^0, P_0^V\) and \(T_0^V\) of \(\mu_v^{\text{id}}\) must be chosen consistently with the adjustable constants of \(g_A^V\) (Feistel et al. (2010a)). The ideal-gas heat capacity of vapour \(c_p^{\text{vd}}(T)\) is available from IAPWS-95. In the ideal-gas limit of infinite dilution, \(f_v\) converges to the partial pressure of vapour (Glasstone (1947)),

\[
\lim_{P \to 0} f_v(A, T, P) = x_v P = P^{\text{vap}}. \tag{3.40.5}
\]

The saturation fugacity is defined by the equilibrium between liquid water (or ice) and vapour in air, \(\mu_v^V(A, T, P) = \mu_w^W(0, T, P)\), that is,

\[
f_v^{\text{sat}} = x_v^{\text{sat}} P \exp \left( \frac{\mu_w^W(0, T, P) - \mu_v^{\text{id}}(A^{\text{sat}}, T, P)}{R_W T} \right), \tag{3.40.6}
\]

\(^1\) CCT: Consultative Committee for Thermometry, www.bipm.org/en/committees/cc/cct/


\(^3\) WMO: World Meteorological Organisation, www.wmo.int
where \( \mu^W = g(0,T,P) \) is the chemical potential of liquid water (or the chemical potential of ice, \( \mu^I \)). The relative fugacity \( \varphi \) of humid air is then defined, dividing Eqn. (3.40.3) by Eqn. (3.40.6) and making use of Eqn. (3.40.4), as

\[
\varphi = \frac{f^V}{f^{\text{sat}}_V} = \exp\left\{ \frac{\mu^V(A,T,P) - \mu^W(0,T,P)}{R_w T} \right\},
\]

(3.40.7)

In the ideal-gas limit, \( \mu^V = \mu^V_{\text{id}} \), and using (3.40.3) we see that the relative fugacity \( \varphi \) coincides with the relative humidity, Eqn. (3.40.1).

Taking Eqn. (3.40.7) at the condensation point, \( A = A^\text{cond} \), Eqn. (3.37.5), it follows that the relative fugacity of humid air at equilibrium with seawater ("sea air" for short) is

\[
\varphi^\text{SA} = \frac{f^V_{\text{sat}}}{f^{\text{sat}}_V} = \exp\left\{ \frac{\mu^W(S_A,T,P) - \mu^W(0,T,P)}{R_w T} \right\}.
\]

(3.40.8)

The chemical potential difference in the exponent is proportional to the osmotic coefficient of seawater, \( \phi \), which is computed from the saline part of the Gibbs function as (Feistel and Marion (2007), Feistel (2008)),

\[
\phi(S_A,T,P) = -\frac{1}{m_{\text{sw}} RT} \left[ g^S - S_A \frac{\partial g^S}{\partial S_A}_{T,P} \right],
\]

(3.40.9)

where \( m_{\text{sw}} \) is the molality of seawater (Millero et al. (2008a)),

\[
m_{\text{sw}} = \frac{S_A}{(1 - S_A) M_S}.
\]

(3.40.10)

From the chemical potential of water in seawater, \( \mu^W = g - S_A g_{\text{sw}} \), and Eqns. (3.40.8) - (3.40.10) we infer for the relative fugacity of sea air the simple formula

\[
\varphi^\text{SA} = \exp(-m_{\text{sw}} M_w \phi),
\]

(3.40.11)

which is identical to the activity \( a_w \) of water in seawater. Similar to the ideal gas approximation, the relative fugacity of sea air is independent of the presence or the properties of air. In Eqn. (3.40.11), the relative fugacity \( \varphi^\text{SA} \leq 1 \) expresses the fact that the vapour pressure of seawater is lower than that of pure water, i.e., that humid air in equilibrium with seawater above its freezing temperature is always sub-saturated.

As a raw practical estimate, using a series expansion of Eqns. (3.40.10) and (3.40.11) with respect to salinity, we can obtain from the molality \( m_{\text{sw}} = S_A / M_S + O(S_A^2) \) and the osmotic coefficient \( \phi = 1 + O(S_A) \) the linear relation

\[
\varphi^\text{SA} \approx 1 - \frac{M_w}{M_S} S_A,
\]

(3.40.12)
i.e., Raoult’s law for the vapour-pressure lowering of seawater, Eqn. (3.37.4).

Below the freezing temperature of pure water at a given pressure, the saturation of vapour is defined by the chemical potential of ice rather than liquid water, i.e. by

\[
f^{\text{sat}}_V = x^\text{sat}_V P \exp\left\{ \frac{\mu^I(T,P) - \mu^V_{\text{id}}(A^\text{sat},T,P)}{R_w T} \right\},
\]

(3.40.13)
rather than Eqn. (3.40.6). Then, the relative fugacity of sea air is

\[
\varphi^\text{SA} = \frac{f^V_{\text{sat}}}{f^{\text{sat}}_V} = \exp\left\{ \frac{\mu^W(S_A,T,P) - \mu^I(T,P)}{R_w T} \right\}.
\]

(3.40.14)

When the temperature is lowered further to the freezing point of seawater, the exponent of (3.40.14) vanishes and sea air is saturated, \( \varphi^\text{SA} = 1 \), for sea-ice air at any lower temperature.
Thermodynamic fluxes in non-equilibrium states are driven by Onsager forces such as the gradient of $\mu / T$ (De Groot and Mazur (1984)). At the sea surface, assuming the same temperature and pressure on both sides of the sea-air interface, the dimensionless Onsager force $X_{SA}(A, S_A, T, P)$ driving the transfer of water is the difference between the chemical potentials of water in humid air and in seawater,

$$X_{SA} = \Delta \left( \frac{\mu}{R_w T} \right) = \frac{\mu_{SW}(A, T, P)}{R_w T} - \frac{\mu_{SW}(S_A, T, P)}{R_w T}. \quad (3.40.15)$$

This difference vanishes at the condensation point, $A = A_{\text{cond}}(S_A, T, P)$, Eqn. (3.37.5), rather than at saturation. $X_{SA}$ can also be expressed in terms of fugacities, Eqns. (3.40.7), (3.40.8) and (3.40.11), in the form

$$X_{SA} = \ln \frac{\phi(A)}{\phi^{SA}(S_A)} = m_{SW} M_w \phi + \ln \phi(A). \quad (3.40.16)$$

Rather than the relative humidity, Eqns. (3.40.1), (3.40.2), the sea-air Onsager force $X_{SA}$, in conjunction with the formula (3.39.7), is relevant for the parameterization of non-equilibrium latent heat fluxes across the sea surface. In the special case of limnological applications, or below the freezing point of seawater, it reduces to $X_{SA} = \ln \phi(A)$, which corresponds to the relative humidity, $\ln(RH_{\text{CCT}})$, in the ideal-gas approximation. All properties required for the calculation of the formula (3.40.16) are available from the TEOS-10 thermodynamic potentials for seawater, ice, and humid air.

### 3.41 Osmotic pressure

If pure water is separated from seawater by a semi-permeable membrane which allows water molecules to pass but not salt particles, water will penetrate into the seawater, thus diluting it and possibly increasing its pressure, until the chemical potential of water in both boxes becomes the same (or the pure water reservoir is exhausted). In the usual model configuration, the two samples are thermally coupled but may possess different pressures; the resulting pressure difference required to maintain equilibrium is the osmotic pressure of seawater. An example of a practical application is desalination by reverse osmosis; if the pressure on seawater in a vessel exceeds its osmotic pressure, freshwater can be “squeezed” out of solution through suitable membrane walls (Sherwood et al. (1967)). The osmotic pressure of seawater is very important for marine organisms; it is considered responsible for the small number of species that can survive in brackish environments.

The defining condition for the osmotic equilibrium is equality of the chemical potentials of pure water at the pressure $p^W$ and of water in seawater at the pressure $p$,

$$g^W(t, p^W) = g(S_A, t, p) - S_A \frac{\partial g}{\partial S_A}(t, p). \quad (3.41.1)$$

The solution of this implicit relation for the osmotic pressure is

$$P^\text{osm}(S_A, t, p) = P - P^W. \quad (3.41.2)$$

The TEOS-10 value for the osmotic pressure of the standard ocean is $P^\text{osm}(S_{SO}, 0^\circ \text{C}, 0 \text{dbar}) = 2354.684$ Pa, computed from Eqn. (3.41.1).
### 3.42 Temperature of maximum density

At about 4 °C and atmospheric pressure, pure water has a density maximum below which the thermal expansion coefficient and the adiabatic lapse rate change their signs (Röntgen (1892), McDougall and Feistel (2003)). At salinities higher than 23.8 g kg⁻¹ the temperature of maximum density $t_{MD}$ is below the freezing point $t_f$ (Table 3.42.1). The seasonal and spatial interplay between density maximum and freezing point is highly important for the stratification stability and the seasonal deep convection for brackish estuaries with permanent vertical and lateral salinity gradients such as the Baltic Sea (Feistel et al. (2008b), Leppäranta and Myrberg (2009), Reissmann et al. (2009)).

The temperature of maximum density $t_{MD}$ is computed from the condition of vanishing thermal expansion coefficient, that is, from the solution of the implicit equation for $t_{MD}(S_A, p)$,

$$g_T(S_A, t_{MD}, p) = 0.$$  \hspace{1cm} (3.42.1)

The temperature of maximum density is available in the GSW computer software library as function `gsw_temps_maxdensity`. This function also returns the potential temperature and the Conservative Temperature at this maximum density point. Selected TEOS-10 values computed from this equation are given in Table 3.42.1.

**Table 3.42.1:** Freezing temperature $t_f$ and temperature of maximum density $t_{MD}$ for air-free brackish seawater with absolute salinities $S_A$ between 0 and 25 g kg⁻¹, computed at the surface pressure from TEOS-10. Values of $t_{MD}$ in parentheses are less than the freezing temperature.

<table>
<thead>
<tr>
<th>$S_A$ g kg⁻¹</th>
<th>$t_f$ °C</th>
<th>$t_{MD}$ °C</th>
<th>$S_A$ g kg⁻¹</th>
<th>$t_f$ °C</th>
<th>$t_{MD}$ °C</th>
<th>$S_A$ g kg⁻¹</th>
<th>$t_f$ °C</th>
<th>$t_{MD}$ °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>+0.003</td>
<td>3.978</td>
<td>8.5</td>
<td>-0.456</td>
<td>2.128</td>
<td>17</td>
<td>-0.912</td>
<td>0.250</td>
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<tr>
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<td>9</td>
<td>-0.483</td>
<td>2.019</td>
<td>17.5</td>
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</tr>
<tr>
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<td>1.909</td>
<td>18</td>
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</tr>
<tr>
<td>1.5</td>
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<td>1.800</td>
<td>18.5</td>
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<td>-0.085</td>
</tr>
<tr>
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<td>13.5</td>
<td>-0.724</td>
<td>1.028</td>
<td>22</td>
<td>-1.184</td>
<td>-0.868</td>
</tr>
<tr>
<td>5.5</td>
<td>-0.296</td>
<td>2.782</td>
<td>14</td>
<td>-0.750</td>
<td>0.917</td>
<td>22.5</td>
<td>-1.212</td>
<td>-0.980</td>
</tr>
<tr>
<td>6</td>
<td>-0.323</td>
<td>2.673</td>
<td>14.5</td>
<td>-0.777</td>
<td>0.807</td>
<td>23</td>
<td>-1.239</td>
<td>-1.092</td>
</tr>
<tr>
<td>6.5</td>
<td>-0.349</td>
<td>2.564</td>
<td>15</td>
<td>-0.804</td>
<td>0.696</td>
<td>23.5</td>
<td>-1.267</td>
<td>-1.204</td>
</tr>
<tr>
<td>7</td>
<td>-0.376</td>
<td>2.456</td>
<td>15.5</td>
<td>-0.831</td>
<td>0.584</td>
<td>24</td>
<td>-1.294</td>
<td>(-1.316)</td>
</tr>
<tr>
<td>7.5</td>
<td>-0.403</td>
<td>2.347</td>
<td>16</td>
<td>-0.858</td>
<td>0.473</td>
<td>24.5</td>
<td>-1.322</td>
<td>(-1.428)</td>
</tr>
<tr>
<td>8</td>
<td>-0.429</td>
<td>2.238</td>
<td>16.5</td>
<td>-0.885</td>
<td>0.362</td>
<td>25</td>
<td>-1.349</td>
<td>(-1.540)</td>
</tr>
</tbody>
</table>
4. Conclusions

The International Thermodynamic Equation of Seawater – 2010 (TEOS-10) allows all the thermodynamic properties of pure water, ice Ih, seawater and moist air to be evaluated in an internally self-consistent manner. Ice Ih is the naturally abundant form of ice, having hexagonal crystals. For the first time the effects of the small variations in seawater composition around the world ocean can be included, especially their effects on the density of seawater (which can be equivalent to ten times the precision of our Practical Salinity measurements at sea).

Perhaps the most apparent change compared to the International Equation of State of seawater (EOS-80) is the adoption of Absolute Salinity $S_A$ instead of Practical Salinity $S_p$ (PSS-78) as the salinity argument for the thermodynamic properties of seawater. Importantly, Practical Salinity is retained as the salinity variable that is stored in databases because Practical Salinity is virtually the measured variable (whereas Absolute Salinity is a calculated variable) and also so that national data bases do not become corrupted with incorrectly labeled and stored salinity data.

The adoption of Absolute Salinity as the argument for all the algorithms used to evaluate the thermodynamic properties of seawater makes sense simply because the thermodynamic properties of seawater depend on $S_A$ rather than on $S_p$; seawater parcels that have the same values of temperature, pressure and of $S_p$ do not have the same density unless the parcels also share the same value of $S_A$. Absolute Salinity is measured in SI units and the calculation of the freshwater concentration and of freshwater fluxes follows naturally from Absolute Salinity, but not from Practical Salinity.

Absolute Salinity is calculated in a two-stage process. First Reference Salinity is calculated from measurements of Practical Salinity using Eqn. (2.4.1). Then the Absolute Salinity Anomaly is estimated from the computer algorithm of McDougall et al. (2010a) or by other means, and Absolute Salinity is formed as the sum of Reference Salinity and the Absolute Salinity Anomaly. There are subtle issues in defining what is exactly meant by “absolute salinity” and at least four different definitions are possible when compositional anomalies are present. We have chosen the definition that yields the most accurate estimates of seawater density since the ocean circulation is sensitive to rather small gradients of density. The algorithm that estimates Absolute Salinity Anomaly represents the state of the art as at 2010, but this area of oceanography is relatively immature. It is likely that the accuracy of this algorithm will improve as more seawater samples from around the world ocean have their density accurately measured. After such future work is published and the results distilled into a revised algorithm for Absolute Salinity Anomaly, such an algorithm will be served from www.TEOS-10.org. Oceanographers should publish the version number of this software that is used to obtain thermodynamic properties in their manuscripts.

Because Absolute Salinity is the appropriate salinity variable for use with the equation of state, Absolute Salinity is the salinity variable that should be published in oceanographic journals. The version number of the software that is 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.
When this is done, it should be clearly stated that the salinity variable that is being graphed is Reference Salinity, not Absolute Salinity.

The treatment of salinity in ocean models is discussed in appendix A.20. The recommended approach is to carry both Preformed Salinity $S_a$ and Absolute Salinity Anomaly $\delta S_a$ as model variables so that Density Salinity can be calculated at each time step of the model and used to accurately evaluate density.

Potential temperature has been used in oceanography as though it is a conservative variable, and yet the specific heat of seawater varies by 5% at the sea surface, and potential temperature suffers from about the same amount of non-conservative production in the ocean as does entropy. The First Law of Thermodynamics can be very accurately regarded as the statement that potential enthalpy is a conservative variable in the ocean. This, together with the knowledge that the air-sea heat flux is exactly the air-sea flux of potential enthalpy (i.e. the air-sea flux of $c_p^\Theta$) means that potential enthalpy can be treated as the “heat content” of seawater and fluxes of potential enthalpy in the ocean can be treated as “heat fluxes”. Just as it is perfectly valid to talk of the flux of salinity anomaly, $(S_a - \text{constant})$, across an ocean section even when the mass flux across the section is non-zero, so it is perfectly valid to treat the flux of $c_p^\Theta$ across an ocean section as the “heat flux” across the section even when the fluxes of mass and of salt across the section are non-zero.

The temperature variable in ocean models is commonly regarded as being potential temperature, but since the non-conservative source terms that are present in the evolution equation for potential temperature are not included in models, it is apparent that the interior of ocean models already treat the prognostic temperature variable as Conservative Temperature $\Theta$. To complete the transition to $\Theta$ in ocean modeling, models should be initialized with $\Theta$ rather than $\theta$, the output temperature must be compared to observed $\Theta$ data rather than to $\theta$ data, and during the model run, any air-sea fluxes that depend on the sea-surface temperature (SST) must be calculated at each model time step using $\Theta = \hat{\theta}(S_a, \Theta)$. The final ingredient needed for an ocean model is a computationally efficient form of density in terms of Conservative Temperature, that is $\rho = \hat{\rho}(S_a, \Theta, \rho)$, such as that described in appendix A.30 and appendix K of this TEOS-10 Manual.

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]. The reader is also referred to the TEOS-10 User’s Guide [IOC, SCOR and IAPSO, 2010: User’s guide to the international thermodynamic equation of seawater – 2010. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56 (abridged edition), UNESCO], which is a succinct summary of the salient features of TEOS-10 and the associated computer software.
APPENDIX A:
Background and theory underlying
the use of the Gibbs function of seawater

A.1 ITS-90 temperature

In order to understand the limitations of conversion between different temperature scales, it is helpful to review the definitions of temperature and of the international scales on which it is reported.

A.1.1 Definition

When considering temperature, the fundamental physical quantity is thermodynamic temperature, symbol \( T \). The unit for temperature is the kelvin. The name of the unit has a lowercase \( k \). The symbol for the unit is uppercase \( K \). One kelvin is \( 1/273.16 \) of the thermodynamic temperature of the triple point of water. (A recent evolution of the definition has been to specify the isotopic composition of the water to be used as that of Vienna Standard Mean Ocean Water, VSMOW.) The Celsius temperature, symbol \( t \), is defined by \( t^\circ C = T/K − 273.15 \), and \( 1 \circ C \) is the same size as \( 1 \mathrm{K} \).

A.1.2 ITS-90 temperature scale

The definition of temperature scales is the responsibility of the Consultative Committee for Thermometry (CCT) which reports to the International Committee for Weights and Measures (often referred to as CIPM for its name in the French language). Over the last 40 years, two temperature scales have been used; the International Practical Temperature Scale 1968 (IPTS-68), followed by the International Temperature Scale 1990 (ITS-90). These are defined by Barber (1969) and Preston-Thomas (1990). For information about the International Temperature Scales of 1948 and 1927 the reader is referred to Preston-Thomas (1990).

In the oceanographic range, temperatures are determined using a platinum resistance thermometer. The temperature scales are defined as functions of the ratio \( W \), namely the ratio of the thermometer resistance at the temperature to be measured \( R(t) \) to the resistance at a reference temperature \( R_0 \). In IPTS-68, \( R_0 \) is \( R(0^\circ C) \), while in ITS-90 \( R_0 \) is \( R(0.01^\circ C) \). The details of these temperature scales and the differences between the two scales are therefore defined by the functions of \( W \) used to calculate \( T \). For ITS-90, and in the range \( 0^\circ C < t_90 < 968.71^\circ C \), \( t_90 \) is described by a polynomial with 10 coefficients given by Table 4 of Preston-Thomas (1990).

We note in passing that the conversions from \( W \) to \( T \) and from \( T \) to \( W \) are both defined by polynomials and these are not perfect inverses of one another. Preston-Thomas points out that the inverses are equivalent to within 0.13mK. In fact the inverses have a difference of 0.13 mK at 861°C, and a maximum error in the range \( 0^\circ C < t_90 < 40^\circ C \) of 0.06 mK at 31°C. That the CCT allowed this discrepancy between the two polynomials immediately provides an indication of the absolute uncertainty in the determination, and indeed in the definition, of temperature.
A second uncertainty in the absolute realization of ITS-90 arises from what is referred to as sub-range inconsistency. The polynomial referred to above describes the behaviour of an ‘ideal’ thermometer. Any practical thermometer has small deviations from this ideal behaviour. ITS-90 allows the deviations to be determined by measuring the resistance of the thermometer at up to five fixed points: the triple point of water (the freezing points of tin, zinc, aluminium and silver, covering the range 0.01 °C < \( t_{90} < 961.78 \) °C). If not all of these points are measured, then it is permissible to estimate the deviation from as many of those points as are measured. The melting point of Gallium (\( t_{90} = 29.7646 \) °C) and the triple point of Mercury (\( t_{90} = -38.8344 \) °C) may also be used if the thermometer is to operate over a smaller temperature range. Hence the manner in which the thermometer may be used to interpolate between the points is not unique. Rather it depends on which fixed points are measured, and there are several possible outcomes, all equally valid within the definition. Sections 3.3.2 and 3.3.3 of Preston-Thomas (1990) give precise details of the formulation of the deviation function. The difference between the deviation functions derived from different sets of fixed points will depend on the thermometer, so it not possible to state an upper bound on this non-uniqueness. Common practice in oceanographic standards laboratories is to estimate the deviation function from measurements at the triple point of water and the melting point of Gallium (\( t_{90} = 29.7646 \) °C). This allows a linear deviation function to be determined, but no higher order terms.

In summary, there is non-uniqueness in the definition of ITS-90, in addition to any imperfections of measurement by any practical thermometer (Rudtsch and Fischer (2008), Feistel et al. (2008a)). It is therefore not possible to seek a unique and perfect conversion between IPTS-68 and ITS-90.

Goldberg and Weir (1992) and Mares and Kalova (2008) have discussed the procedures needed to convert measured thermophysical quantities (such as specific heat) from one temperature definition to another. When mechanical or electrical energy is used in a laboratory to heat a certain sample, this energy can be measured in electrical or mechanical units by appropriate instruments such as an ampere meter, independent of any definition of a temperature scale. It is obvious from the fundamental thermodynamic relation (at constant Absolute Salinity), \( du = T \, d\eta + P \, dv \), that the same energy difference \( T \, d\eta \) results in different values for the entropy \( \eta \), depending on the number read for \( T \) from a thermometer calibrated on the 1990 compared with one calibrated on the 1968 scale. A similar dependence is found for numbers derived from entropy, for example, for the heat capacity,

\[
c_p = T \, \eta |_{S_A,P}.
\]

Douglas (1969) listed a systematic consideration of the quantitative relations between the measured values of various thermal properties and the particular temperature scale used in the laboratory at the time the measurement was conducted. Conversion formulas to ITS-90 of readings on obsolete scales are provided by Goldberg and Weir (1992) and Weir and Goldberg (1996).

Any thermal experimental data that entered the construction of the thermodynamic potentials that form TEOS-10 were carefully converted by these rules, in addition to the conversion between the various older definitions of for example calories and joules. This must be borne in mind when properties computed from TEOS-10 are combined with historical measurements from the literature.
A.1.3 Theoretical conversion between IPTS-68 and ITS-90

Having understood that the conversion between IPTS-68 and ITS-90 is not uniquely defined, we review the sources of uncertainty, or even flexibility, in the conversion between \( t_{90} \) and \( t_{68} \).

Consider first why \( t_{90} \) and \( t_{68} \) temperatures differ:

1) The fixed points have new temperature definitions in ITS-90, due to improvements in determining the absolute thermodynamic temperatures of the melting/freezing physical states relative to the triple point of water.

2) For some given resistance ratio \( W \) the two scales have different algorithms for interpolating between the fixed points.

Now consider why there is non-uniqueness in the conversion:

3) In some range of ITS-90, the conversion of \( W \) to \( t_{90} \) can be undertaken with a choice of coefficients that is made by the user (Preston-Thomas (1990) Sections 3.3.2.1 to 3.3.3), referred to as sub-range inconsistency.

4) The impact of the ITS-90 deviation function on the conversion is non-linear. Therefore the size of the coefficients in the deviation function will affect the difference, \( t_{90} - t_{68} \). The formal conversion is different for each actual thermometer that has been used to acquire data.

The group responsible for developing ITS-90 was well aware of the non-uniqueness of the conversion. Table 6 of Preston-Thomas (1990) gives differences \( (t_{90} - t_{68}) \) with a resolution of 1 mK, because

(a) the true thermodynamic temperature \( T \) was known to have uncertainties of order 1 mK or larger in some ranges,

(b) the sub-range inconsistency of ITS-90 using the same calibration data gave an uncertainty of several tenths of 1 mK.

Therefore to attempt to define a generic conversion of \( (t_{90} - t_{68}) \) with a resolution of say 0.1 mK would probably be meaningless and possibly misleading as there isn’t a unique generic conversion function.

A.1.4 Practical conversion between IPTS-68 and ITS-90

Rusby (1991) published an 8th order polynomial that was a fit to Table 6 of Preston-Thomas (1990). This fit is valid in the range 73.15 K to 903.89 K (−200 °C to 630.74 °C). He reports that the polynomial fits the table to within 1 mK, commensurate with the non-uniqueness of IPTS-68.

Rusby’s 8th order polynomial is in effect the ‘official recommended’ conversion between IPTS-68 and ITS-90. This polynomial has been used to convert historical IPTS-68 data to ITS-90 for the preparation of the new thermodynamic properties of seawater that are the main subject of this manual.

As a convenient conversion valid in a narrower temperature range, Rusby (1991) also proposed

\[
(T_{90} - T_{68})/K = -0.00025(T_{68} / K - 273.15)
\]

(A.1.1)
in the range 260 K to 400 K (−13 °C to 127 °C). Rusby (1991) also explicitly reminds readers (see his page 1158) that compound quantities that involve temperature intervals such as heat capacity and thermal conductivity are affected by their dependence on the derivative \( d(T_{90} - T_{68})/dT_{68} \). About the same time that Rusby published his conversion from \( t_{68} \) to \( t_{90} \), Saunders (1990) made a recommendation to oceanographers that in the common oceanographic temperature range −2 °C < \( t_{68} \) < 40 °C, conversion could be achieved using

\[
(t_{90}/°C) = (t_{68}/°C)/1.00024.
\]

(A.1.2)
The difference between Saunders (1990) and Rusby (1991) arises from the best slope being 1.00024 near 0 °C and 1.00026 near 100 °C (recall that \( t_{08} \) for the boiling point of water was 100 °C while its \( t_{09} \) is 99.974 °C). Thus Rusby (1991) chose 1.00025 over the wider range of 0 °C to 100 °C.

In considering what is a ‘reasonable’ conversion between the two temperature scales, we must recall that the uncertainty in conversion between measured resistance and either temperature scale is of order a few tenths of mK, and the uncertainty in the absolute thermodynamic temperature \( T \) is probably at least as large, and may be larger than 1 mK in some parts of the oceanographic range. For all practical purposes data converted using Saunders’ 1.00024 cannot be improved upon; conversions using Rusby’s (1991) 8th order fit are fully consistent with Saunders’ 1.00024 in the oceanographic temperature range within the limitations of the temperature scales.

**A.1.5 Recommendation regarding temperature conversion**

The ITS-90 scale was introduced to correct differences between true thermodynamic temperature \( T \), and temperatures reported in IPTS-68.

There are remaining imperfections and residuals in \( T - T_{09} \) (Rusby, pers. comm.), which may be as high as a couple of mK in the region of interest. This is being investigated by the Consultative Committee for Thermometry (CCT). At a meeting in 2000 (Rusby and White (2003)) the CCT considered introducing a new temperature scale to incorporate the known imperfections, referred to at that time as ITS-XX. Further consideration by CCT WG1 has moved thinking away from the desirability of a new scale. The field of thermometry is undergoing rapid advances at present. Instead of a new temperature scale, the known limitations of the ITS-90 can be addressed in large part through the ITS-90 Technical Annex, and documentation from time to time of any known differences between thermodynamic temperature and ITS-90 (Ripple et al. (2008)).

The two main conversions currently in use are Rusby’s 8th order fit valid over a wide range of temperatures, and Saunders’ 1.00024 scaling widely used in the oceanographic community. They are formally indistinguishable because they differ by less than both the uncertainty in thermodynamic temperature, and the uncertainty in the practical application of the IPTS-68 and ITS-90 scales. Nevertheless we note that Rusby (1991) suggests a linear fit with slope 1.00025 in the range -13 °C to 127 °C, and that Saunders’ slope 1.00024 is a better fit in the range -2 °C to 40 °C while Rusby’s 8th order fit is more robust for temperatures outside the oceanographic range. The difference between Saunders (1990) and Rusby (1991) is less than 1 mK everywhere in the range -2 °C to 40 °C and less than 0.03mK in the range -2 °C to 10 °C.

In conclusion, the algorithms for PSS-78 require \( t_{08} \) as the temperature argument. In order to use these algorithms with \( t_{09} \) data, \( t_{08} \) may be calculated using Eqn. (A.1.3) thus

\[
(t_{08}/°C) = 1.00024 (t_{09}/°C). \tag{A.1.3}
\]
A.2 Sea pressure, gauge pressure and absolute pressure

Sea pressure $p$ is defined to be the Absolute Pressure $P$ less the Absolute Pressure of one standard atmosphere, $P_0 = 101\,325\,\text{Pa}$; that is

$$p = P - P_0. \quad \text{(A.2.1)}$$

Also, it is common oceanographic practice to express sea pressure in decibars (dbar). Another common pressure variable that arises naturally in the calibration of sea-board instruments is gauge pressure $p^{\text{gauge}}$ which is Absolute Pressure less the Absolute Pressure of the atmosphere at the time of the instrument’s calibration (perhaps in the laboratory, or perhaps at sea). Because atmospheric pressure changes in space and time, sea pressure $p$ is preferred as a thermodynamic variable as it is unambiguously related to Absolute Pressure. The seawater Gibbs function is naturally a function of sea pressure $p$ (or functionally equivalently, of Absolute Pressure $P$); it is not a function of gauge pressure.

Table A.2.1 Pressure unit conversion table

<table>
<thead>
<tr>
<th></th>
<th>Pascal (Pa)</th>
<th>decibar</th>
<th>bar (bar)</th>
<th>Technical atmosphere (at)</th>
<th>atmosphere (atm)</th>
<th>torr (Torr)</th>
<th>pound-force per square inch (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pa</td>
<td>= 1 N/m²</td>
<td>$10^{-4}$</td>
<td>$10^{-5}$</td>
<td>$10.197 \times 10^{-6}$</td>
<td>$9.8692 \times 10^{-6}$</td>
<td>$7.5006 \times 10^{-3}$</td>
<td>$145.04 \times 10^{-6}$</td>
</tr>
<tr>
<td>1 dbar</td>
<td>$10^4$</td>
<td>$10^5$ dyn/cm²</td>
<td>0.1</td>
<td>0.10197</td>
<td>0.98692</td>
<td>75.006</td>
<td>1.45037744</td>
</tr>
<tr>
<td>1 bar</td>
<td>100 000</td>
<td>10</td>
<td>$10^6$ dyn/cm²</td>
<td>1.0197</td>
<td>0.98632</td>
<td>750.06</td>
<td>14.5037744</td>
</tr>
<tr>
<td>1 at</td>
<td>98 066.5</td>
<td>9.80665</td>
<td>0.980665</td>
<td>$1 \text{ kgf/cm}^2$</td>
<td>0.967841</td>
<td>735.56</td>
<td>14.223</td>
</tr>
<tr>
<td>1 atm</td>
<td>101 325</td>
<td>10.1325</td>
<td>1.01325</td>
<td>$1 \text{ atm}$</td>
<td>1.0332</td>
<td>760</td>
<td>14.696</td>
</tr>
<tr>
<td>1 torr</td>
<td>133.322</td>
<td>$1.3332 \times 10^{-3}$</td>
<td>$1.3332 \times 10^{-3}$</td>
<td>$1.3595 \times 10^{-3}$</td>
<td>$1.3158 \times 10^{-3}$</td>
<td>= 1 Torr</td>
<td>$19.337 \times 10^{-3}$</td>
</tr>
<tr>
<td>1 psi</td>
<td>6 894.757</td>
<td>0.68948</td>
<td>68.948</td>
<td>$70.307 \times 10^{-3}$</td>
<td>$68.046 \times 10^{-3}$</td>
<td>51.715</td>
<td>= 1 lbf/in²</td>
</tr>
</tbody>
</table>

Example: $1\,\text{Pa} = 1\,\text{N/m}^2 = 10^{-4}\,\text{dbar} = 10^{-5}\,\text{bar} = 10.197 \times 10^{-6}\,\text{at} = 9.8692 \times 10^{-6}\,\text{atm}$, etc.

The difference between sea pressure and gauge pressure is quite small and probably insignificant for many oceanographic applications. Nevertheless it would be best practice to ensure that the CTD pressure that is used in the seawater Gibbs function is calibrated on deck to read the atmospheric pressure as read from the ship’s bridge barometer, less the absolute pressure of one standard atmosphere, $P_0 = 101\,325\,\text{Pa}$. (When the CTD is lowered from the sea surface, the monitoring software may well display gauge pressure, indicating the distance from the surface.)

Since there are a variety of different units used to express atmospheric pressure, we present a table (Table A.2.1) to assist in converting between these different units of pressure (see ISO (1993)). Note that one decibar (1 dbar) is exactly 0.1 bar, and that 1 mmHg is very similar to 1 torr with the actual relationship being $1\,\text{mmHg} = 1.000\,000\,142\,466\,321\ldots$ torr. The torr is defined as exactly 1/760 of the Absolute Pressure of one standard atmosphere, so that one torr is exactly equal to $(101\,325/760)\,\text{Pa}$. 

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A.3 Reference Composition and the Reference-Composition Salinity Scale

As mentioned in the main text, the Reference Composition of seawater is defined by Millero et al. (2008a) as the exact mole fractions given in Table D.3 of appendix D below. This composition model was determined from the most accurate measurements available of the properties of Standard Seawater, which is filtered seawater from the surface waters of the North Atlantic as made available by the IAPSO Standard Seawater Service. The Reference Composition is perfectly consistent with charge balance of ocean waters and the most recent atomic weight estimates (Wieser (2006)). For seawater with this reference composition the Reference-Composition Salinity $S_R$ as defined below provides our best estimate of the Absolute Salinity.

The Reference Composition includes all important components of seawater having mass fractions greater than about 0.001 g kg$^{-1}$ (i.e. 1.0 mg kg$^{-1}$) that can significantly affect either the conductivity or the density of seawater having a Practical Salinity of 35. The most significant ions not included are Li$^+$ (~0.18 mg kg$^{-1}$) and Rb$^+$ (~0.12 mg kg$^{-1}$). Dissolved gases N$_2$ (~16 mg kg$^{-1}$) and O$_2$ (up to 8 mg kg$^{-1}$ in the ocean) are not included as neither have a significant effect on density or on conductivity. In addition, N$_2$ remains within a few percent of saturation at the measured temperature in almost all laboratory and in situ conditions. However, the dissolved gas CO$_2$ (~0.7 mg kg$^{-1}$), and the ion OH$^-$ (~0.08 mg kg$^{-1}$) are included in the Reference Composition because of their important role in the equilibrium dynamics of the carbonate system. Changes in pH which involve conversion of CO$_2$ to and from ionic forms affect conductivity and density. Concentrations of the major nutrients Si(OH)$_4$, NO$_3^-$ and PO$_4^{3-}$ are assumed to be negligible in Standard Seawater; their concentrations in the ocean range from 0-16 mg kg$^{-1}$, 0-2 mg kg$^{-1}$, and 0-0.2 mg kg$^{-1}$ respectively. The Reference Composition does not include organic matter. The composition of Dissolved Organic Matter (DOM) is complex and poorly known. DOM is typically present at concentrations of 0.5-2 mg kg$^{-1}$ in the ocean.

Reference-Composition Salinity is defined to be conservative during mixing or evaporation that occurs without removal of sea salt from solution. Because of this property, the Reference-Composition Salinity of any seawater sample can be defined in terms of products determined from the mixture or separation of two precisely defined end members. Pure water and KCl-normalized seawater are defined for this purpose. Pure water is defined as Vienna Standard Mean Ocean Water, VSMOW, which is described in the 2001 Guideline of the International Association for the Properties of Water and Steam (IAPWS (2005), BIPM (2005)); it is taken as the zero reference value. KCl-normalized seawater (or normalized seawater for short) is defined to correspond to a seawater sample with a Practical Salinity of 35. Thus, any seawater sample that has the same electrical conductivity as a solution of potassium chloride (KCl) in pure water with the KCl mass fraction of 32.4356 g kg$^{-1}$ when both are at the ITS-90 temperature $t = 14.996$ °C and one standard atmosphere pressure, $P = 101325$ Pa is referred to as normalized seawater. Here, KCl refers to the normal isotopic abundances of potassium and chlorine as described by the International Union of Pure and Applied Chemistry (Wieser (2006)). As discussed below, any normalized seawater sample has a Reference-Composition Salinity of 35.165 04 g kg$^{-1}$.

Since Reference-Composition Salinity is defined to be conservative during mixing, if a seawater sample of mass $m_1$ and Reference-Composition Salinity $S_{R1}$ is mixed with another seawater sample of mass $m_2$ and Reference-Composition Salinity $S_{R2}$, the final Reference-Composition Salinity $S_{R12}$ of this sample is

$$S_{R12} = \frac{m_1 S_{R1} + m_2 S_{R2}}{m_1 + m_2}. \quad (A.3.1)$$
Negative values of $m_1$ and $m_2$, corresponding to the removal of seawater with the appropriate salinity are permitted, so long as $m_1(1-S_{R1}) + m_2(1-S_{R2}) > 0$. In particular, if $S_{R2} = 0$ (pure water) and $m_2$ is the mass of pure water needed to normalize the seawater sample (that is, $m_2$ is the mass needed to achieve $S_{R1} = 35.165$ g kg$^{-1}$), then the original Reference-Composition Salinity of sample 1 is given by

$$S_{R1} = [1 + (m_2 / m_1)] \times 35.16504 \text{ g kg}^{-1}. \quad (A.3.2)$$

The definitions and procedures above allow one to determine the Reference Salinity of any seawater sample at the ITS-90 temperature $t = 14.996$ °C and one standard atmosphere pressure. To complete the definition, we note that the Reference-Composition Salinity of a seawater sample at given temperature and pressure is equal to the Reference-Composition Salinity of the same sample at any other temperature and pressure provided the transition process is conducted without exchange of matter, in particular, without evaporation, precipitation or degassing of substance from the solution. Note that this property is shared by Practical Salinity to the accuracy of the algorithms used to define this quantity in terms of the conductivity ratio $R_{15}$.

We noted above that a Practical Salinity of 35 is associated with a Reference Salinity of 35.165 04 g kg$^{-1}$. This value was determined by Millero et al. (2008a) using the reference composition model, the most recent atomic weights (Wieser (2006)) and the relation $S = 1.80655 Cl/(g \text{ kg}^{-1})$ which was used in the original definition of Practical Salinity to convert between measured Chlorinity values and Practical Salinity. Since the relation between Practical Salinity and conductivity ratio was defined using the same conservation relation as satisfied by Reference Salinity, the Reference Salinity can be determined to the same accuracy as Practical Salinity wherever the latter is defined (that is, in the range 2 < $S_p$ < 42), as

$$S_R \approx u_{ps} S_p \quad \text{where} \quad u_{ps} = (35.165 04/35) \text{ g kg}^{-1}. \quad (A.3.3)$$

For practical purposes, this relationship can be taken to be an equality since the approximate nature of this relation only reflects the accuracy of the algorithms used in the definition of Practical Salinity. This follows from the fact that the Practical Salinity, like Reference Salinity, is intended to be precisely conservative during mixing and also during changes in temperature and pressure that occur without exchange of mass with the surroundings.

The Reference-Composition Salinity Scale is defined such that a seawater sample whose Practical Salinity $S_p$ is 35 has a Reference-Composition Salinity $S_R$ of precisely 35.165 04 g kg$^{-1}$. Millero et al. (2008a) estimate that the absolute uncertainty associated with using this value as an estimate of the Absolute Salinity of Reference Composition Seawater is ±0.007 g kg$^{-1}$. Thus the numerical difference between the Reference Salinity expressed in g kg$^{-1}$ and Practical Salinity is about 24 times larger than this estimate of uncertainty. The difference is also large compared to our ability to measure Practical Salinity at sea (which can be as precise as ±0.002). Understanding how this discrepancy was introduced requires consideration of some historical details that influenced the definition of Practical Salinity. The details are presented in Millero et al. (2008a) and in Millero (2010) and are briefly reviewed below.

There are two primary sources of error that contribute to this discrepancy. First, and most significant, in the original evaporation technique used by Sørensen in 1900 (Forch et al. 1902) to estimate salinity, some volatile components of the dissolved material were lost so the amount of dissolved material was underestimated. Second, the approximate relation determined by Knudsen (1901) to determine $S(\%o)$ from measurements of $Cl(\%o)$ was based on analysis of only nine samples (one from the Red Sea, one from the North Atlantic, one from the North Sea and six from the Baltic Sea). Both the errors in estimating absolute Salinity by evaporation and the bias towards Baltic Sea conditions, where strong
composition anomalies relative to North Atlantic conditions are found, are reflected in Knudsen’s formula,

\[ S_k(\%) = 0.03 + 1.805 \ C I(\%) \]  \hspace{1cm} (A.3.4)

When the Practical Salinity Scale was decided upon in the late 1970s it was known that this relation included significant errors, but it was decided to maintain numerical consistency with this accepted definition of salinity for typical mid-ocean conditions (Millero (2010)). To achieve this consistency while having salinity directly proportional to Chlorinity, the Joint Panel for Oceanographic Tables and Standards (JPOTS) decided to determine the proportionality constant from Knudsen’s formula at \( S_k = 35 \ \text{‰} \ (CI = 19.3740 \ \text{‰}) \) (Wooster et al., 1969). This resulted in the conversion formula

\[ S(\%) = 1.80655 \ C I(\%) \]  \hspace{1cm} (A.3.5)

being used in the definition of the practical salinity scale as if it were an identity, thus introducing errors that have either been overlooked or accepted for the past 30 years. We now break with this tradition in order to define a salinity scale based on a composition model for Standard Seawater that was designed to give a much improved estimate of the mass-fraction salinity for Standard Seawater and for Reference-Composition Seawater. The introduction of this salinity scale provides a more physically meaningful measure of salinity and simplifies the task of systematically incorporating the influence of spatial variations of seawater composition into the procedure for estimating Absolute Salinity.

Finally, we note that to define the Reference-Composition Salinity Scale we have introduced the quantity \( u_{ps} \) in Eqn. (A.3.3), defined by \( u_{ps} = (35.165 \ 04/35) \ \text{g kg}^{-1} \). This value was determined by the requirement that the Reference-Composition Salinity gives the best estimate of the mass-fraction Absolute Salinity (that is, the mass-fraction of non-\( \text{H}_2\text{O} \) material) of Reference-Composition Seawater. However, the uncertainty in using \( S_k \) to estimate the Absolute Salinity of Reference Composition Seawater is at least 0.007 \( \text{g kg}^{-1} \) at \( S = 35 \) (Millero et al. (2008b)). Thus, although \( u_{ps} \) is precisely specified in the definition of the Reference-Composition Salinity Scale, it must be noted that using the resulting definition of the Reference Salinity to estimate the Absolute Salinity of Reference Composition Seawater does have a non-zero uncertainty associated with it. This and related issues are discussed further in the next subsection.

### A.4 Absolute Salinity

Millero et al. (2008a) list the following six advantages of adopting Reference Salinity \( S_k \) and Absolute Salinity \( S_A \) in preference to Practical Salinity \( S_p \).

1. The definition of Practical Salinity \( S_p \) on the PSS-78 scale is separate from the system of SI units (BIPM (2006)). Reference Salinity can be expressed in the unit (\( \text{g kg}^{-1} \)) as a measure of Absolute Salinity. Adopting Absolute Salinity and Reference Salinity will terminate the ongoing controversies in the oceanographic literature about the use of “PSU” or “PSS” and make research papers more readable to the outside scientific community and consistent with SI.

2. The freshwater mass fraction of seawater is not \((1 - 0.001 \ S_p)\). Rather, it is \((1 - 0.001 \ S_A/(\text{g kg}^{-1}))\), where \( S_A \) is the Absolute Salinity, defined as the mass fraction of dissolved material in seawater. The values of \( S_A/(\text{g kg}^{-1}) \) and \( S_p \) are known to differ by about 0.5%. There seems to be no good reason for continuing to ignore this known difference, for example in ocean models.

3. PSS-78 is limited to the range \( 2 < S_p < 42 \). For a smooth crossover on one side to pure water, and on the other side to concentrated brines up to saturation, as for...
example encountered in sea ice at very low temperatures, salinities beyond these limits need to be defined. While this poses a challenge for \( S_p \), it is trivial for \( S_R \).

4. The theoretical Debye-Hückel limiting laws of seawater behavior at low salinities, used for example in the determination of the Gibbs function of seawater, can only be computed from a chemical composition model, which is available for \( S_R \) but not for \( S_p \).

5. For artificial seawater of Reference Composition, \( S_R \) has a fixed relation to Chlorinity, independent of conductivity, salinity, temperature, or pressure.

6. Stoichiometric anomalies can be specified accurately relative to Reference-Composition Seawater with its known composition, but only uncertainly with respect to IAPSO Standard Seawater with its unknown composition. These variations in the composition of seawater cause significant (a few percent) variations in the horizontal density gradient.

Regarding point number 2, Practical Salinity \( S_p \) is a dimensionless number of the order of 35 in the open ocean; no units or their multiples are permitted. There is however more freedom in choosing the representation of Absolute Salinity \( S_A \) since it is defined as the mass fraction of dissolved material in seawater. For example, all the following quantities are equal (see ISO (1993) and BIPM (2006)),

\[
34 \text{ g/kg} = 34 \text{ mg/g} = 0.034 \text{ kg/kg} = 0.034 = 3.4 \% = 34,000 \text{ ppm} = 34,000 \text{ mg/kg}.
\]

In particular, it is strictly correct to write the freshwater fraction of seawater as either \((1 - 0.001 \ S_A/\text{(g kg}^{-1}\text{)})\) or as \((1 - S_A)\) but it would be incorrect to write it as \((1 - 0.001 \ S_A)\).

Clearly it is essential to consider the units used for Absolute Salinity in any particular application. If this is done, there should be no danger of confusion, but to maintain the numerical value of Absolute Salinity close to that of Practical Salinity \( S_p \) we adopt the first option above, namely \( \text{g kg}^{-1} \) as the preferred unit for \( S_A \) (as in \( S_A = 35.165 \text{ 04 g kg}^{-1} \)).

The Reference Salinity, \( S_R \), is defined to have the same units and follows the same conventions as \( S_A \). Salinity “\( S_{\%} \)” measured prior to PSS-78 available from the literature or from databases is usually reported in \( \% \) or ppt (part per thousand) and is converted to the Reference Salinity, \( S_R = u_{ps} S_{\%} \), by the numerical factor \( u_{ps} \) from (A.3.3).

Regarding point number 5, Chlorinity \( Cl \) is the concentration variable that was used in the laboratory experiments for the fundamental determinations of the equation of state and other properties, but has seldom been measured in the field since the definition of PSS-78 (Millero, 2010). Since the relation \( S = 1.806 \text{ 55 Cl} \) for Standard Seawater was used in the definition of Practical Salinity this may be taken as an exact relation for Standard Seawater and it is also our best estimate for Reference Composition Seawater. Thus, Chlorinity expressed in \( \% \) can be converted to Reference-Composition Salinity by the relation, \( S_R = u_{cl} Cl \), with the numerical factor \( u_{cl} = 1.806 \text{ 55 u_{ps}} \). These constants are recommended for the conversion of historical (pre 1900) data. The primary source of error in using this relation will be the possible presence of composition anomalies in the historical data relative to Standard Seawater.

Regarding point number 6, the composition of dissolved material in seawater is not constant but varies a little from one ocean basin to another, and the variation is even stronger in estuaries, semi-enclosed or even enclosed seas. Brewer and Bradshaw (1975) and Millero (2000) point out that these spatial variations in the relative composition of seawater impact the relationship between Practical Salinity (which is essentially a measure of the conductivity of seawater at a fixed temperature and pressure) and density. All the thermophysical properties of seawater as well as other multicomponent electrolyte solutions are directly related to the concentrations of the major components, not the salinity determined by conductivity; note that some of the variable nonelectrolytes (e.g.,
Si(OH)$_4$, CO$_2$ and dissolved organic material) do not have an appreciable conductivity signal. It is for this reason that the new TEOS-10 thermodynamic description of seawater (Millero et al. (2008a), Millero (2010)) has the Gibbs function $g$ of seawater expressed as a function of Absolute Salinity as $g(S_A,t,p)$ rather than as a function of Practical Salinity $S_p$ or of Reference Salinity, $S_R$. The issue of the spatial variation in the composition of seawater is discussed more fully in appendix A.5.

Regarding point number 2, we note that it is perhaps debatable which of $(1 - 0.001\; S_A^{\text{dm}}/(\text{g kg}^{-1}))$, $(1 - 0.001\; S_A^{\text{en}}/(\text{g kg}^{-1}))$, $(1 - 0.001\; S_A^{\text{dd}}/(\text{g kg}^{-1}))$ or $(1 - 0.001\; S_A/(\text{g kg}^{-1}))$ is the most appropriate measure of the freshwater mass fraction. (These different versions of absolute salinity are defined in section 2.5 and also later in this appendix.) This is a minor point compared with the present use of $S_p$ in this context, and the choice of which of these expressions may depend on the use for the freshwater mass fraction. For example, in the context of ocean modelling, if $S_p$ is the salinity variable that is treated as a conservative variable in an ocean model, then $(1 - 0.001\; S_p/(\text{g kg}^{-1}))$ is probably the most appropriate version of freshwater mass fraction.

It should be noted that the quantity $S_A$ appearing as an argument of the function $g(S_A,t,p)$ is the Absolute Salinity (the “Density Salinity” $S_A = S_A^{\text{dm}}$) measured on the Reference-Composition Salinity Scale. This is important since the Gibbs function has been fitted to laboratory and field measurements with the Absolute Salinity values expressed on this scale. Thus, for example, it is possible that sometime in the future it will be determined that an improved estimate of the mass fraction of dissolved material in Standard Seawater can be obtained by multiplying $S_R$ by a factor slightly different from 1 (uncertainties permit values in the range 1 ± 0.002). We emphasize that since the Gibbs function is expressed in terms of the Absolute Salinity expressed on the Reference-Composition Salinity Scale, use of any other scale (even one that gives more accurate estimates of the true mass fraction of dissolved substances in Standard Seawater) will reduce the accuracy of the thermodynamic properties determined from the Gibbs function. In part for this reason, we recommend that the Reference-Composition Salinity continue to be measured on the scale defined by Millero et al. (2008a) even if new results indicate that improved estimates of the true mass fraction can be obtained using a modified scale. That is, we recommend that the value of $u_{\text{PS}}$ used in (A.3.3) not be updated. If a more accurate mass fraction estimate is required for some purpose in the future, such a revised estimate should definitely not be used as an argument of the TEOS-10 Gibbs function.

Finally, we note a second reason for recommending that the value assigned to $u_{\text{PS}}$ not be modified without very careful consideration. Working Group 127 is recommending that the practice of expressing salinity as Practical Salinity in publications be phased out in favour of using Absolute Salinity for this purpose. It is critically important that this new measure of salinity remain stable into the future. In particular, we note that any change in the value of $u_{\text{PS}}$ used in the determination of Reference Salinity would result in a change in reported salinity values that would be unrelated to any real physical change. For example, a change in $u_{\text{PS}}$ from 35.16504/35 to (35.16504/35) x 1.001 for example, would result in changes of the reported salinity values of order 0.035 g kg$^{-1}$ which is more than ten times larger than the precision of modern salinometers. Thus changes associated with a series of improved estimates of $u_{\text{PS}}$ (as a measure of the mass fraction of dissolved salts in Standard Seawater) could cause very serious confusion for researchers who monitor salinity as an indicator of climate change. Based on this concern and the fact that the Gibbs function is expressed as a function of Absolute Salinity measured on the Reference-Composition Salinity Scale as defined by Millero et al. (2008a), we strongly recommend that the Reference-Composition Salinity continue to be expressed on this scale; no changes in the value of $u_{\text{PS}}$ should be introduced.
For seawater of Reference Composition, Reference Salinity $S_R$ is the best available estimate of the mass-fraction of non-H$_2$O material in seawater. As discussed in sections 2.4 and 2.5, under TEOS-10 $S_R$ was determined to provide the best available estimate of the mass-fraction of non-H$_2$O material in Standard Seawater by Millero et al. (2008a). Subsequently, Pawlowicz (2010) has argued that the DIC content of the Reference Composition is probably about 117 $\mu$mol kg$^{-1}$ low for SSW and also for the North Atlantic surface water from which it was prepared. This difference in DIC causes a negligible effect on both conductivity and density, and hence on Reference Salinity and Density Salinity. The influence on Solution Salinity is nearly a factor of 10 larger (Pawlowicz et al., 2010) but at 0.0055 g kg$^{-1}$ it is still just below the uncertainty of 0.007 g kg$^{-1}$ assigned to the estimated Absolute Salinity by Millero et al. (2008a). In fact, the largest uncertainties in Reference Salinity as a measure of the Absolute Salinity of SSW are associated with uncertainties in the mass fractions of other constituents such as sulphate, which may be as large as 0.05 g kg$^{-1}$ (Seitz et al., 2010a). Nevertheless, it seems that the sulphate value of Reference-Composition Seawater lies within the 95% uncertainty range of the best laboratory-determined estimates of SSW’s sulphate concentration, so there is no justification for an update of the Reference Composition at this time.

When the composition of seawater differs from that of Standard Seawater, there are several possible definitions of the absolute salinity of a seawater sample, as discussed in section 2.5. Conceptually the simplest definition is “the mass fraction of dissolved non-H$_2$O material in a seawater sample at its temperature and pressure”. One drawback of this definition is that because the equilibrium conditions between H$_2$O and several carbon compounds depends on temperature and pressure, this mass-fraction would change as the temperature and pressure of the sample is changed, even without the addition or loss of any material from the sample. This drawback can be overcome by first bringing the sample to the constant temperature $t = 25^\circ$C and the fixed sea pressure 0 dbar, and when this is done, the resulting mass-fraction of non-H$_2$O material is called “Solution Absolute Salinity” (usually shortened to “Solution Salinity”), $S_{\text{soln}}^A$. Another measure of absolute salinity is the “Added-Mass Salinity” $S_{\text{add}}^A$ which is $S_R$ plus the mass fraction of material that must be added to Standard Seawater to arrive at the concentrations of all the species in the given seawater sample, after chemical equilibrium has been reached, and after the sample has been brought to $t = 25^\circ$C and $p = 0$ dbar.

Another form of absolute salinity, “Preformed Absolute Salinity” (usually shortened to “Preformed Salinity”), $S_P$ has been defined by Pawlowicz et al. (2010) and Wright et al. (2010b). Preformed Salinity $S_P$ is designed to be as close as possible to being a conservative variable. That is, $S_P$ is designed to be insensitive to biogeochemical processes that affect the other types of salinity to varying degrees. $S_P$ is formed by first estimating the contribution of biogeochemical processes to one of the salinity measures $S_A$, $S_{\text{soln}}^A$, or $S_{\text{add}}^A$, and then subtracting this contribution from the appropriate salinity variable. Because it is designed to be a conservative oceanographic variable, $S_P$ will find a prominent role in ocean modeling.

There is still no simple means to measure either $S_{\text{soln}}^A$ or $S_{\text{add}}^A$ for the general case of the arbitrary addition of many components to Standard Seawater. Hence a more precise and easily determined measure of the amount of dissolved material in seawater is required and TEOS-10 adopts “Density Salinity” $S_{\text{dens}}^A$ for this purpose. “Density Salinity” $S_{\text{dens}}^A$ is defined as the value of the salinity argument of the TEOS-10 expression for density which gives the sample’s actual measured density at the temperature $t = 25^\circ$C and at the sea pressure $p = 0$ dbar. When there is no risk of confusion, “Density Salinity” is also called Absolute Salinity with the label $S_A$, that is $S_A = S_{\text{dens}}^A$. There are two clear advantages of $S_A = S_{\text{dens}}^A$ over both $S_{\text{soln}}^A$ and $S_{\text{add}}^A$. First, it is possible to measure the density of a seawater sample very accurately and in an SI-traceable manner, and second, the use of
$S_A = S_A^{\text{dens}}$ yields the best available estimates of the density of seawater. This is important because in the field of physical oceanography, it is density that needs to be known to the highest relative accuracy.

Pawlowicz et al. (2010) and Wright et al. (2010b) found that while the nature of the ocean’s composition variations changes from one ocean basin to another, the five different salinity measures $S_R$, $S_A^{\text{dens}}$, $S_A^{\text{soln}}$, $S_A^{\text{add}}$ and $S_s$ are approximately related by the following simple linear relationships, (obtained by combining equations (55) – (57) and (62) of Pawlowicz et al. (2010))

$$S_s - S_R \approx -0.35 \delta S_R^{\text{dens}}, \quad (A.4.1)$$

$$S_A^{\text{dens}} - S_R \approx 1.0 \delta S_R^{\text{dens}}, \quad (A.4.2)$$

$$S_A^{\text{soln}} - S_R \approx 1.75 \delta S_R^{\text{dens}}, \quad (A.4.3)$$

$$S_A^{\text{add}} - S_R \approx 0.78 \delta S_R^{\text{dens}}. \quad (A.4.4)$$

Eqn. (A.4.2) is simply the definition of the Absolute Salinity Anomaly, $\delta S_A = \delta S_R^{\text{dens}} = S_A^{\text{dens}} - S_R$. Note that in many TEOS-10 publications, the simpler notation $\delta S_A$ is used for $\delta S_R^{\text{dens}} = S_A^{\text{dens}} - S_R$, a salinity difference for which a global atlas is available (McDougall et al. (2010a)). In the context of ocean modelling, it is more convenient to cast these salinity differences with respect to the Preformed Salinity $S_s$ as follows (using the above equations)

$$S_R - S_s \approx 0.35 \delta S_R^{\text{dens}}, \quad (A.4.5)$$

$$S_A^{\text{dens}} - S_s \approx 1.35 \delta S_R^{\text{dens}}, \quad (A.4.6)$$

$$S_A^{\text{soln}} - S_s \approx 2.1 \delta S_R^{\text{dens}}, \quad (A.4.7)$$

$$S_A^{\text{add}} - S_s \approx 1.13 \delta S_R^{\text{dens}}. \quad (A.4.8)$$

These relationships are illustrated on the number line of salinity in Figure A.4.1. For SSW, all five salinity variables $S_R$, $S_A^{\text{dens}}$, $S_A^{\text{soln}}$, $S_A^{\text{add}}$ and $S_s$ are equal. It should be noted that the simple relationships of Eqns. (A.4.1) – (A.4.8) are derived from simple linear fits to model calculations that show more complex variations. However, the variation about these relationships is not larger than the typical uncertainty of ocean measurements. These linear relationships provide a way by which the effects of anomalous seawater composition may be addressed in ocean models (see appendix A.20).

**Figure A.4.1.** Number line of salinity, illustrating the differences between various forms of salinity for seawater whose composition differs from that of Standard Seawater.

If measurements are available of the Total Alkalinity, Dissolved Inorganic Carbon, and the nitrate and silicate concentrations, but not of density anomalies, then alternative formulae are available for the four salinity differences that appear on the left-hand sides of
Eqns. (A.4.1) – (A.4.8). Pawlowicz et al. (2010) have used a chemical model of conductivity and density to estimate how the many salinity differences introduced above depend on the measured properties of seawater. The following equations correspond to Eqns. (A.4.1) – (A.4.4) above, and come from equations (51) – (54) and (59) of Pawlowicz et al. (2010). These equations are written in terms of the values of the nitrate and silicate concentrations in the seawater sample (measured in mol kg$^{-1}$), the difference between the Total Alkalinity (TA) and Dissolved Inorganic Carbon (DIC) of the sample and the corresponding values of our best estimates of TA and DIC in Standard Seawater, $\Delta$TA and $\Delta$DIC, both measured in mol kg$^{-1}$. For Standard Seawater our best estimates of TA and DIC are 0.0023 ($S_T/35$) mol kg$^{-1}$ and 0.00208 ($S_T/35$) mol kg$^{-1}$ respectively (see Pawlowicz (2010), Pawlowicz et al. (2010) and the discussion of this aspect of SSW versus RCSW in Wright et al. (2010b)).

\[
(S_R - S_S)/(g \text{ kg}^{-1}) = \left(-18.1 \Delta \text{TA} - 7.1 \Delta \text{DIC} - 43.0 \text{NO}_3^- + 0.1 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}), \quad \text{(A.4.9)}
\]

\[
(S_A^{\text{dens}} - S_S)/(g \text{ kg}^{-1}) = \left(55.6 \Delta \text{TA} + 4.7 \Delta \text{DIC} + 38.9 \text{NO}_3^- + 50.7 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}), \quad \text{(A.4.10)}
\]

\[
(S_A^{\text{soln}} - S_S)/(g \text{ kg}^{-1}) = \left(7.2 \Delta \text{TA} + 47.0 \Delta \text{DIC} + 36.5 \text{NO}_3^- + 96.0 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}), \quad \text{(A.4.11)}
\]

\[
(S_A^{\text{add}} - S_S)/(g \text{ kg}^{-1}) = \left(25.9 \Delta \text{TA} + 4.9 \Delta \text{DIC} + 16.1 \text{NO}_3^- + 60.2 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}). \quad \text{(A.4.12)}
\]

The standard error of the model fits in Eqns. (A.4.9) – (A.4.11) are given by Pawlowicz et al. (2010) at less than $10^{-6}$ kg m$^{-3}$ (in terms of density) which is equivalent to a factor of 20 smaller than the accuracy to which Practical Salinity can be measured at sea. It is clear that if measurements of TA, DIC, nitrate and silicate are available (and recognizing that these measurements will come with their own error bars), these expressions will likely give more accurate estimates of the salinity differences than the approximate linear expressions presented in Eqns. (A.4.1) – (A.4.8). The coefficients in Eqn. (A.4.10) are reasonably similar to the corresponding expression of Brewer and Bradshaw (1975) (as corrected by Millero et al. (1976a)):- when expressed as the salinity anomaly $S_A^{\text{dens}} - S_R$ rather than as the corresponding density anomaly $\rho - \rho_R$, their expression corresponding to Eqn. (A.4.10) had the coefficients 71.4, -12.8, 31.9 and 59.9 compared with the coefficients 55.6, 4.7, 38.9 and 50.7 respectively in Eqn. (A.4.10).

The salinity differences expressed with respect to Preformed Salinity $S_S$ which correspond to Eqns. (A.4.5) – (A.4.8) can be found by linear combinations of Eqns. (A.4.9) – (A.4.12) as follows

\[
(S_S - S_A)/(g \text{ kg}^{-1}) = \left(18.1 \Delta \text{TA} + 7.1 \Delta \text{DIC} + 43.0 \text{NO}_3^- - 0.1 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}), \quad \text{(A.4.13)}
\]

\[
(S_A^{\text{dens}} - S_S)/(g \text{ kg}^{-1}) = \left(73.7 \Delta \text{TA} + 11.8 \Delta \text{DIC} + 81.9 \text{NO}_3^- + 50.6 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}), \quad \text{(A.4.14)}
\]

\[
(S_A^{\text{soln}} - S_S)/(g \text{ kg}^{-1}) = \left(25.3 \Delta \text{TA} + 54.1 \Delta \text{DIC} + 79.5 \text{NO}_3^- + 95.9 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}), \quad \text{(A.4.15)}
\]

\[
(S_A^{\text{add}} - S_S)/(g \text{ kg}^{-1}) = \left(44.0 \Delta \text{TA} + 12.0 \Delta \text{DIC} + 59.1 \text{NO}_3^- + 60.1 \text{Si(OH)}_4\right)/(\text{mol kg}^{-1}). \quad \text{(A.4.16)}
\]
A.5 Spatial variations in seawater composition

When the oceanographic data needed to evaluate Eqn. (A.4.10) for $S^\text{dens}_{A} - S_R$ is not available, the look-up table method of McDougall et al. (2010a) is recommended to evaluate $\delta S_A = \delta S^\text{dens}_R = S^\text{dens}_{A} - S_R$. The following paragraphs describe how this method was developed.

In a series of papers Millero et al. (1976a, 1978, 2000, 2008b) and McDougall et al. (2010a) have reported on density measurements made in the laboratory on samples collected from around the world’s oceans. Each sample has had its Practical Salinity measured in the laboratory as well as its density (measured with a vibrating tube densimeter at 25 °C and atmospheric pressure). The Practical Salinity yields a Reference Salinity $S_R$ according to Eqn. (A.3.3), while the density measurement $\rho^\text{meas}$ implies an Absolute Salinity $S_A = S^\text{dens}_{A}$ by using the equation of state and the equality $\rho^\text{meas} = \rho(S^\text{dens}_{A}, 25 \, ^\circ\text{C}, 0\text{dbar})$. The difference $S^\text{dens}_{A} - S_R$ between these two salinity measures is taken to be due to the composition of the sample being different to that of Standard Seawater. In these papers Millero established that the salinity difference $S_A - S_R$ could be estimated approximately from knowledge of just the silicate concentration of the fluid sample. The reason for the explaining power of silicate alone is thought to be that (a) it is itself substantially correlated with other relevant variables (e.g. total alkalinity, nitrate concentration, DIC [often called total carbon dioxide]), (b) it accounts for a substantial fraction (about 0.6) of the typical variations in concentrations (g kg$^{-1}$) of the above species and (c) being essentially non-ionic; its presence has little effect on conductivity while having a direct effect on density.

When the existing data on $\delta S_A$, based on laboratory measurements of density, was regressed against the silicate concentration of the seawater samples, McDougall et al. (2010a) found the simple relation

$$\delta S_A / (\text{g kg}^{-1}) = (S_A - S_R) / (\text{g kg}^{-1}) = 98.24 \left( \text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right) \quad \text{Global (A.5.1)}$$

This regression was done over all available density measurements from the world ocean, and the standard error in the fit was 0.0054 g kg$^{-1}$.

The dependence of $\delta S_A$ on silicate concentration is observed to be different in each ocean basin, and this aspect was exploited by McDougall et al. (2010a) to obtain a more accurate dependence of $\delta S_A$ on location in space. For data in the Southern Ocean south of 30°S the best simple fit was found to be

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 \left( \text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Southern Ocean (A.5.2)}$$

and the associated standard error is 0.0026 g kg$^{-1}$.

The data north of 30°S in each of the Pacific, Indian and Atlantic Oceans was treated separately. In each of these three regions the fit was constrained to match (A.5.2) at 30°S and the slope of the fit was allowed to vary linearly with latitude. The resulting fits were (for latitudes north of 30°S, that is for $\lambda \geq -30^\circ$)

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 \left[ 1 + 0.3622 \left( \lambda / 30^\circ + 1 \right) \right] \left( \text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Pacific (A.5.3)}$$

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 \left[ 1 + 0.3861 \left( \lambda / 30^\circ + 1 \right) \right] \left( \text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Indian (A.5.4)}$$

$$\delta S_A / (\text{g kg}^{-1}) = 74.884 \left[ 1 + 1.0028 \left( \lambda / 30^\circ + 1 \right) \right] \left( \text{Si(OH)}_4 / (\text{mol kg}^{-1}) \right), \quad \text{Atlantic (A.5.5)}$$

These relationships between the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ and silicate concentration have been used by McDougall, Jackett and Millero (2010a) in a computer algorithm that uses an existing global data base of silicate (Gouretski and Koltermann (2004)) and provides an estimate of Absolute Salinity when given a seawater sample's
Practical Salinity as well as its spatial location in the world ocean. This computer algorithm accounts for the latest understanding of Absolute Salinity in the Baltic Sea, but it is silent on the influence of compositional variations in other marginal seas. The Absolute Salinity Anomaly in the Baltic Sea has been quite variable over the past few decades of observation (Feistel et al. (2010c)). The computer algorithm of McDougall et al. (2010a) uses the relationship found by Feistel et al. (2010c) that applies in the years 2006-2009, namely

\[ \delta S_A = S_A - S_R = 0.087 \, \text{g kg}^{-1} \times (1 - S_R / S_{SO}), \]  

(A.5.6)

where \( S_{SO} = 35.165 \, \text{g kg}^{-1} \) is the standard-ocean Reference Salinity that corresponds to the Practical Salinity of 35.

In order to gauge the importance of the spatial variation of seawater composition, the northward gradient of density at constant pressure is shown in Fig. A.5.1 for the data in a world ocean hydrographic atlas deeper than 1000m. The vertical axis in this figure is the magnitude of the difference between the northward density gradient at constant pressure when the TEOS-10 algorithm for density is called with \( S_A = S_{A}^{\text{dens}} \) (as it should be) compared with calling the same TEOS-10 density algorithm with \( S_{R} \) as the salinity argument. Figure A.5.1 shows that the “thermal wind” is misestimated by more than 2% for 58% of the data in the world ocean below a depth of 1000m if the effects of the variable seawater composition are ignored.

![Figure A.5.1](image)

**Figure A.5.1.** The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for \( p > 1000 \, \text{dbar} \). The vertical axis is the magnitude of the difference between evaluating the density gradient using \( S_A \) versus \( S_{R} \) as the salinity argument in the TEOS-10 expression for density.

The importance of the spatial variations in seawater composition illustrated in Fig. A.5.1 can be compared with the corresponding improvement achieved by the TEOS-10 Gibbs function for Standard Seawater compared with using EOS-80. This is done by ignoring spatial variations in seawater composition in both the evaluation of TEOS-10 and in EOS80 by calling TEOS-10 with \( S_{R} \) and EOS-80 with \( S_{P} \). Figure A.5.2 shows the magnitude of the improvement in the “thermal wind” in the part of the ocean that is deeper than 1000m through the adoption of TEOS-10 but ignoring the influence of
compositional variations. By comparing Figs. A.5.1 and A.5.2 it is seen that the main benefit that TEOS-10 delivers to the evaluation of the “thermal wind” is through the incorporation of spatial variations in seawater composition; the greater accuracy of TEOS-10 over EOS-80 for Standard Seawater is only 18% as large as the improvement gained by the incorporation of compositional variations into TEOS-10 (i. e. the rms value of the vertical axis in Fig. A.5.2 is 18% of that of the vertical axis of Fig. A.5.1). If the Atlantic were excluded from this comparison, the relative importance of compositional variations would be even larger.

![Graph](image)

**Figure A.5.2.** The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for \( p > 1000 \) dbar . The vertical axis is the magnitude of the difference between evaluating the density gradient using \( S_R \) as the salinity argument in the TEOS-10 expression for density compared with using \( S_p \) in the EOS-80 algorithm for density.

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. The adoption of TEOS-10 has recognized that this technique of estimating Absolute Salinity from readily measured quantities is perhaps the least mature aspect of the TEOS-10 thermodynamic description of seawater. The present computer software, in both FORTRAN and MATLAB, which evaluates Absolute Salinity \( S_A \), given the input variables Practical Salinity \( S_p \), longitude \( \lambda \), latitude \( \phi \) and sea pressure \( p \) is available at [www.TEOS-10.org](http://www.TEOS-10.org). It is expected, as new data (particularly density data) become available, that the determination of Absolute Salinity will 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 such an updated algorithm will appear on the [www.TEOS-10.org](http://www.TEOS-10.org) web site. Users of this software should state in their published work which version of the software was used to calculate Absolute Salinity.
A.6 Gibbs function of seawater

The Gibbs function of seawater \( g(S_A,t,p) \) is defined as the sum of the Gibbs function for pure water \( g^W(t,p) \) and the saline part of the Gibbs function \( g^S(S_A,t,p) \) so that

\[
g(S_A,t,p) = g^W(t,p) + g^S(S_A,t,p). \tag{A.6.1}
\]

In this way at zero Absolute Salinity, the thermodynamic properties of seawater are equal to those of pure water. This consistency is also maintained with respect to the Gibbs function for ice so that the properties along the equilibrium curve can be accurately determined (such as the freezing temperature as a function of Absolute Salinity and pressure). The careful alignment of the thermodynamic potentials of pure water, ice \( I_{\text{f}} \) and seawater is described in Feistel et al. (2008a).

The internationally accepted thermodynamic description of the properties of pure water (IAPWS-95) is the official pure-water basis upon which the Gibbs function of seawater is built according to (A.6.1). This \( g^W(t,p) \) Gibbs function of liquid water is valid over extended ranges of temperature and pressure from the freezing point to the critical point \((-22 \, ^\circ\text{C} < t < 374 \, ^\circ\text{C} \text{ and } 600 \, \text{Pa} < p + P_0 < 1000 \, \text{MPa}\)) however it is a computationally expensive algorithm. Part of the reason for this computational intensity is that the IAPWS-95 formulation is in terms of a Helmholtz function which has the pressure as a function of temperature and density, so that an iterative procedure is need to for the Gibbs function \( g^W(t,p) \) (see for example, Feistel et al. (2008a))

For practical oceanographic use in the oceanographic ranges of temperature and pressure, from less than the freezing temperature of seawater (at any pressure), up to \( 40 \, ^\circ\text{C} \) (specifically from \(-2.65 + (p + P_0) \times 5 \times 10^{-4} \, ^\circ\text{C} \text{ to } 40 \, ^\circ\text{C}\), and in the pressure range \( 0 < p < 10^4 \, \text{dbar} \) we also recommend the use of the pure water part of the Gibbs function of Feistel (2003) which has been approved by IAPWS as the Supplementary Release, IAPWS-09. The IAPWS-09 release discusses the accuracy to which the Feistel (2003) Gibbs function fits the underlying thermodynamic potential of IAPWS-95; in summary, for the variables density, thermal expansion coefficient and specific heat capacity, the rms misfit between IAPWS-09 and IAPWS-95, in the region of validity of IAPWS-09, are a factor of between 20 and 100 less than the corresponding error in the laboratory data to which IAPWS-95 was fitted. Hence, in the oceanographic range of parameters, IAPWS-09 and IAPWS-95 may be regarded as equally accurate thermodynamic descriptions of pure liquid water.

All of the thermodynamic properties of seawater that are described in this Manual are available as both FORTRAN and MATLAB implementations. These implementations are available for \( g^W(t,p) \) being IAPWS-95 and IAPWS-09, both being equally accurate relative to the laboratory-determined known properties, but with the computer code based on IAPWS-09 being approximately a factor of 65 faster than that based on IAPWS-95.

Most of the experimental seawater data that were already used for the construction of EOS-80 were exploited again for the IAPWS-08 formulation after their careful adjustment to the new temperature and salinity scales and the improved pure-water reference IAPWS-95. Additionally, IAPWS-08 was significantly improved (compared with EOS-80) by making use of theoretical relations such as the ideal-solution law and the Debye-Hückel limiting law, as well as by incorporating additional accurate measurements such as the temperatures of maximum density, vapour pressures and mixing heats, and implicitly by the enormous background data set which had entered the determination of IAPWS-95 (Wagner and Pruß (2002), Feistel (2003, 2008)). For example, Millero and Li (1994) concluded that the pure-water part of the EOS-80 sound-speed formula of Chen and Millero (1977) was responsible for a deviation of 0.5 \( \text{m s}^{-1} \) from Del Grosso’s (1974) formula for seawater at high pressures and temperature below 5 \( ^\circ\text{C} \). Chen and Millero (1977) only measured the differences in the sound speeds of seawater and pure water. The
new Gibbs function in which we use IAPWS-95 for the pure-water part as well as sound speeds from Del Grosso (1974), is perfectly consistent with Chen and Millero’s (1976) densities and Bradshaw and Schleicher’s (1970) thermal expansion data at high pressures. The accuracy of high-pressure seawater densities has increased with the use of IAPWS-95, directly as the pure-water part, and indirectly by correcting earlier seawater measurements, making them "new" seawater data. In this manner the known sound-speed inconsistency of EOS-80 has been resolved in a natural manner.

A.7 The fundamental thermodynamic relation

The fundamental thermodynamic relation for a system composed of a solvent (water) and a solute (sea salt) relates the total differentials of thermodynamic quantities for the case where the transitions between equilibrium states are reversible. This restriction is satisfied for infinitesimally small changes of an infinitesimally small seawater parcel. The fundamental thermodynamic relation is

\[ dh - v dP = (T_0 + t) d\eta + \mu dS_\lambda. \]  \hspace{1cm} (A.7.1)

A derivation of the fundamental thermodynamic relation can be found in Warren (2006) (his equation (8)). The left-hand side of Eqn. (A.7.1) is often written as \( du + (p + P_0) dv \) where \( (p + P_0) \) is the absolute pressure. Here \( h \) is the specific enthalpy (i.e. enthalpy per unit mass of seawater), \( u \) is the specific internal energy, \( v = \rho^{-1} \) is the specific volume, \( (T_0 + t) \) is the absolute temperature, \( \eta \) is the specific entropy and \( \mu \) is the relative chemical potential. In fluid dynamics we usually deal with material derivatives, \( d/dt \), that is, derivatives defined following the fluid motion, \( d/dt = \partial / \partial t + \mathbf{u} \cdot \nabla \) where \( \mathbf{u} \) is the fluid velocity. In terms of this type of derivative, and assuming local thermodynamic equilibrium (i.e. that local thermodynamic equilibrium is maintained during the temporal change), the fundamental thermodynamic relation is

\[ \frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} = (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_\lambda}{dt}. \]  \hspace{1cm} (A.7.2)

Note that the constancy of entropy does not imply the absence of irreversible processes because, for example, there can be irreversible changes of both salinity and enthalpy at constant pressure in just the right ratio so as to have equal effects in Eqns. (A.7.1) or (A.7.2) so that the change of entropy in these equations is zero.

A.8 The “conservative” and “isobaric conservative” properties

A thermodynamic variable \( C \) is said to be “conservative” if its evolution equation (that is, its prognostic equation) has the form

\[ (\rho C)_t + \nabla \cdot (\rho \mathbf{u} C) = \rho \frac{dC}{dt} = - \nabla \cdot \mathbf{F}^C. \]  \hspace{1cm} (A.8.1)

For such a “conservative” property, in the absence of fluxes \( \mathbf{F}^C \) at the boundary of a control volume, the total amount of \( C \)-stuff is constant inside the control volume. The middle part of Eqn. (A.8.1) has used the continuity equation (which is the equation for the conservation of mass)

\[ \partial \rho / \partial t |_{\text{v,\,y,\,z}} + \nabla \cdot (\rho \mathbf{u}) = 0. \]  \hspace{1cm} (A.8.2)

In the special case when the material derivative of a property is zero (that is, the middle part of Eqn. (A.8.1) is zero) the property is said to be “materially conserved”.

The only quantity that can be regarded as 100% conservative in the ocean is mass [equivalent to taking \( C=1 \) and \( \mathbf{F}^C = \mathbf{0} \) in Eqn. (A.8.1)]. In fact, looking ahead to
appendices A.20 and A.21, if we strictly interpret \( \rho \mathbf{u} \) as the mass flux per unit area of pure seawater (i.e. of only pure water plus dissolved material) and specifically, that \( \rho \mathbf{u} \) excludes the flux of particulate matter, then the right-hand side of the continuity equation (A.8.2) should be \( \rho \mathbf{S}^{3}_{\lambda} \), the non-conservative source of mass due to biogeochemical processes. It can be shown that the influence of this source term \( \rho \mathbf{S}^{3}_{\lambda} \) in the continuity equation on the evolution equation for Absolute Salinity is less important by the factor \( \tilde{S}_{\lambda}/[1 - \tilde{S}_{\lambda}] \) than the same source term that appears in this evolution equation for Absolute Salinity, Eqn. (A.21.8). Hence the current practice of assuming that the non-particulate part of the ocean obeys the conservative form (A.8.2) of the continuity equation is confirmed even in the presence of biogeochemical processes.

Two other variables, total energy \( \mathcal{E} = u + 0.5 \mathbf{u} \cdot \mathbf{u} + \Phi \) (see Eqn. (B.15)) and Conservative Temperature \( \Theta \) (or equivalently, potential enthalpy \( h^b \)) are not completely conservative, but the error in assuming them to be conservative is negligible (see appendix A.21). Other variables such as Reference Salinity \( S_R \), Absolute Salinity \( S_{\lambda} \), potential temperature \( \theta \), enthalpy \( h \), internal energy \( u \), entropy \( \eta \), density \( \rho \), potential density \( \rho^0 \), specific volume anomaly \( \delta \) and the Bernoulli function \( B = h + 0.5 \mathbf{u} \cdot \mathbf{u} + \Phi \) (see Eqn. (B.17)) are not conservative variables.

While both Absolute Salinity and Reference Salinity are conservative under the turbulent mixing process, both are affected in a non-conservative way by the remineralization process. Because the dominant variations of the composition of seawater are due to species which do not have a strong signature in conductivity, in some situations it may be sufficiently accurate to take Reference Salinity \( S_R \) to be a conservative variable. However, we note that the error involved with assuming that \( S_R \) is a conservative variable is a factor of approximately 40 larger (in terms of its effects on density) than the error in assuming that \( \Theta \) is a conservative variable. Preformed Salinity \( S_* \) is constructed so that it contains no signature of the biogeochemical processes that cause the spatial variation of seawater composition. In this way \( S_* \) is specifically designed to be a conservative oceanic salinity variable. Having said that, the accuracy with which we can construct Preformed Salinity \( S_* \) from ocean observations is presently limited by our knowledge of the biogeochemical processes (see appendices A.4 and A.5 and Pawlowicz et al. (2010)).

Summarizing this discussion thus far, the quantities that can be considered conservative in the ocean are (in descending order of accuracy) (i) mass, (ii) total energy \( \mathcal{E} = u + 0.5 \mathbf{u} \cdot \mathbf{u} + \Phi \), (iii) Conservative Temperature \( \Theta \), and (iv) Preformed Salinity \( S_* \).

A different form of “conservation” attribute, namely “isobaric conservation” occurs when the total amount of the quantity is conserved when two fluid parcels are mixed at constant pressure without external input of heat or matter. This “isobaric conservative” property is a very valuable attribute for an oceanographic variable. Any “conservative” variable is also “isobaric conservative”, thus the four conservative variables listed above, namely mass, Conservative Temperature \( \Theta \), Preformed Salinity \( S_* \), and total energy \( \mathcal{E} \) are “isobaric conservative”. In addition, the Bernoulli function \( B \) and specific enthalpy \( h \) are also “isobaric conservative” (see Eqn. (B.17) and the discussion thereafter).

Some variables that are not “isobaric conservative” include potential temperature \( \theta \), internal energy \( u \), entropy \( \eta \), density \( \rho \), potential density \( \rho^0 \), and specific volume anomaly \( \delta \). Enthalpy \( h \) and Conservative Temperature \( \Theta \) are not exactly “isobaric conservative” because enthalpy increases when the kinetic energy of fluid motion is dissipated by molecular viscosity inside the control volume and when there is a salinity source term due to the remineralization of particulate matter. However, these are tiny effects in the First Law of Thermodynamics (see appendix A.21) and traditionally we regard enthalpy \( h \) as an “isobaric conservative” variable. Note that while \( h \) is “isobaric conservative”, it is not a “conservative” variable.
Appendices A.18 and A.21 show that for all practical purposes we can treat $\Theta$ and $h^0$ as being “conservative” variables (and hence also “isobaric conservative” variables); doing so ignores the dissipation of mechanical energy $\epsilon$ and other terms of similar or smaller magnitude. Hence for all practical purposes in oceanography we have mass and the following three other variables that are “conservative” and “isobaric conservative”;

1. Conservative Temperature $\Theta$, (and potential enthalpy $h^0$),
2. Preformed Salinity $S_\text{p}$, and
3. total energy $Z'$.

Here we comment briefly on the likely errors involved with assuming variables other than $S_\text{p}$ and $\Theta$ to be conservative variables in ocean models. If one took Absolute Salinity $S_A$ as an ocean model’s salinity variable and treated it as being conservative, the salinity error would (after a long spin-up time) be approximately as large as the Absolute Salinity Anomaly (as shown in Figure 2), which is larger than 0.025 g kg$^{-1}$ in the North Pacific, implying density errors of 0.020 kg m$^{-3}$. As a measure of the importance of this type of density error, we note that if the equation of state in an ocean model were called with $S_\text{p}$ instead of with $S_A$, the northward density gradient at fixed pressure (i.e., the thermal wind) would be misestimated by more than 2% for more than 58% of the data below a pressure of 1000 dbar in the world ocean. It is clearly desirable not to have this type of systematic error in the dynamical equations of the ocean component of coupled climate models. Appendix A.20 discusses practical ways of including the effects of the non-conservative remineralization source term in ocean models. The recommended option is that ocean models carry Preformed Salinity $S_\text{p}$ as the model’s conservative salinity model variable, and that they also carry an evolution equation for an Absolute Salinity Anomaly as described in section A.20.1 and Eqns. (A.20.3) – (A.20.5).

The errors incurred in ocean models by treating potential temperature $\theta$ as being conservative have not yet been thoroughly investigated, but McDougall (2003) and Tailleux (2010) have made a start on this topic. McDougall (2003) found that typical errors in $\theta$ are $\pm 0.1^\circ$C while in isolated regions such as where the fresh Amazon water discharges into the ocean, the error can be as large as $1.4^\circ$C. The corresponding error in the meridional heat flux appears to be about 0.005 PW (or a relative error of 0.4%). The use of Conservative Temperature $\Theta$ in ocean models reduces these errors by approximately two orders of magnitude.

If the ocean were in thermodynamic equilibrium, its temperature would be the same everywhere as would the chemical potentials of water and of each dissolved species, while the entropy and the concentrations of each species would be functions of pressure. Turbulent mixing acts in the complementary direction, tending to make salinity and entropy constant but in the process causing gradients in temperature and the chemical potentials as functions of pressure. That is, turbulent mixing acts to maintain a non-equilibrium state. This difference between the roles of molecular versus turbulent mixing results from the symmetry breaking role of the gravity field; for example, in a laboratory without gravity, turbulent and molecular mixing would have indistinguishable effects.

Note that the molecular flux of salt $F^s$ is given by equation (58.11) of Landau and Lifshitz (1959) and by Eqn. (B.23) below. $F^s$ consists not only of the usual molecular diffusivity and $-\rho \nabla S_A$, but also contains two other terms that are proportional to the gradients of temperature and pressure respectively. It is these terms that cause the equilibrium vertical gradients of the dissolved solutes in a non-turbulent ocean to be different and non-zero; the last term being called the baro-diffusion effect. The presence of turbulent mixing in the real ocean renders this process moot as turbulence tends to homogenize the ocean and maintains a relatively constant sea-salt composition.

Note that the description “conservation equation” of a particular quantity is often used for the equation that describes how this quantity changes in response to the
divergence of various fluxes of the quantity and to non-conservative “source” terms. For example, it is usual to refer to the “conservation equation” for entropy or for “potential temperature”. Since these variables are not conservative variables it seems unnatural to refer to their evolution equations as “conservation equations”. Hence here we will use the term “conservation equation” only for a variable that is (for all practical purposes) conserved. For other variables we will refer to their “evolution equation” or their “prognostic equation” or their “local balance equation”.

A.9 The “potential” property

Any thermodynamic property of seawater that remains constant when a parcel of seawater is moved from one pressure to another adiabatically, without exchange of mass and without interior conversion between its turbulent kinetic and internal energies, is said to possess the “potential” property, or in other words, to be a “potential” variable. Prime examples of “potential” variables are entropy η and all types of salinity. The constancy of entropy η can be seen from the First Law of Thermodynamics in Eqn. (B.19) below; with the right-hand side of Eqn. (B.19) being zero, and with no change in Absolute Salinity, it follows that entropy is also constant. Any thermodynamic property that is a function of only Absolute Salinity and entropy also remains unchanged by this procedure and is said to have the “potential” property. Thermodynamic properties that posses the “potential” attribute include potential temperature θ, potential enthalpy h°, Conservative Temperature Θ and potential density ρ° (no matter what fixed reference pressure is chosen). Some thermodynamic properties that do not posses the potential property are temperature t, enthalpy h, internal energy u, specific volume v, density ρ, specific volume anomaly δ, total energy E and the Bernoulli function B. From Eqn. (B.17) we notice that in the absence of molecular fluxes and the source term of Absolute Salinity, the Bernoulli function B is constant following the fluid flow only if the pressure field is steady; in general this is not the case. The non-potential nature of E is explained in the discussion following Eqn. (B.17).

Some authors have used the term “quasi-material” to describe a variable that has the “potential” property. The name “quasi-material” derives from the idea that the variable only changes as a result of irreversible mixing processes and does not change in response to adiabatic and isohaline changes in pressure.

The word “adiabatic” is traditionally taken to mean a process during which there is no exchange of heat between the environment and the fluid parcel one is considering. With this definition of “adiabatic” it is still possible for the entropy η, the potential temperature θ and the Conservative Temperature Θ of a fluid parcel to change during an isohaline and adiabatic process. This is because the dissipation of mechanical energy ε causes increases in η, θ and Θ (see the First Law of Thermodynamics, Eqns. (A.13.3) - (A.13.5)). While the dissipation of mechanical energy is a small term whose influence is routinely neglected in the First Law of Thermodynamics in oceanography, it seems advisable to modify the meaning of the word “adiabatic” in oceanography so that our use of the word more accurately reflects the properties we normally associate with an adiabatic process. Accordingly we propose that the word “adiabatic” in oceanography be taken to describe a process occurring without exchange of heat and also without the internal dissipation of mechanical energy. With this definition of “adiabatic”, a process that is both isohaline and adiabatic does imply that the entropy η, potential temperature θ and Conservative Temperature Θ are all constant.

Using this more restrictive definition of the word “adiabatic” we can restate the definition of a “potential” property as follows; any thermodynamic property of seawater that remains constant when a parcel of seawater is moved from one pressure to another
“adiabatically” and without exchange of mass, is said to possess the “potential” property, or in other words, to be a “potential” variable.

In appendix A.8 above we concluded that only mass, and the three variables $E$, $S$, and $\Theta$ (approximately) are “conservative” (and hence also “isobaric conservative”). Since $E$ does not possess the “potential” property, we now conclude that only mass and the two variables $S_\lambda$ and $\Theta$ possess all three highly desired properties, namely that they are “conservative”, “isobaric conservative” and are “potential” variables. In the case of Conservative Temperature $\Theta$, its “conservative” (and therefore its “isobaric conservative”) nature is approximate: while $\Theta$ is not a 100% conservative variable, it is approximately two orders of magnitude closer to being a totally conservative variable than are either potential temperature or entropy. Similarly, Preformed Salinity $S_\eta$ is in principle 100% conservative, but our ability to evaluate $S_\eta$ from hydrographic observations is limited (for example, by the approximate relations (A.4.1) or (A.4.9)).

**Table A.9.1** The “potential”, “conservative”, “isobaric conservative” and the functional nature of various oceanographic variables

<table>
<thead>
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<th>Variable</th>
<th>“potential”?</th>
<th>“conservative”?</th>
<th>“isobaric conservative”?</th>
<th>function of $(S_\lambda, t, p)$?</th>
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<td>$h$</td>
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<td>×</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>$\Theta, h^0$</td>
<td>✓</td>
<td>×</td>
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<td>$u$</td>
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<td>$B$</td>
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<td>$E$</td>
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<td>$\rho, v$</td>
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<tr>
<td>$\rho^0$</td>
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<td>$\delta$</td>
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<td>$\rho_s$</td>
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<tr>
<td>$\gamma^n$</td>
<td>×</td>
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<td>×</td>
</tr>
</tbody>
</table>

1. The remineralization of organic matter changes $S_R$ less than it changes $S_\lambda$.
2. Taking $\varepsilon$ and the effects of remineralization to be negligible.
3. Taking $\varepsilon$ and other terms of similar size to be negligible (see the discussion following Eqn. (A.21.13)).
4. Taking the effects of remineralization to be negligible.
5. Once the reference sound speed function $c_0(p, \rho)$ has been decided upon.

In Table A.9.1 various oceanographic variables are categorized according to whether they possess the “potential” property, whether they are “conservative” variables, whether they are “isobaric conservative” variables, and whether they are functions of only $(S_\lambda, t, p)$. 

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Note that \( \Theta \) is the only variable that achieve four “ticks” in this table, while Preformed Salinity \( S_p \) has ticks in the first three columns, but not in the last column since it is a function not only of \( (S_p, t, p) \) but also of the composition of seawater. Hence \( \Theta \) is the most “ideal” thermodynamic variable. If it were not for the non-conservation of Absolute Salinity, it too would be an “ideal” thermodynamic variable, but in this sense, Preformed Salinity is superior to Absolute Salinity. Conservative Temperature \( \Theta \) and Preformed Salinity \( S_p \) are the only two variables in this table to be both “potential” and “conservative”. The last four rows of Table A.9.1 are for potential density, \( \rho^p \) (see section 3.4), specific volume anomaly, \( \delta \) (see section 3.7), orthobaric density, \( \rho_o \) (see appendix A.28) and Neutral Density \( \gamma^n \) (see section 3.14 and appendix A.29).

**A.10 Proof that \( \theta = \theta(S_p, \eta) \) and \( \Theta=\Theta(S_p, \theta) \)**

Consider changes occurring at the sea surface, (specifically at \( p = 0 \) dbar) where the temperature is the same as the potential temperature referenced to 0 dbar and the increment of pressure \( dp \) is zero. Regarding specific enthalpy \( h \) and chemical potential \( \mu \) to be functions of entropy \( \eta \), (in place of temperature \( t \), that is, considering the functional form of \( h \) and \( \mu \) to be \( h = h(S_p, \eta, p) \) and \( \mu = \mu(S_p, \eta, p) \), it follows from the fundamental thermodynamic relation (Eqn. (A.7.1)) that

\[
\hat{h}_\eta(S_p, \eta, 0) \, d\eta + \hat{h}_{S_p}(S_p, \eta, 0) \, dS_p = (T_0 + \theta) d\eta + \mu(S_p, \eta, 0) \, dS_p.
\] (A.10.1)

which shows that specific entropy \( \eta \) is simply a function of Absolute Salinity \( S_p \) and potential temperature \( \theta \), that is \( \eta = \eta(S_p, \theta) \), with no separate dependence on pressure. It follows that \( \theta = \theta(S_p, \eta) \).

Similarly, from the definition of potential enthalpy and Conservative Temperature in Eqns. (3.2.1) and (3.3.1), at \( p = 0 \) dbar it can be seen that the fundamental thermodynamic relation (A.7.1) implies

\[
c_p^0 \, d\Theta = (T_0 + \theta) d\eta + \mu(S_p, \theta, 0) \, dS_p.
\] (A.10.2)

This shows that Conservative Temperature is also simply a function of Absolute Salinity and potential temperature, \( \Theta=\Theta(S_p, \theta) \), with no separate dependence on pressure. It then follows that \( \Theta \) may also be expressed as a function of only \( S_p \) and \( \eta \). It follows that \( \Theta \) has the “potential” property.

**A.11 Various isobaric derivatives of specific enthalpy**

Because of the central role of enthalpy in the transport and the conservation of “heat” in the ocean, the derivatives of specific enthalpy at constant pressure are here derived with respect to Absolute Salinity and with respect to the three “temperature-like” variables \( \eta, \theta \) and \( \Theta \) as well as in situ temperature \( t \).

We begin by noting that the three standard derivatives of \( h = h(S_p, t, p) \) when in situ temperature \( t \) is taken as the “temperature-like” variable are

\[
\frac{\partial h}{\partial S_p} \bigg|_{S_p, t, p} = \mu(S_p, t, p) - (T_0 + t) \mu_T(S_p, t, p),
\] (A.11.1)

\[
\frac{\partial h}{\partial T} \bigg|_{S_p, t, p} = c_p(S_p, t, p) = (T_0 + t) \eta_T(S_p, t, p),
\] (A.11.2)

and

\[
\frac{\partial h}{\partial P} \bigg|_{S_p, t, p} = v(S_p, t, p) - (T_0 + t) v_T(S_p, t, p).
\] (A.11.3)
Now considering specific enthalpy to be a function of entropy (rather than of temperature \( t \)), that is, taking \( h = \hat{h}(S_A, \eta, p) \), the fundamental thermodynamic relation (A.7.1) becomes
\[
\hat{h}_\eta \, d\eta + \hat{h}_{S_A} \, dS_A = (T_0 + t) \, d\eta + \mu \, dS_A \quad \text{while} \quad \partial \hat{h}/\partial p \bigg|_{S_A, \eta} = \nu, \quad (A.11.4)
\]
so that
\[
\partial \hat{h}/\partial \eta \bigg|_{S_A, \rho} = (T_0 + t) \quad \text{and} \quad \partial \hat{h}/\partial S_A \bigg|_{\eta, p} = \mu. \quad (A.11.5)
\]

Now taking specific enthalpy to be a function of potential temperature (rather than of temperature \( t \)), that is, taking \( h = \hat{h}(S_A, \theta, p) \), the fundamental thermodynamic relation (A.7.1) becomes
\[
\hat{h}_\theta \, d\theta + \hat{h}_{S_A} \, dS_A = (T_0 + t) \, d\theta + \mu \, dS_A \quad \text{while} \quad \partial \hat{h}/\partial p \bigg|_{S_A, \theta} = \nu. \quad (A.11.6)
\]
To evaluate the \( \hat{h}_\theta \) partial derivative, it is first written in terms of the derivative with respect to entropy as
\[
\hat{h}_\theta \bigg|_{S_A, p} = \eta_0 \bigg|_{S_A, \rho} \hat{h}_\theta \bigg|_{S_A, \rho} = \eta_0 \bigg|_{S_A} (T_0 + t), \quad (A.11.7)
\]
where (A.11.5) has been used. This equation can be evaluated at \( p = 0 \) when it becomes (the potential temperature used here is referenced to \( p_r = 0 \))
\[
\hat{h}_\theta \bigg|_{S_A, p=0} = c_p \big( S_A, \theta, 0 \big) = \eta_0 \bigg|_{S_A} (T_0 + \theta). \quad (A.11.8)
\]
These two equations are used to arrive at the desired expression for \( \hat{h}_\theta \) namely
\[
\hat{h}_\theta \bigg|_{S_A, \rho} = c_p \big( S_A, \theta, 0 \big) \frac{(T_0 + t)}{(T_0 + \theta)}. \quad (A.11.9)
\]
To evaluate the \( \hat{h}_{S_A} \) partial derivative, we first write specific enthalpy in the functional form \( h = \hat{h}(S_A, \eta(S_A, \theta), p) \) and then differentiate it, finding
\[
\hat{h}_{S_A} \big|_{\theta, p} = \hat{h}_{S_A} \big|_{\eta, p} + \hat{h}_{S_A} \big|_{\eta, \rho} \eta_0 \big|_{\theta}. \quad (A.11.10)
\]
The partial derivative of specific entropy \( \eta = -g_T \) (Eqn. (2.10.1)) with respect to Absolute Salinity, \( \eta_0 = -g_{S,T} \), is also equal to \( -\mu_T \) since chemical potential is defined by Eqn. (2.9.6) as \( \mu = g_{S_A} \). Since the partial derivative of entropy with respect to \( S_A \) in (A.11.10) is performed at fixed potential temperature (rather than at fixed \( \text{situ} \) temperature), this is equal to \( -\mu_T \) evaluated at \( p = 0 \). Substituting both parts of (A.11.5) into (A.11.10) we have the desired expression for \( \hat{h}_{S_A} \) namely
\[
\hat{h}_{S_A} \big|_{\theta, p} = \mu \big( S_A, \theta, p \big) - (T_0 + t) \mu_T \big( S_A, \theta, 0 \big). \quad (A.11.11)
\]
Notice that this expression contains some things that are evaluated at the general pressure \( p \) and one evaluated at the reference pressure \( p_r = 0 \).

Now considering specific enthalpy to be a function of Conservative Temperature (rather than of temperature \( t \)), that is, taking \( h = \hat{h}(S_A, \Theta, p) \), the fundamental thermodynamic relation (A.7.1) becomes
\[
\hat{h}_\Theta \, d\Theta + \hat{h}_{S_A} \, dS_A = (T_0 + t) \, d\Theta + \mu \, dS_A \quad \text{while} \quad \partial \hat{h}/\partial p \bigg|_{S_A, \Theta} = \nu. \quad (A.11.12)
\]
The partial derivative \( \hat{h}_\Theta \) follows directly from this equation as
\[
\hat{h}_\Theta \bigg|_{S_A, p} = (T_0 + t) \eta_0 \bigg|_{S_A, \rho} = (T_0 + t) \eta_0 \bigg|_{S_A}. \quad (A.11.13)
\]
At \( p = 0 \) this equation reduces to
\[
\hat{h}_\Theta \bigg|_{S_A, p=0} = c_p^0 \big( T_0 + \theta \big) \eta_0 \bigg|_{S_A}. \quad (A.11.14)
\]
and combining these two equations gives the desired expression for \( \hat{h}_\Theta \) namely
To evaluate the \( \hat{h}_{SA} \) partial derivative we first write \( h \) in the functional form
\[
h = \hat{h}\left(S_A, \eta(S_A, \Theta), p\right)
\]
and then differentiate it, finding (using both parts of Eqn. (A.11.5))
\[
\hat{h}_{SA} \big|_{\Theta, p} = \mu(S_A, \eta, p) + (T_0 + t) \eta_{SA} \big|_{\Theta}.
\]

The differential expression Eqn. (A.11.12) can be evaluated at \( p = 0 \) where the left-hand side is simply \( c_p^0 d\Theta \) so that from Eqn. (A.11.12) we find that
\[
\eta_{SA} \big|_{\Theta} = \frac{-\mu(S_A, \Theta, 0)}{(T_0 + \Theta)},
\]
so that the desired expression for \( \hat{h}_{SA} \) is
\[
\hat{h}_{SA} \big|_{\Theta, p} = \mu(S_A, \eta, p) - \frac{(T_0 + t)}{(T_0 + \Theta)} \mu(S_A, \Theta, 0).
\]

The above boxed expressions for four different isobaric derivatives of specific enthalpy are important as they are integral to forming the First Law of Thermodynamics in terms of potential temperature and in terms of Conservative Temperature.

### A.12 Differential relationships between \( \eta, \theta, \Theta \) and \( S_A \)

Evaluating the fundamental thermodynamic relation in the forms (A.11.6) and (A.11.12) and using the four boxed equations in appendix A.11, we find the relations
\[
(T_0 + t) d\eta + \mu(p) dS_A = \frac{(T_0 + t)}{(T_0 + \Theta)} c_p^0(0) d\Theta + \left[ \mu(p) - (T_0 + t) \mu_T(0) \right] dS_A
\]
\[= \frac{(T_0 + t)}{(T_0 + \Theta)} c_p^0 d\Theta + \left[ \mu(p) - \frac{(T_0 + t)}{(T_0 + \Theta)} \mu(0) \right] dS_A.\]

The quantity \( \mu(p) dS_A \) is now subtracted from each of these three expressions and the whole equation is then multiplied by \( (T_0 + \Theta)/(T_0 + t) \) obtaining
\[
(T_0 + \Theta) d\eta = c_p^0(0) d\Theta - (T_0 + \Theta) \mu_T(0) dS_A = c_p^0 d\Theta - \mu(0) dS_A.\]

From this follows all the following partial derivatives between \( \eta, \theta, \Theta \) and \( S_A \),
\[
\Theta_{\Theta} |_{S_A} = c_p^0(S_A, \Theta, 0)/c_p^0,
\]
\[
\Theta_{S_A} |_{\Theta} = \left[ \mu(S_A, \Theta, 0) - (T_0 + \Theta) \mu_T(S_A, \Theta, 0) \right]/c_p^0,
\]
\[
\theta_{\Theta} |_{S_A} = (T_0 + \Theta)/c_p^0,
\]
\[
\theta_{S_A} |_{\Theta} = \left[ \mu(S_A, \Theta, 0) - (T_0 + \Theta) \mu_T(S_A, \Theta, 0) \right]/c_p^0,
\]
\[
\eta_{\Theta} |_{S_A} = c_p^0(S_A, \Theta, 0)/(T_0 + \Theta),
\]
\[
\eta_{S_A} |_{\Theta} = -\left[ \mu(S_A, \Theta, 0) - (T_0 + \Theta) \mu_T(S_A, \Theta, 0) \right]/c_p^0(S_A, \Theta, 0),\]
\[
\theta_{\Theta} |_{S_A} = c_p^0(S_A, \Theta, 0)/(T_0 + \Theta),
\]
\[
\eta_{S_A} |_{\Theta} = -\mu_T(S_A, \Theta, 0),
\]
\[
\Theta_{\theta} |_{S_A} = \frac{(T_0 + t)}{(T_0 + \Theta)} c_p^0(S_A, \Theta, 0),
\]
\[
\Theta_{S_A} |_{\Theta} = \frac{(T_0 + t)}{(T_0 + \Theta)} c_p^0(S_A, \Theta, 0),
\]
\[
\theta_{\theta} |_{S_A} = c_p^0(S_A, \Theta, 0)/(T_0 + \Theta),
\]
\[
\eta_{S_A} |_{\Theta} = -\mu_T(S_A, \Theta, 0)/(T_0 + \Theta).
\]

The three second order derivatives of \( \eta(S_A, \Theta) \) are listed in Eqns. (P.14) and (P.15) of appendix P. The corresponding derivatives of \( \Theta(S_A, \Theta) \), namely \( \Theta_{\theta}, \Theta_{\Theta}, \Theta_{\theta} \Theta, \Theta_{\theta \Theta}, \Theta_{\theta \Theta}, \Theta_{\theta \Theta}, \Theta_{\theta \Theta} \) and \( \Theta_{\theta \Theta \Theta} \) can also be derived using Eqn. (P.13), obtaining
\[ \dot{\theta} = \frac{1}{\rho} \frac{d \rho}{dt}, \quad \dot{\theta}_s = -\frac{\dot{\Theta}_s}{\rho}, \quad \dot{\theta}_{\theta\theta} = -\frac{\partial \rho}{\partial \theta} \left( \frac{\dot{\Theta}_s}{\rho} \right)^2, \quad \dot{\theta}_{\theta^2} = -\frac{\partial \rho}{\partial \theta} \left( \frac{\dot{\Theta}_s}{\rho} \right)^2, \quad (A.12.9a,b,c,d) \]

and

\[ \dot{\theta}_{\theta^2 s} = -\frac{\partial \rho}{\partial \theta^2} s_{\theta^2 s} + 2 \frac{\partial \rho}{\partial \theta} \frac{\dot{\Theta}_s}{\rho} \left( \frac{\dot{\Theta}_s}{\rho} \right)^2, \quad (A.12.10) \]

in terms of the partial derivatives \( \dot{\Theta}_s, \dot{\theta}_s, \dot{\theta}_{\theta\theta}, \dot{\theta}_{\theta^2}, \) and \( \dot{\theta}_{\theta^2 s} \) which can be obtained by differentiating the polynomial \( \Theta(S_s, \theta) \) from the TEOS-10 Gibbs function.

**A.13 The First Law of Thermodynamics**

The law of the conservation of energy for thermodynamic equilibrium states was discovered in the 19th century by Gibbs (1873) and other early pioneers. It was formulated as a balance between internal energy, heat and work, similar to the fundamental equation (A.7.1), and referred to as the First Law of Thermodynamics (Thomson (1851), Clausius (1876), Alberty (2001)). Under the weaker condition of a local thermodynamic equilibrium (Glansdorff and Prigogine (1971)), the original thermodynamic concepts can be suitably generalized to describe irreversible processes of fluid dynamics which are subject to molecular fluxes and macroscopic motion (Landau and Lifshitz (1959), De Groot and Mazur (1984)).

In some circles the “First Law of Thermodynamics” is used to describe the evolution equation for total energy, being the sum of internal energy, potential energy and kinetic energy. Here we follow the more common practice of regarding the First Law of Thermodynamics as the difference between the conservation equation of total energy and the evolution equation for kinetic energy plus potential energy, leaving what might loosely be termed the evolution equation of “heat”, Eqn. (A.13.1) (Landau and Lifshitz (1959), McDougall (2003), Griffies (2004)).

The First Law of Thermodynamics can therefore be written as (see Eqn. (B.19) and the other Eqns. (A.13.3), (A.13.4) and (A.13.5) of this appendix; all of these equations are equally valid incarnations of the First Law of Thermodynamics)

\[ \rho \left( \frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon + h_{\theta^2} \rho S^{\theta^2}, \quad (A.13.1) \]

where \( \mathbf{F}^R \) is the sum of the boundary and radiative heat fluxes and \( \mathbf{F}^Q \) is the sum of all molecular diffusive fluxes of heat, being the normal molecular heat flux directed down the temperature gradient plus a term proportional to the molecular flux of salt (the Dufour Effect, see Eqn. (B.24) below). Lastly, \( \varepsilon \) is the rate of dissipation of mechanical energy per unit mass, transformed into internal energy and \( h_{\theta^2} \rho S^{\theta^2} \) is the rate of increase of enthalpy due to the interior source term of Absolute Salinity caused by remineralization. The derivation of (A.13.1) is summarized in appendix B below, where we also discuss the related evolution equations for total energy and for the Bernoulli function.

Following Fofonoff (1962) we note that an important consequence of (A.13.1) is that when two finite sized parcels of seawater are mixed at constant pressure and under ideal conditions, the total amount of enthalpy is conserved. To see this one combines (A.13.1) with the continuity equation \( \partial \rho / \partial t + \nabla \cdot (\rho \mathbf{u}) = 0 \) to find the following divergence form of the First Law of Thermodynamics,

\[ \partial (\rho h) / \partial t + \nabla \cdot (\rho \mathbf{u} h) - \frac{dP}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon + h_{\theta^2} \rho S^{\theta^2}. \quad (A.13.2) \]

One then integrates over the volume that encompasses both fluid parcels while assuming there to be no radiative, boundary and molecular fluxes across the boundary of the control volume. This control volume may change with time as the fluid moves (at constant
pressure), mixes and contracts. The dissipation of mechanical energy by viscous friction and the source term due to the production of Absolute Salinity are also commonly ignored during such mixing processes but in fact these terms do cause a small increase in the enthalpy of the mixture with respect to that of the two original parcels. Apart from these non-conservative source terms, under these assumptions Eqn. (A.13.2) reduces to the statement that the volume integrated amount of $\rho h$ is the same for the two initial fluid parcels as for the final mixed parcel, that is, the total amount of enthalpy is unchanged.

This result of non-equilibrium thermodynamics is of the utmost importance in oceanography. The fact that enthalpy is conserved when fluid parcels mix at constant pressure is the central result upon which all of our understanding of “heat fluxes” and of “heat content” in the ocean rests. The importance of this result cannot be overemphasized; it must form part of all our introductory courses on oceanography and climate dynamics. As important as this result is, it does not follow that enthalpy is the best variable to represent “heat content” in the ocean. Enthalpy is a very poor representation of “heat content” in the ocean because it does not posses the “potential” property. It will be seen that potential enthalpy $h^0$ (referenced to zero sea pressure) is the best thermodynamic variable to represent “heat content” in the ocean.

The First Law of Thermodynamics (A.13.1) can be written (using Eqn. (A.7.2)) as an evolution equation for entropy as follows

$$\rho\left(\frac{T_0 + t}{T_0 + \theta}\right)\frac{d\eta}{dt} + \mu \frac{dS}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon + h_{s_{\lambda}} \rho \mathbf{S}^{S_{\lambda}} \tag{A.13.3}$$

The First Law of Thermodynamics (A.13.1) can also be written in terms of potential temperature $\theta$ (with respect to reference pressure $p_r$) by substituting Eqsns. (A.11.9) and (A.11.11) into Eqn. (A.13.1) as (from Bacon and Fofonoff (1996) and McDougall (2003))

$$\rho\left(\frac{T_0 + t}{T_0 + \theta}\right)\frac{c_p}{c_p} \left[\frac{d\theta}{dt} + \mu (p) \frac{dS}{dt}\right] = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon + h_{s_{\lambda}} \rho \mathbf{S}^{S_{\lambda}} \tag{A.13.4}$$

where $T_0$ is the Celsius zero point ($T_0$ is exactly 273.15 K), while in terms of Conservative Temperature $\Theta$, the First Law of Thermodynamics is (from McDougall (2003), using Eqns. (A.11.15) and (A.11.18) above)

$$\rho\left(\frac{T_0 + t}{T_0 + \Theta}\right)\frac{c_p}{c_p} \left[\frac{d\Theta}{dt} + \mu (p) \frac{dS}{dt}\right] = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon + h_{s_{\lambda}} \rho \mathbf{S}^{S_{\lambda}} \tag{A.13.5}$$

where $c_p^0$ is the fixed constant defined by the exact 15-digit number in Eqn. (3.3.3).

In appendices A.16, A.17 and A.18 the non-conservative production of entropy, potential temperature and Conservative Temperature are quantified, both as Taylor series expansions which identify the relevant non-linear thermodynamic terms that cause the production of these variables, and also on the $S_{\lambda} - \Theta$ diagram where variables are contoured which graphically illustrate the non-conservation of these variables. In other words, appendices A.16, A.17 and A.18 quantify the non-ideal nature of the left-hand sides of Eqns. (A.13.3) - (A.13.5). That is, these appendices quantify the deviations of the left-hand sides of these equations from being proportional to $\rho d\eta/dt$, $\rho d\theta/dt$ and $\rho d\Theta/dt$.

A quick ranking of these three variables, $\eta$, $\theta$ and $\Theta$, from the viewpoint of the amount of their non-conservation, can be gleaned by examining the range of the terms (at fixed pressure) that multiply the material derivatives on the left-hand sides of the above Eqns. (A.13.3), (A.13.4) and (A.13.5). The ocean circulation may be viewed as a series of adiabatic and isohaline movements of seawater parcels interrupted by a series of isolated turbulent mixing events. During any of the adiabatic and isohaline transport stages every
“potential” property is constant, so each of the above variables, entropy, potential temperature and Conservative Temperature are 100% ideal during these adiabatic and isohaline advection stages. The turbulent mixing events occur at fixed pressure so the non-conservative production of say entropy depends on the extent to which the coefficients \((T_0 + t)\) and \(\mu\) in Eqn. (A.13.3) vary at fixed pressure. Similarly the non-conservative production of potential temperature depends on the extent to which the coefficients \(c_p(p_t)(T_0 + t)/(T_0 + \theta)\) and \(\left[\mu(p) - (T_0 + t)\mu_f(p_t)\right]\) in Eqn. (A.13.4) vary at fixed pressure, while the non-conservative production of Conservative Temperature depends on the extent to which the coefficients \((T_0 + t)/(T_0 + \theta)\) and \(\left[\mu(p) - \mu(0)(T_0 + t)/(T_0 + \theta)\right]\) in Eqn. (A.13.5) vary at fixed pressure.

According to this way of looking at these equations we note that the material derivative of entropy appears in Eqn. (A.13.3) multiplied by the absolute temperature \((T_0 + t)\) which varies by about 15% at the sea surface \((273.15 + 40)/273.15 \approx 1.146\), the term that multiplies \(\frac{d\theta}{dt}\) in (A.13.4) is dominated by the variations in the isobaric specific heat \(c_p(S_A, t, p_t)\) which is mainly a function of \(S_A\) and which varies by 5% at the sea surface (see Figure 4), while the material derivative of Conservative Temperature \(\frac{d\Theta}{dt}\) in Eqn. (A.13.5) is multiplied by the product of a constant “heat capacity” \(c_p^0\) and the factor \((T_0 + t)/(T_0 + \theta)\) which varies very little in the ocean, especially when one realizes that it is only the variation of this ratio at each pressure level that is of concern. This factor is unity at the sea surface and is also very close to unity in the deep ocean.

![Figure A.13.1. Contours (in °C) of the difference θ−Θ between potential temperature θ and Conservative Temperature Θ at the sea surface of the annually-averaged atlas of Gouretski and Koltermann (2004).](image)

Fortunately, Conservative Temperature is not only much more accurately conserved in the ocean than potential temperature but it is also relatively easy to use in oceanography. Because Conservative Temperature also possesses the “potential” property, it is a very accurate representation of the “heat content” of seawater. The difference \(\theta−\Theta\) between potential temperature \(\theta\) and Conservative Temperature \(\Theta\) at the sea surface is shown in Figure A.13.1 (after McDougall, 2003). If an ocean model is
written with potential temperature as the prognostic temperature variable rather than Conservative Temperature, and is run with the same constant value of the isobaric specific heat capacity ($c_p^0$ as given by Eqn. (3.3.3)), the neglect of the non-conservative source terms that should appear in the prognostic equation for $\theta$ means that such an ocean model incurs errors in the model output. These errors will depend on the nature of the surface boundary condition; for flux boundary conditions the errors are as shown in Figure A.13.1.

This appendix has largely demonstrated the benefits of potential enthalpy and Conservative Temperature from the viewpoint of conservation equations, but the benefits can also be proven by the following parcel-based argument. First, the air-sea heat flux needs to be recognized as a flux of potential enthalpy which is exactly $c_p^0$ times the flux of Conservative Temperature. Second, the work of appendix A.18 shows that while it is the in situ enthalpy that is conserved when parcels mix, a negligible error is made when potential enthalpy is assumed to be conserved during mixing at any depth. Third, note that the ocean circulation can be regarded as a series of adiabatic and isohaline movements during which $\Theta$ is absolutely unchanged (because of its “potential” nature) followed by a series of turbulent mixing events during which $\Theta$ is almost totally conserved. Hence it is clear that $\Theta$ is the quantity that is advected and diffused in an almost conservative fashion and whose surface flux is exactly proportional to the air-sea heat flux.

### A.14 Advective and diffusive “heat” fluxes

In section 3.23 and appendices A.8 and A.13 the First Law of Thermodynamics is shown to be practically equivalent to the conservation equation (A.21.15) for Conservative Temperature $\Theta$. We have emphasized that this means that the advection of “heat” is very accurately given as the advection of $c_p^0 \Theta$. In this way $c_p^0 \Theta$ can be regarded as the “heat content” per unit mass of seawater and the error involved with making this association is approximately 1% of the error in assuming that either $c_p^0 \theta$ or $c_p(S, \theta, 0 \text{dbar}) \theta$ is the “heat content” per unit mass of seawater (see also appendix A.21 for a discussion of this point).

The conservative form (A.21.15) implies that the turbulent diffusive flux of heat should be directed down the mean gradient of Conservative Temperature rather than down the mean gradient of potential temperature. In this appendix we quantity the difference between these mean temperature gradients.

Consider first the respective temperature gradients along the neutral tangent plane. From Eqn. (3.11.2) we find that

$$ \left( \frac{\alpha^0}{\beta^0} \right) \nabla_n \theta = \nabla_n S_L = \left( \frac{\alpha^0}{\beta^0} \right) \nabla_n \Theta, $$

(A.14.1)

so that the epineutral gradients of $\theta$ and $\Theta$ are related by the ratios of their respective thermal expansion and saline contraction coefficients, namely

$$ \nabla_n \theta = \left( \frac{\alpha^0}{\beta^0} \right) \nabla_n \Theta. $$

(A.14.2)

This proportionality factor between the parallel two-dimensional vectors $\nabla_n \theta$ and $\nabla_n \Theta$ is readily calculated and illustrated graphically. Before doing so we note two other equivalent expressions for this proportionality factor.

The epineutral gradients of $\theta$, $\Theta$ and $S_L$ are related by (using $\theta = \hat{\theta}(S_L, \Theta)$)

$$ \nabla_n \theta = \hat{\theta} \nabla_n S_L + \hat{S}_L \nabla_n S_L, $$

(A.14.3)

and using the neutral relationship $\nabla_n S_L = \left( \frac{\alpha^0}{\beta^0} \right) \nabla_n \Theta$ we find
\[ \nabla_s \theta = \left( \hat{\theta}_\alpha + \left[ \alpha^\theta / \beta^\theta \right] \hat{\theta}_{S_A} \right) \nabla_n \Theta. \]  
\( \text{(A.14.4)} \)

Also, in section 3.13 we found that \( T_k^\theta \nabla_s \theta = T_k^\theta \nabla_n \Theta \), so that we can write the equivalent expressions

\[ \frac{\left| \nabla_s \theta \right|}{\left| \nabla_n \Theta \right|} = \frac{\left( \alpha^\theta / \beta^\theta \right)}{\left( \alpha^\theta / \beta^\theta \right)} = \frac{T_k^\theta}{T_k^\theta} \left( \hat{\theta}_\alpha + \left[ \alpha^\theta / \beta^\theta \right] \hat{\theta}_{S_A} \right), \]
\( \text{(A.14.5)} \)

and it can be shown that \( \alpha^\theta / \alpha^\theta = \hat{\theta}_\alpha \) and \( \beta^\theta / \beta^\theta = \frac{1 + \left[ \alpha^\theta / \beta^\theta \right] \hat{\theta}_{S_A} / \hat{\theta}_\alpha} \), that is, \( \beta^\theta = \beta^\theta + \alpha^\theta \hat{\theta}_{S_A} / \hat{\theta}_\alpha \). The partial derivatives \( \hat{\theta}_\alpha \) and \( \hat{\theta}_{S_A} \) in the last part of Eqn. (A.14.5) are both independent of pressure while \( \alpha^\theta / \beta^\theta \) is a function of pressure. This ratio, Eqn. (A.14.5), of the epineutral gradients of \( \theta \) and \( \Theta \) is shown in Figure A.14.1 at \( p = 0 \), indicating that the epineutral gradient of potential temperature is sometimes more than 1% different to that of Conservative Temperature. This ratio \( \left| \nabla_s \theta \right| / \left| \nabla_n \Theta \right| \) is only a weak function of pressure. This ratio, \( \left| \nabla_s \theta \right| / \left| \nabla_n \Theta \right| \) (i.e. Eqn. (A.14.5)), is available in the GSW computer software library as function gsw_ntp_pt_to_CT_gradient.

Similarly to Eqn. (A.14.3), the vertical gradients are related by

\[ \theta_z = \hat{\theta}_\alpha \Theta_z + \hat{\theta}_{S_A} S_A, \]
\( \text{(A.14.6)} \)

and using the definition, Eqn. (3.15.1), of the stability ratio we find that

\[ \frac{\theta_z}{\Theta_z} = \hat{\theta}_\alpha + R_p^{-1} \left[ \alpha^\theta / \beta^\theta \right] \hat{\theta}_{S_A}. \]
\( \text{(A.14.7)} \)

For values of the stability ratio \( R_p \) close to unity, the ratio \( \theta_z / \Theta_z \) is close to the values of \( \left| \nabla_s \theta \right| / \left| \nabla_n \Theta \right| \) shown in Figure A.14.1. For other values of \( R_p \), Eqn. (A.14.7) can be calculated and plotted.

**Figure A.14.1.** Contours of \( \left( \left| \nabla_s \theta \right| / \left| \nabla_n \Theta \right| - 1 \right) \times 100\% \) at \( p = 0 \), showing the percentage difference between the epineutral gradients of \( \theta \) and \( \Theta \). The blue dots are from the ocean atlas of Gouretski and Koltermann (2004) at \( p = 0 \).

As noted in section 3.8 the dianeutral advection of thermobaricity is the same when quantified in terms of potential temperature as when done in terms of Conservative Temperature. The same is not true of the dianeutral velocity caused by cabling. The ratio of the cabling dianeutral velocity calculated using potential temperature to that using Conservative Temperature is given by \( \left( C^\theta_{\nabla_n \Theta} \cdot \nabla_n \Theta \right) / \left( C^\theta_{\nabla_n \Theta} \cdot \nabla_n \Theta \right) \) (see section 3.9) which can be expressed as

\[ \]
\[
\frac{C_b^\theta \nabla_{\theta} \theta^2}{C_b^\theta \nabla_{\Theta} \Theta^2} = \frac{C_b^\theta (\alpha^\theta / \beta^\theta)^2}{C_b^\theta (\alpha^\Theta / \beta^\Theta)^2} = \frac{C_b^\theta (T_b^\Theta)^2}{C_b^\theta (T_b^\theta)^2} = \frac{C_b^\theta}{C_b^\Theta} \left( \theta_{\bar{k}} + \left[ \alpha^\Theta / \beta^\Theta \right] \theta_{\bar{k}} \right)^2,
\]

(A.14.8)

and this is contoured in Fig. A.14.2. While the ratio of Eqn. (A.14.8) is not exactly unity, it varies relatively little in the oceanographic range, indicating that the dianeutral advection due to cabbeling estimated using \( \theta \) or \( \Theta \) are within half a percent of each other at \( p = 0 \).

Figure A.14.2. Contours of the percentage difference of \( \left( \frac{C_b^\theta \nabla_{\theta} \theta^2}{C_b^\theta \nabla_{\Theta} \Theta^2} \right) / \left( \frac{C_b^\theta \nabla_{\theta} \theta^2}{C_b^\theta \nabla_{\Theta} \Theta^2} \right) \) from unity at \( p = 0 \) dbar.

### A.15 Derivation of the expressions for \( \alpha^\theta, \beta^\theta, \alpha^\Theta \) and \( \beta^\Theta \)

This appendix derives the expressions in Eqns. (2.18.2) – (2.18.3) and (2.19.2) – (2.19.3) for the thermal expansion coefficients \( \alpha^\theta \) and \( \alpha^\Theta \) and the haline contraction coefficients \( \beta^\theta \) and \( \beta^\Theta \).

In order to derive Eqn. (2.18.2) for \( \alpha^\theta \) we first need an expression for \( \partial \theta / \partial t \) at \( S_A, p \). This is found by differentiating with respect to \( \text{in situ} \) temperature the entropy equality \( \eta(S_A, t, p) = \eta(S_A, \theta[S_A, t, p, p_I], p_I) \) which defines potential temperature, obtaining

\[
\frac{\partial \theta}{\partial t} \bigg|_{S_A, p} = \frac{\eta_r(S_A, t, p)}{\eta_r(S_A, \theta, p_I)} = \frac{g_{TT}(S_A, t, p)}{g_{TT}(S_A, \theta, p_I)}.
\]

(A.15.1)

This is then used to obtain the desired expression Eqn. (2.18.2) for \( \alpha^\theta \) as follows

\[
\alpha^\theta = \frac{1}{v} \left( \frac{\partial \Theta}{\partial t} \right)_{S_A, p} = \frac{1}{v} \left( \frac{\partial \theta}{\partial t} \right)_{S_A, p} \left( \frac{\partial \Theta}{\partial \theta} \right)_{S_A, p}^{-1} = \frac{g_{TT}(S_A, t, p)}{g_{TT}(S_A, \theta, p_I)} \frac{g_{TT}(S_A, \theta, p_I)}{g_{TT}(S_A, t, p)}.
\]

(A.15.2)

In order to derive Eqn. (2.18.3) for \( \alpha^\Theta \) we first need an expression for \( \partial \Theta / \partial t \) at \( S_A, p \). This is found by differentiating with respect to \( \text{in situ} \) temperature the entropy equality \( \eta(S_A, t, p) = \eta(S_A, \Theta[S_A, t, p]) \) obtaining

\[
\frac{\partial \Theta}{\partial t} \bigg|_{S_A, p} = \frac{\eta_r(S_A, t, p)}{\eta_r(S_A, \Theta)} \frac{\partial \Theta}{\partial \Theta} \bigg|_{S_A, p} = - (T_0 + \theta) g_{TT}(S_A, t, p) / c_p^\theta.
\]

(A.15.3)

where the second part of this equation has used Eqn. (A.12.4) for \( \Theta \bigg|_{S_A, p} \). This is then used to obtain the desired expression Eqn. (2.18.3) for \( \alpha^\Theta \) as follows
In order to derive Eqn. (2.19.2) for $\beta^\theta$ we first need an expression for $\partial \theta / \partial S_{A,\rho}$. This is found by differentiating with respect to Absolute Salinity the entropy equality $\eta(S_{A,t}, p) = \eta(S_{A,\rho}[S_{A,t}, p, p_t], p_t)$ which defines potential temperature, obtaining

$$\frac{\partial \theta}{\partial S_{A,\rho}} = \frac{\partial \Theta}{\partial S_{A,\rho}} \left[ \eta_{S_{A}}(S_{A,t}, p) - \eta_{S_{A}}(S_{A,\rho}, p_t) \right]$$

$$= \frac{(T_0 + \theta)}{c_p(S_{A,\rho}, \rho, p_t)} \left[ \mu_T(S_{A,\rho}, \rho, p_t) - \mu_T(S_{A,t}, p_t) \right]$$

$$= \left[ g_{S_{A,T}}(S_{A,t}, p) - g_{S_{A,T}}(S_{A,\rho}, \rho, p_t) \right] / g_{TT}(S_{A,t}, p_t),$$

where Eqns. (A.12.5) and (A.12.7) have been used with a general reference pressure $p_t$ rather than with $p_t = 0$. By differentiating $\rho = \tilde{\rho}(S_{A,\rho}[S_{A,t}, p, p_t], p)$ with respect to Absolute Salinity it can be shown that (Gill (1982), McDougall (1987a))

$$\beta^\theta = \frac{1}{\rho} \frac{\partial \rho}{\partial S_{A,\rho}} = \frac{1}{\rho} \frac{\partial \rho}{\partial S_{A,\rho}} + \alpha^\theta \frac{\partial \Theta}{\partial S_{A,\rho}},$$

and using Eqn. (A.15.5) we arrive at the desired expression Eqn. (2.19.2) for $\beta^\theta$

$$\beta^\theta = -\frac{g_{S_{A,p}}(S_{A,t}, p)}{g_p(S_{A,t}, p)} + \frac{g_{TT}(S_{A,t}, p)}{g_p(S_{A,t}, p)} \frac{g_{S_{A,T}}(S_{A,t}, p) - g_{S_{A,T}}(S_{A,\rho}, \rho, p_t)}{g_{TT}(S_{A,t}, p)}.$$

Note that the terms in the natural logarithm of the square root of Absolute Salinity cancel from the two parts of the square brackets in Eqns. (A.15.5) and (A.15.7).

In order to derive Eqn. (2.19.3) for $\beta^\theta$ we first need an expression for $\partial \Theta / \partial S_{A,\rho}$. This is found by differentiating with respect to Absolute Salinity the entropy equality $\eta(S_{A,t}, p) = \tilde{\eta}(S_{A,\rho}[S_{A,t}, p, p_t])$ obtaining (using Eqns. (A.12.4) and (A.12.8))

$$\frac{\partial \Theta}{\partial S_{A,\rho}} = \Theta \left[ \eta_{S_{A}}(S_{A,t}, p) - \tilde{\eta}_{S_{A}} \right]$$

$$= \left[ \mu(S_{A,\rho}, \rho, 0) - (T_0 + \theta) \mu_T(S_{A,t}, p) \right] / c_p^\theta$$

$$= \left[ g_{S_{A}}(S_{A,\rho}, \rho, 0) - (T_0 + \theta) g_{S_{A,T}}(S_{A,t}, p) \right] / c_p^\theta.$$

Differentiating $\rho = \tilde{\rho}(S_{A,\rho}[S_{A,t}, p, p_t], p)$ with respect to Absolute Salinity leads to

$$\beta^\theta = \frac{1}{\rho} \frac{\partial \rho}{\partial S_{A,\rho}} = \frac{1}{\rho} \frac{\partial \rho}{\partial S_{A,\rho}} + \alpha^\theta \frac{\partial \Theta}{\partial S_{A,\rho}},$$

and using Eqn. (A.15.8) we arrive at the desired expression (2.19.3) for $\beta^\theta$ namely

$$\beta^\theta = -\frac{g_{S_{A,p}}(S_{A,t}, p)}{g_p(S_{A,t}, p)} + \frac{g_{TT}(S_{A,t}, p)}{g_p(S_{A,t}, p)} \frac{g_{S_{A,T}}(S_{A,t}, p) - g_{S_{A,T}}(S_{A,\rho}, \rho, 0)}{(T_0 + \theta) g_{TT}(S_{A,t}, p)}.$$

Note that the terms in the natural logarithm of the square root of Absolute Salinity cancel from the two parts of the square brackets in Eqns. (A.15.8) and (A.15.10).
A.16 Non-conservative production of entropy

In this and the following three appendices (A.16 – A.19) the non-conservative nature of several thermodynamic variables (entropy, potential temperature, Conservative Temperature and potential density) will be quantified by considering the mixing of pairs of seawater parcels at fixed pressure. The mixing is taken to be complete so that the end state is a seawater parcel that is homogeneous in Absolute Salinity and entropy. That is, we will be considering mixing to completion by a turbulent mixing process. In appendix A.20 the non-conservative production of Absolute Salinity by the remineralization of particulate organic matter is considered. This process is not being considered in appendices A.16 – A.19. The non-conservative production which is quantified in appendices A.16 – A.19 occurs in the absence of any variation in seawater composition.

Following Fofonoff (1962), consider mixing two fluid parcels (parcels 1 and 2) that have initially different temperatures and salinities. The mixing process occurs at pressure $p$. The mixing is assumed to happen to completion so that in the final state Absolute Salinity, entropy and all the other properties are uniform. Assuming that the mixing happens with a vanishingly small amount of dissipation of mechanical energy, the $\varepsilon$ term can be dropped from the First Law of Thermodynamics, (A.13.1), this equation becoming

$$\left(\rho h\right) + \nabla \cdot (\rho u h) = -\nabla \cdot F^R - \nabla \cdot F^Q.$$  \hspace{1cm} at constant pressure (A.16.1)

Note that this equation has the form (A.8.1) and so $h$ is conserved during mixing at constant pressure, that is, $h$ is “isobaric conservative”. In the case we are considering of mixing the two seawater parcels, the system is closed and there are no radiative, boundary or molecular heat fluxes coming through the outside boundary so the integral over space and time of the right-hand side of Eqn. (A.16.1) is zero. The surface integral of $(\rho u h)$ through the boundary is also zero. Hence it is apparent that the volume integral of $\rho h$ is the same at the final state as it is at the initial state, that is, enthalpy is conserved. Hence during the mixing process the mass, salt content and enthalpy are conserved, that is

$$m_1 + m_2 = m, \hspace{1cm} (A.16.2)$$
$$m_1 S_{\lambda 1} + m_2 S_{\lambda 2} = m S_{\lambda}, \hspace{1cm} (A.16.3)$$
$$m_1 h_1 + m_2 h_2 = m h, \hspace{1cm} (A.16.4)$$

while the non-conservative nature of entropy means that it obeys the equation,

$$m_1 \eta_1 + m_2 \eta_2 + m \delta \eta = m \eta. \hspace{1cm} (A.16.5)$$

Here $S_{\lambda}, h$ and $\eta$ are the values of Absolute Salinity, enthalpy and entropy of the final mixed fluid and $\delta \eta$ is the production of entropy, that is, the amount by which entropy is not conserved during the mixing process. Entropy $\eta$ is now regarded as the functional form $\eta = \eta(S_{\lambda}, h, p)$ and is expanded in a Taylor series of $S_{\lambda}$ and $h$ about the values of $S_{\lambda}$ and $h$ of the mixed fluid, retaining terms to second order in $[S_{\lambda 2} - S_{\lambda 1}] = \Delta S_{\lambda}$ and in $[h_2 - h_1] = \Delta h$. Then $\eta_1$ and $\eta_2$ are evaluated and (A.16.4) and (A.16.5) used to find

$$\delta \eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \bar{\eta}_{hh} (\Delta h)^2 + 2 \bar{\eta}_{hS_{\lambda}} \Delta h \Delta S_{\lambda} + \bar{\eta}_{S_{\lambda}S_{\lambda}} (\Delta S_{\lambda})^2 \right\}. \hspace{1cm} (A.16.6)$$

Towards the end of this section the implications of the production (A.16.6) of entropy will be quantified, but for now we ask what constraints the Second Law of Thermodynamics might place on the form of the Gibbs function $g(S_{\lambda}, t, p)$ of seawater. The Second Law of Thermodynamics tells us that the entropy excess $\delta \eta$ must not be negative for all possible combinations of the differences in enthalpy and salinity between the two fluid parcels. From (A.16.6) this requirement implies the following three inequalities,

$$\bar{\eta}_{hh} < 0,$$  \hspace{1cm} (A.16.7)
\[ \bar{\eta}_{SA_A} < 0 , \quad (A.16.8) \]
\[ \left( \bar{\eta}_{hSA_A} \right)^2 < \bar{\eta}_{hh} \bar{\eta}_{SA_A} , \quad (A.16.9) \]

where the last requirement reflects the need for the discriminant of the quadratic in (A.16.6) to be negative. Since entropy is already a first derivative of the Gibbs function, the constraints would seem to be three different constraints on various third derivative of the Gibbs function. In fact, we will see that they amount to only two rather well-known constraints on second order derivatives of the Gibbs function.

From the fundamental thermodynamic relation (A.7.1) we find that (where \( T \) is the absolute temperature, \( T = T_0 + t \))
\[ \bar{\eta}_h = \left. \frac{\partial \eta}{\partial h} \right|_{S_A, p} = T^{-1} , \quad (A.16.10) \]
\[ \bar{\bar{\eta}}_{SA} = \left. \frac{\partial \eta}{\partial S_A} \right|_{h, p} = - \frac{\mu}{T} , \quad (A.16.11) \]

and from these relations the following expressions for the second order derivatives of \( \eta \) can be found,
\[ \bar{\eta}_{hh} = \left( \frac{\partial^2 \eta}{\partial h^2} \right)_{S_A, p} = \frac{\partial T}{\partial h} \left. \right|_{S_A, p} = - \frac{T^{-1} c_p}{c_p} , \quad (A.16.12) \]
\[ \bar{\bar{\eta}}_{SA, h} = \left( \frac{\partial^2 \eta}{\partial h \partial S_A} \right)_{p} = \left. \frac{\partial (-\mu / T)}{\partial h} \right|_{S_A, p} = - \frac{1}{c_p} \left( \frac{\mu}{T} \right)_T , \quad (A.16.13) \]

and
\[ \bar{\bar{\eta}}_{SA, S} = \left( \frac{\partial^2 \eta}{\partial S_A^2} \right)_{h, p} = \left. \frac{\partial (-\mu / T)}{\partial S_A} \right|_{h, p} \left. \frac{\partial h}{\partial S_A} \right|_{h, p} = - \frac{\mu_{SA_A} c_p}{T} - \frac{T^2}{c_p} \left[ \left( \frac{\mu}{T} \right)_T \right]^2 . \quad (A.16.14) \]

The last equation comes from regarding \( \bar{\eta}_{SA_A} \) as \( \bar{\eta}_{SA} = \bar{\eta}_{SA_A} \left( S_A, h \left[ S_A, t, p \right], p \right) \).

The constraint (A.16.7) that \( \bar{\eta}_{hh} < 0 \) simply requires (from (A.16.12)) that the isobaric heat capacity \( c_p \) is positive, or that \( g_{TT} < 0 \). The constraint (A.16.8) that \( \bar{\eta}_{SA_A} < 0 \), requires (from (A.16.14)) that
\[ g_{SA_A} > - \frac{T^3}{c_p} \left[ \left( \frac{\mu}{T} \right)_T \right]^2 , \quad (A.16.15) \]

that is, the second derivative of the Gibbs function with respect to Absolute Salinity \( g_{SA_A} \) must exceed some negative number. The constraint (A.16.9) that \( \left( \bar{\eta}_{hSA_A} \right)^2 < \bar{\eta}_{hh} \bar{\eta}_{SA_A} \) requires that (substituting from (A.16.12), (A.16.13) and (A.16.14))
\[ \frac{g_{SA_A}}{T^2 c_p} > 0 , \quad (A.16.16) \]

and since the isobaric heat capacity must be positive, this requirement is that \( g_{SA_A} > 0 \), and so is more demanding than (A.16.15).

We conclude that while there are the three requirements (A.16.7) to (A.16.9) on the functional form of entropy \( \eta = \eta \left( S_A, h, p \right) \) in order to satisfy the constraint of the Second Law of Thermodynamics that entropy be produced when water parcels mix, these three constraints are satisfied by the following two constraints on the form of the Gibbs function \( g \left( S_A, t, p \right) \),
\[ g_{TT} < 0 \quad (A.16.17) \]
and
\[ g_{SA_A} > 0 . \quad (A.16.18) \]
The Second Law of Thermodynamics does not impose any additional requirement on the cross derivatives \( g_{\Delta T} \) nor on any third order derivatives of the Gibbs function.

The constraint (A.16.18) can be understood by considering the molecular diffusion of salt which is known to be directed down the gradient of chemical potential \( \mu(S, t, p) \) (Landau and Lifshitz (1959)). That is, the molecular flux of salt is proportional to \( -\nabla \mu \). Expanding \( -\nabla \mu \) in terms of gradients of Absolute Salinity, of temperature, and of pressure, one finds that the first term is \( -\mu_{\Delta S} \nabla S \) and in order to avoid an unstable explosion of salt one must have \( \mu_{\Delta S} = g_{\Delta S} > 0 \). So the constraint (A.16.18) amounts to the requirement that the molecular diffusivity of salt is positive.

The two constraints (A.16.17) and (A.16.18) on the Gibbs function are well known in the thermodynamics literature. Landau and Lifshitz (1959) derive them on the basis of the contribution of molecular fluxes of heat and salt to the production of entropy (their equations 58.9 and 58.13). Alternatively, Planck (1935) as well as Landau and Lifshitz (1980) in their §96 (this is §98 in editions before the 1976 extension made by Lifshitz and Pitayevski) inferred such inequalities from thermodynamic stability considerations. It is pleasing to obtain the same constraints on the seawater Gibbs function from the above Non-Equilibrium Thermodynamics approach of mixing fluid parcels since this approach involves turbulent mixing which is the type of mixing that dominates in the ocean; (molecular diffusion has the complementary role of dissipating tracer variance).

In addition to the Second Law requirements (A.16.17) and (A.16.18) there are other constraints which the seawater Gibbs function must obey. One is that the adiabatic (and isohaline) compressibility must be positive for otherwise the fluid would expand in response to an increase in pressure which is an unstable situation. Taking \( g_p > 0 \) (since specific volume needs to be positive) the requirement that the adiabatic (and isohaline) compressibility be positive imposes the following two constraints (from (2.16.1))

\[
g_{pp} < 0 \tag{A.16.19}
\]

and

\[
(g_{TT})^2 < g_{pp} g_{TT}, \tag{A.16.20}
\]

recognizing that \( g_{TT} \) is negative (\( g_{pp} \) may, and does, take either sign). Equation (A.16.20) is more demanding of \( g_{pp} \) than is (A.16.19), requiring \( g_{pp} \) to be less than a negative number rather than simply being less than zero. This last inequality can also be regarded as a constraint on the thermal expansion coefficient \( \alpha' \), implying that its square must be less than \( g_p^2 \frac{g_{pp} g_{TT}}{g_{pp} g_{TT}} \) or otherwise the relevant compressibility \( (\kappa) \) would be negative and the sound speed complex.

The constraints on the seawater Gibbs function \( g(S, t, p) \) that have been discussed above are summarized as

\[
g_p > 0, \quad g_{\Delta S} > 0, \quad g_{pp} < 0, \quad g_{TT} < 0, \quad \text{and} \quad (g_{TT})^2 < g_{pp} g_{TT}. \tag{A.16.21}
\]

We return now to quantify the non-conservative production of entropy in the ocean. When the mixing process occurs at \( p = 0 \), the expression (A.16.6) for the production of entropy can be expressed in terms of Conservative Temperature \( \Theta \) (since \( \Theta \) is simply proportional to \( h \) at \( p = 0 \)) as follows (now entropy is taken to be the functional form \( \eta = \dot{\eta}(S, \Theta) \))

\[
\delta \eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \dot{\eta}_{\Theta_0} (\Delta \Theta)^2 + 2 \dot{\eta}_{\Theta_0} \Delta \Theta \Delta S + \dot{\eta}_{S_0 S_0} (\Delta S)^2 \right\}. \tag{A.16.22}
\]

The maximum production occurs when parcels of equal mass are mixed so that \( \frac{1}{2} m_1 m_2 m^2 = \frac{1}{8} \) and we adopt this value in what follows. To illustrate the magnitude of this non-conservation of entropy we first scale entropy by a dimensional constant so that the resulting variable ("entropic temperature") has the value 25 °C at \( (S, \Theta) = (S_{01}, 25 \, \text{°C}) \) and then \( \Theta \) is subtracted. The result is contoured in \( S - \Theta \) space in Figure A.16.1.
The fact that the variable in Figure A.16.1 is not zero over the whole $S_\lambda - \Theta$ plane is because entropy is not a conservative variable. The non-conservative production of entropy can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels and then reading off the production (in °C) of entropy from the figure. Taking the most extreme situation with one parcel at $(S_\lambda, \Theta) = (0 \text{ g kg}^{-1}, 0 \text{ °C})$ and the other at the warmest and saltiest corner of the figure, the non-conservative production of $\eta$ on mixing parcels of equal mass is approximately 0.9 °C.

Since entropy can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature $\eta = \hat{\eta}(S_\lambda, \Theta)$, and since at any pressure in the ocean both $S_\lambda$ and $\Theta$ may be considered conservative variables (see appendix A.18 below), it is clear that the non-conservative production given by (A.16.22) and illustrated in Figure A.16.1 is equivalent to the slightly more accurate expression (A.16.6) which applies at any pressure. The only discrepancy between the production of entropy calculated from (A.16.22) and that from (A.16.6) is due to the very small non-conservative production of $\Theta$ at pressures other than zero (as well as the fact that both expressions contain only the second order terms in an infinite Taylor series).

### A.17 Non-conservative production of potential temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved during the mixing process are mass, Absolute Salinity and enthalpy. As in section A.16 we again consider two parcels being mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again Eqns. (A.16.2) – (A.16.4). Potential temperature $\theta$ is not conserved during the mixing process and the production of potential temperature is given by

$$m_1 \theta_1 + m_2 \theta_2 + m \delta \theta = m \theta. \quad (A.17.1)$$

Enthalpy in the functional form $h = \tilde{h}(S_\lambda, \theta, \rho)$ is expanded in a Taylor series of $S_\lambda$ and $\theta$ about the values $S_\lambda$ and $\theta$ of the mixed fluid, retaining terms to second order in
\[ [S_{A2} - S_{A1}] = \Delta S_A \text{ and in } [\theta_2 - \theta_1] = \Delta \theta. \] Then \( h_1 \) and \( h_2 \) are evaluated and Eqns. (A.16.4) and (A.17.1) used to find

\[
\delta \theta = \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\hat{h}_{\theta \theta}}{\bar{h}_\theta} (\Delta \theta)^2 + 2 \frac{\hat{h}_{\theta S_A}}{\bar{h}_\theta} \Delta \theta \Delta S_A + \frac{\hat{h}_{S_A S_A}}{\bar{h}_\theta} (\Delta S_A)^2 \right\}, \tag{A.17.2}
\]

The maximum production occurs when parcels of equal mass are mixed so that \( \frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8} \). The “heat capacity” \( \bar{h}_\theta \) is not a strong function of \( \theta \) but is a much stronger function of \( S_A \) so the first term in the curly brackets in Eqn. (A.17.2) is generally small compared with the second term. Also, the third term in Eqn. (A.17.2) which causes the so-called “dilution heating”, is usually small compared with the second term. A typical value of \( \hat{h}_{S_A S_A} \) is approximately -5.4 J kg\(^{-1}\) K\(^{-1}\)(g kg\(^{-1}\))\(^{-1}\) (see the dependence of isobaric heat capacity on \( S_A \) in Figure 4 of section 2.20) so that an approximate expression for the production of potential temperature \( \delta \theta \) is

\[
\frac{\delta \theta}{\Delta \theta} \approx \frac{1}{8} \hat{h}_{S_A S_A} / \bar{h}_\theta \approx -3.4 \times 10^{-4} \left( \Delta S_A / [\text{g kg}\(^{-1}\)] \right). \tag{A.17.3}
\]

Since potential temperature \( \theta = \hat{\theta}(S_A, \Theta) \) can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature, and since during turbulent mixing both \( S_A \) and \( \Theta \) may be considered conservative variables (see section A.18 below), it is clear that the non-conservative production given by (A.17.2) can be approximated by the corresponding production of potential temperature that would occur if the mixing had occurred at \( p = 0 \), namely

\[
\delta \theta = \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\Theta_{\theta \theta}}{\bar{\theta}_\theta} (\Delta \theta)^2 + 2 \frac{\Theta_{\theta S_A}}{\bar{\theta}_\theta} \Delta \theta \Delta S_A + \frac{\Theta_{S_A S_A}}{\bar{\theta}_\theta} (\Delta S_A)^2 \right\}, \tag{A.17.4}
\]

where the exact proportionality between potential enthalpy and Conservative Temperature \( h^\Theta = \phi^\Theta_\theta \) has been exploited. The maximum production occurs when parcels of equal mass are mixed so that \( \frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8} \) and we adopt this value in what follows.

Equations (A.17.2) or (A.17.4) may be used to evaluate the non-conservative production of potential temperature due to mixing a pair of fluid parcels across a front at which there are known differences in salinity and temperature. The temperature difference \( \theta - \Theta \) is contoured in Figure A.17.1 and can be used to illustrate Eqn. (A.17.4). \( \delta \theta \) can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels (along which both Absolute Salinity and Conservative Temperature are conserved) and then calculating the production (in \( ^\circ C \)) of \( \theta \) from the contoured values of \( \theta - \Theta \). Taking the most extreme situation with one parcel at \( (S_A, \Theta) = (0 \text{ g kg}^{-1}, 0 ^\circ C) \) and the other at the warmest and saltiest corner of Figure A.17.1, the non-conservative production of \( \theta \) on mixing parcels of equal mass is approximately -0.55 \( ^\circ C \). This is to be compared with the corresponding maximum production of entropy, as discussed above in connection with Figure A.16.1, of approximately 0.9 \( ^\circ C \).

If Figure A.17.1 were to be used to quantify the errors in oceanographic practice incurred by assuming that \( \theta \) is a conservative variable, one might select property contrasts that were typical of a prominent oceanic front and decide that because \( \delta \theta \) is small at this one front, that the issue can be ignored (see for example, Warren (2006)). But the observed properties in the ocean result from a large and indeterminate number of such prior mixing events and the non-conservative production of \( \theta \) accumulates during each of these mixing events, often in a sign-definite fashion. How can we possibly estimate the error that is made by treating potential temperature as a conservative variable during all of these unknowably many past individual mixing events? This seemingly difficult issue is partially resolved by considering what is actually done in ocean models today. These models carry a temperature conservation equation that does not have non-conservative source terms, so that the model’s temperature variable is best interpreted as being \( \Theta \). This
being the case, the temperature difference contoured in Figure A.17.1 illustrates the error that is made by interpreting the model temperature as being \( \theta \). That is, the values contoured in Figures A.16.1 and A.17.1 are representative of the error, expressed in °C, associated with assuming that \( \eta \) and \( \theta \) respectively are conservative variables. These contoured values of temperature difference encapsulate the accumulated non-conservative production that has occurred during all the many mixing processes that have lead to the ocean’s present state. The maximum such error for \( \eta \) is approximately -1.0 °C (from Figure A.16.1) while for \( \theta \) the maximum error is approximately -1.8 °C (from Figure A.17.1). One percent of the data at the sea surface of the world ocean have values of \( \theta - \Theta \) that lie outside a range that is 0.25 °C wide (McDougall (2003)), implying that this is the magnitude of the error incurred by ocean models when they treat \( \theta \) as a conservative quantity. From the curvature of the isolines on Figure A.17.1 it is clear that the non-conservative production of potential temperature takes both positive and negative signs.

![Figure A.17.1](image)

**Figure A.17.1.** Contours (in °C ) of the difference between potential temperature and Conservative Temperature \( \theta - \Theta \). This plot illustrates the non-conservative production of potential temperature \( \theta \) in the ocean.

### A.18 Non-conservative production of Conservative Temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved during the mixing process are mass, Absolute Salinity and enthalpy. As in sections A.16 and A.17 we consider two parcels being mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again Eqns. (A.16.2) – (A.16.4). Potential enthalpy \( h^0 \) and Conservative Temperature \( \Theta \) are not exactly conserved during the mixing process and the production of \( \Theta \) is given by
\[ m_1 \Theta_1 + m_2 \Theta_2 + m \Theta = m \Theta. \]

(A.18.1)

Enthalpy in the functional form \( h = \hat{h}(S_A, \Theta, p) \) is expanded in a Taylor series of \( S_A \) and \( \Theta \) about the values \( S_A \) and \( \Theta \) of the mixed fluid, retaining terms to second order in \( [S_{A2} - S_{A1}] = \Delta S_A \) and in \( [\Theta_2 - \Theta_1] = \Delta \Theta \). Then \( h_1 \) and \( h_2 \) are evaluated and Eqns. (A.16.4) and (A.18.1) are used to find

\[ \Theta = \frac{m_1 m_2}{m \Theta} \left( \frac{\hat{h}_{\Theta \Theta}(\Delta \Theta)^2}{\hat{h}_\Theta} + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \Delta \Theta \Delta S_A + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} (\Delta S_A)^2 \right). \]

(A.18.2)

In order to evaluate these partial derivatives, we first write enthalpy in terms of potential enthalpy (i.e. \( c^0_p \Theta \)) using Eqn. (3.2.1), as

\[ h = \hat{h}(S_A, \Theta, p) = c_p^0 \Theta + \int_{\hat{h}_\Theta}^{\hat{h}_\Theta}(S_A, \Theta, p') dP'. \]

(A.18.3)

This is differentiated with respect to \( \Theta \) giving

\[ \hat{h}_{\Theta}\Big|_{S_A, p} = \hat{h}_\Theta = c_p^0 + \int_{\hat{h}_\Theta}^{\hat{h}_\Theta} \frac{\alpha^0}{\rho} dP'. \]

(A.18.4)

The right-hand side of Eqn. (A.18.4) scales as \( c_p^0 + \rho^{-1}(P - P_0) \alpha^0 \), which is more than \( c_p^0 \) by only about \( 0.0015 c_p^0 \) for \( (P - P_0) \) of \( 4 \times 10^7 \) Pa (4,000 dbar). Hence, to a very good approximation, \( \hat{h}_\Theta \) in Eqn. (A.18.2) may be taken to be simply \( c_p^0 \). It is interesting to examine why this approximation is so accurate when the difference between enthalpy, \( h \), and potential enthalpy, \( h^0 \), as given by Eqns. (3.2.1) and (A.18.3), scales as \( \rho^{-1} \) which is as large as typical values of potential enthalpy. The reason is that the integral in Eqns. (3.2.1) or (A.18.3) is dominated by the integral of the mean value of \( \rho^{-1} \), so causing a significant offset between \( h \) and \( h^0 \) as a function of pressure but not affecting the partial derivative \( \hat{h}_\Theta \) which is taken at fixed pressure. Even the dependence of density on pressure alone does not affect \( \hat{h}_\Theta \).

The second order derivatives of \( \hat{h} \) are needed in Eqn. (A.18.2), and these can be estimated in terms of the strength of cabling as follows. Equation (A.18.4) is differentiated with respect to Conservative Temperature, giving

\[ \hat{h}_{\Theta \Theta} = \int_{\hat{h}_\Theta}^{\hat{h}_\Theta} \frac{\alpha^0}{\rho} dP' \approx \rho^{-1} \int_{\hat{h}_\Theta}^{\hat{h}_\Theta} \left( \frac{\alpha^0}{\rho} \right)_\Theta dP'. \]

(A.18.5)

so that we may write Eqn. (A.18.2) approximately as (assuming \( m_1 = m_2 \))

\[ \Theta = \frac{(P - P_0)}{8 \rho c_p^0} \left( \alpha^0_\Theta (\Delta \Theta)^2 + 2 \alpha^0_{S_A} \Delta \Theta \Delta S_A - \beta^0_{S_A} (\Delta S_A)^2 \right). \]

(A.18.6)

Equation (A.18.6) shows that the non-conservative production of Conservative Temperature is approximately proportional to the non-conservative production of density at fixed pressure (see Eqn. (A.19.4) below), often referred to loosely as "cabling" (McDougall, 1987b),

\[ \delta \rho = \frac{1}{2} \rho \left( \alpha^0_\Theta (\Delta \theta)^2 + 2 \alpha^0_{S_A} \Delta \theta \Delta S_A - \beta^0_{S_A} (\Delta S_A)^2 \right). \]

(A.18.7)

The production of \( \Theta \) causes an increase (or decrease) and a consequent change in density of \(-\rho \alpha^0 \Theta \). The ratio of this increase in density (using Eqn. (A.18.6)) to that caused by cabling (from Eqn. (A.18.7)) is \(-\frac{(P - P_0)}{\rho \alpha_p^0} \) which is about 0.0015 for a value of pressure \((P - P_0)\) of 40 MPa (4000 dbar). Hence it is clear that cabling has a much larger effect on density than does the non-conservation of \( \Theta \). Nevertheless, from Eqn. (A.18.6) we see that the non-conservative production of \( \Theta \) is proportional to the product of sea pressure and the strength of cabling.
The first term in the bracket in Eqn. (A.18.6) is usually about a factor of ten larger than the other two terms (McDougall (1987b)), so the production of Conservative Temperature $\partial$ as a ratio of the contrast in Conservative Temperature $\Delta\Theta = \Theta_2 - \Theta_1$ may be approximated as

$$\frac{\partial \Theta}{\Delta \Theta} \approx \frac{(P - P_0) \alpha_\Theta^\partial \Delta \Theta}{8 p c_p^\theta} \approx 3.3 \times 10^{-9} \left( \frac{\Delta \Theta}{K} \right).$$  \hfill (A.18.8)$$

where $\alpha_\Theta^\partial$ has been taken to be $1.1 \times 10^{-5} \text{K}^{-2}$ (McDougall, 1987b).

At the sea surface Conservative Temperature $\Theta$ is totally conserved ($\partial \Theta = 0$). The non-conservative production of Conservative Temperature, $\partial \Theta$, increases linearly with pressure (see Eqn. (A.18.6)) but at larger pressure the range of temperature and salinity in the ocean decreases, and from the above equations it is clear that the magnitude of $\partial \Theta$ decreases proportionally to the square of the temperature and salinity contrasts. McDougall (2003) concluded that the production $\partial \Theta$ between extreme seawater parcels at each pressure is largest at 600 dbar, and the magnitude of the non-conservative production of Conservative Temperature, $\partial \Theta$, is illustrated in Figure A.18.1 for data at this pressure. The quantity contoured on this figure is the difference between $\Theta$ and the following totally conservative quantity at $p = 600$ dbar. This conservative quantity was constructed by taking the conservative property enthalpy $h$ at this pressure and adding the linear function of $S_A$ which makes the result equal to zero at $(S_A=0, \Theta=0 \degree C)$ and at $(S_A=35.165 \ 04\text{gkg}^{-1}, \Theta=0 \degree C)$. This quantity is then scaled so that it becomes $25 \degree C$ at $(S_A=35.165 \ 04\text{gkg}^{-1}, \Theta=25 \degree C)$. In this manner the quantity that is contoured in Figure A.18.1 has units of $\degree C$ and represents the amount by which Conservative Temperature $\Theta$ is not a totally conservative variable at a pressure of 600 dbar. The maximum amount of production by mixing seawater parcels at the boundaries of Figure A.18.1 is about $4\times10^{-3} \degree C$ although the range of values encountered in the real ocean at this pressure is actually quite small, as indicated in Figure A.18.1. McDougall (2003) concludes that the maximum non-conservation of $\Theta$ in the real ocean is a factor of approximately a hundred less than the maximum non-conservative production of potential temperature $\theta$.

![Figure A.18.1. Contours (in $\degree C$) of a variable that is used to illustrate the non-conservative production of Conservative Temperature $\Theta$ at $p = 600$ dbar. The cloud of points show where most of the oceanic data reside at $p = 600$ dbar. The three points that are forced to be zero are shown with black dots.](image)
From the curvature of the isolines on Figure A.18.1 it is clear that the non-conservative production of Conservative Temperature at \( p = 600 \) dbar is positive, so that an ocean model that ignores this production of Conservative Temperature will slightly underestimate \( \Theta \). From Eqn. (A.18.2) one sees the non-conservative production of Conservative Temperature is always positive if \( \hat{h}_{\Theta\Theta} > 0 \), \( \hat{h}_{\Theta S} > 0 \) and \( (\hat{h}_{\Theta\Theta})^2 < \hat{h}_{\Theta\Theta} \hat{h}_{SS} \) everywhere, and it can be shown that these requirements are in fact met.

From Eqns. (A.18.8) and (A.17.3) we can write the ratio of the production of Conservative Temperature to the production of potential temperature when two seawater parcels mix as the approximate expression

\[
\frac{\partial \Theta}{\partial \theta} \approx -10^{-5} \left( \frac{p}{\text{dbar}} \right) \left( \frac{\Delta \Theta}{K} \right) \left( \frac{\Delta S_A}{[\text{g kg}^{-1}]} \right)^{-1}.
\] (A.18.9)

Taking a typical ratio of temperature differences to salinity differences in the deep ocean to be 10 K/\([\text{g kg}^{-1}]\), Eqn. (A.18.9) becomes \( \partial \Theta/\partial \theta \approx -10^{-4} \left( \frac{p}{\text{dbar}} \right) \). At a pressure of 4000 dbar this ratio is \( \partial \Theta/\partial \theta \approx -0.4 \) implying that Conservative Temperature is almost as non-conservative as is potential temperature. While this is the case, the temperature and salinity contrasts in the deep ocean are small, so the non-conservation of both types of temperature amount to very small temperature increments of both \( \partial \theta \) and \( \partial \Theta \). The largest non-conservative increment of Conservative Temperature \( \partial \Theta \) seems to occur at a pressure of about 600 dbar (McDougall (2003)) and this value of \( \partial \Theta \) is two orders of magnitude less than the maximum value of \( \partial \theta \) which occurs at the sea surface. The material in appendices A.16 - A.18 has closely followed the paper of McDougall (2003).

A.19 Non-conservative production of density and of potential density

For the purpose of calculating the non-conservative production of density we take both Absolute Salinity \( S_A \) and Conservative Temperature \( \Theta \) to be 100% conservative (see appendix A.18 above). Density is written in the functional form

\[
\rho = \tilde{\rho}(S_A, \Theta, p)
\] (A.19.1)

and the same mixing process between two fluid parcels is considered as in the previous appendices. Mass and Absolute Salinity are conserved during the turbulent mixing process (Eqns. (A.16.2) and (A.16.3)) as is Conservative Temperature, that is

\[
m_1 \Theta_1 + m_2 \Theta_2 = m \Theta,
\] (A.19.2)

while the non-conservative nature of density means that it obeys the equation,

\[
m_1 \rho_1 + m_2 \rho_2 + m \delta \rho = m \rho.
\] (A.19.3)

Density is expanded in a Taylor series of \( S_A \) and \( \Theta \) about the values of \( S_A \) and \( \Theta \) of the mixed fluid, retaining terms to second order in \( [S_{A2} - S_{A1}] = \Delta S_A \) and in \( [\Theta_2 - \Theta_1] = \Delta \Theta \). Then \( \rho_1 \) and \( \rho_2 \) are evaluated and (A.19.3) is used to find

\[
\delta \rho = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \tilde{\rho}_{\Theta \Theta} (\Delta \Theta)^2 + 2 \tilde{\rho}_{\Theta S} \Delta \Theta \Delta S_A + \tilde{\rho}_{SS} (\Delta S_A)^2 \right\}.
\] (A.19.4)

The non-conservative production of density \( \delta \rho \) of Eqn. (A.19.4) is illustrated in Figure A.19.1 for mixing at \( p = 0 \) dbar. That is, this figure shows the production \( \delta \rho^\theta \) of potential density \( \rho^\theta \) (note that the symbol \( \rho^\theta \) could equally well be used for potential density). The quantity contoured on this figure is formed as follows. First the linear function of \( S_A \) is found that is equal to \( \rho^\theta \) at \( (S_A = 0, \Theta = 0 \degree C) \) and at \( (S_A = 35.165 \text{ g kg}^{-1}, \Theta = 0 \degree C) \). This linear function of \( S_A \) is subtracted from \( \rho^\theta \) and the result is scaled to equal 25 \degree C at \( (S_A = 35.165 \text{ g kg}^{-1}, \Theta = 25 \degree C) \). The variable that is contoured in Figure A.19.1 is the difference between this scaled linear combination of \( \rho^\theta \) and \( S_A \), and Conservative Temperature. This figure allows the non-conservative nature
of density to be understood in temperature units. The mixing of extreme fluid parcels on Figure A.19.1 causes the same increase in density as a cooling of approximately 10 °C. From Figure A.18.1 it is seen that the (tiny) non-conservative nature of $\Theta$ is a factor of approximately 4000 smaller than this.

Figure A.19.1. Contours (in °C) of a variable that is used to illustrate the non-conservative production of potential density $\rho^\theta$. The three points that are forced to be zero are shown with black dots.

A.20 The representation of salinity in numerical ocean models

Ocean models need to evaluate salinity at every time step as a necessary prelude to using the equation of state to determine density and its derivatives for use in the hydrostatic relationship and frequently in neutral mixing algorithms. The current practice in numerical models is to treat salinity as a perfectly conserved quantity in the interior of the ocean; salinity changes at the surface and at coastal boundaries due to evaporation, precipitation, brine rejection, ice melt and river runoff and satisfies an advection-diffusion equation away from these boundaries. The inclusion of composition anomalies necessitates several changes to this approach. These changes can be divided into two broad categories. First, in addition to fresh water inputs and brine rejection, all sources of dissolved material entering through the surface and coastal boundaries of the model should be considered as possible sources of composition anomalies. Second, within the interior of the model, changes due to the growth, decay and remineralization of biological material must be considered. Here, we focus on this second issue. While the ultimate resolution of these issues will involve biogeochemical models, in this appendix we discuss some practical ways forward based on the approximate relations (A.4.5) and (A.4.6) between the salinity variables $S_R$, $S_A$ and $S_A = S_{\text{dens}}$ that were discussed in section A.4. At the time of writing, the suggested approaches here have not been tested, so it must be acknowledged that the treatment of seawater composition anomalies in ocean models is currently a work in progress.

We begin by restating Eqns. (A.4.5) and (A.4.6), namely

$$S_R - S_A \approx \eta_1 \delta S_{\text{dens}},$$

(A.20.1)
\[ S_A^{\text{dens}} - S_* \approx (1 + r_1) \, \delta S_R^{\text{dens}}, \]  
(A.20.2)

where \( r_1 \) will be taken to be the constant 0.35 based on the work of Pawlowicz et al. (2010), and in this section these approximate relations will be taken to be exact. The Absolute Salinity Anomaly \( \delta S_R^{\text{dens}} \equiv S_A^{\text{dens}} - S_R \) is the salinity difference that can be directly measured from seawater samples using a vibrating beam densimeter and knowledge of the sample’s Practical Salinity, and a global look-up table exists for this quantity (McDougall et al. (2010a)). Because this particular salinity difference is based on direct measurements, it is the natural measure of the anomalous composition of seawater to use in developing the following options for numerical modeling of composition anomalies.

### A.20.1 Using Preformed Salinity as the conservative salinity variable

Because Preformed Absolute Salinity \( S_* \) (henceforth referred to by the shortened name, Preformed Salinity) is designed to be a conservative salinity variable, blind to the effects of biogeochemical processes, its evolution equation will be in the conservative form (A.8.1).

When this type of conservation equation is averaged in the appropriate manner (see appendix A.21) the conservation equation for Preformed Salinity becomes (from Eqn. (A.21.7)),

\[
\frac{d \hat{S}_*/d t} = \frac{1}{h} \nabla_n \cdot (hK \nabla_n \hat{S}_*) + \left( D \frac{\partial \hat{S}_*/\partial z} \right) z. 
\]  
(A.20.3)

As explained in appendix A.21, the over-tildes of \( \hat{S}_* \) indicates that this variable is the thickness-weighted average Preformed Salinity, having been averaged between a pair of closely spaced neutral tangent planes. The material derivative on the left-hand side of Eqn. (A.20.3) is with respect to the sum of the Eulerian and quasi-Stokes velocities of height coordinates (equivalent to the description in appendix A.21 in terms of the thickness-weighted average horizontal velocity and the mean dianeutral velocity), while the right-hand side of this equation is the standard notation indicating that \( \hat{S}_* \) is being diffused along neutral tangent planes with the diffusivity \( K \) and in the vertical direction with the diapycnal diffusivity \( D \) (and \( h \) here is the average thickness between two closely spaced neutral tangent planes).

In order to evaluate density during the running of an ocean model, Density Salinity must be evaluated. This can be done from Eqn. (A.20.2) as the sum of the model’s salinity variable \( \hat{S}_* \) and \( (1 + r_1) \, \delta S_R^{\text{dens}} \). This could be done by simply adding to the model’s salinity variable \( (1 + r_1) \) times the fixed spatial map of \( \delta S_R^{\text{dens}} \) (obs) as observed today (and as is available from the computer algorithm of McDougall et al. (2010a)). However experience has shown that even a smooth field of density errors can result in significant anomalies in diagnostic model calculations, primarily due to the misalignment of the density errors and the model bottom topography. Indeed, even if the correct mean density could somehow be determined, approximations associated with the specification of the model bottom topography would result in significant errors in bottom pressure torques that can degrade the model solution. One way to minimize such errors is to allow some dynamical adjustment of the specified density field so that, for example, density contours tend to align with bottom depth contours where the flow is constrained to follow bottom topography. This simple idea is the key to the success of the robust diagnostic approach (Sarmiento and Bryan (1982)). To allow dynamical adjustment of the Absolute Salinity Anomalies \( \delta S_R^{\text{dens}}(x,y,p) \) while not permitting them to develop large differences from the observed values \( \delta S_R^{\text{dens}} \) (obs), we recommend carrying an evolution equation for \( \delta S_R^{\text{dens}} \) so that it becomes an extra model variable which evolves according to

\[
\frac{d \delta S_R^{\text{dens}}}{d t} = \frac{1}{h} \nabla_n \cdot (hK \nabla_n \delta S_R^{\text{dens}}) + \left( D \frac{\partial \delta S_R^{\text{dens}}/\partial z} \right) z + v^{-1} \left( \delta S_R^{\text{dens}} \text{(obs)} - \delta S_R^{\text{dens}} \right). 
\]  
(A.20.4)
Here the model variable $\delta S_R^{\text{dens}}$ would be initialized based on observations, $\delta S_R^{\text{dens}}(\text{obs})$, and advected and diffused like any other tracer, but in addition, there is a non-conservative source term $\tau^{-1}(\delta S_R^{\text{dens}}(\text{obs}) - \delta S_R^{\text{dens}})$ which serves to restore the model variable $\delta S_R^{\text{dens}}$ towards the observed value with a restoring time $\tau$ that can be chosen to suit particular modeling needs. It should be at least 30 days to permit significant adjustment, but it might prove appropriate to allow a much longer adjustment period (up to several years) if drift from observations is sufficiently slow. The lower bound is based on a very rough estimate of the time required for the density field to be aligned with topography by advective processes. The upper bound is set by the requirement to have the restoring time relatively short compared to vertical and basin-scale horizontal redistribution times.

Ideally one would like the non-conservative source term to reflect the actual physical and chemical processes responsible for remineralization in the ocean interior, but until our knowledge of these processes improves such that this is possible, the approach of Eqn. (A.20.4) provides a way forward. An indication of how this approach might be improved in the future can be gleaned from looking at Eqn. (A.4.14) for $S_A^\text{dens} - S$, (taken from Pawlowicz et al. (2010)). If a biogeochemical model produces estimates of the quantities on the right-hand side of this equation, it could be immediately integrated into an ocean model to diagnose the effects of the included biogeochemical processes on the model’s density and its circulation.

In summary, the approach suggested here carries the evolution Eqns. (A.20.3) and (A.20.4) for $\delta S_r$ and $\delta S_A^{\text{dens}}$, while $\delta S_A^{\text{dens}}$ is calculated by the model at each time step according to

$$\delta S_A^{\text{dens}} = \delta S_r + (1 + \eta) \delta S_A^{\text{dens}},$$

with our best present estimate of $(1 + \eta)$ being 1.35. The model is initialized with values of Preformed Salinity using Eqn. (A.20.1) (namely $\delta S_r = \delta S_R - \eta \delta S_A^{\text{dens}}$) based on observations of Reference Salinity and on the global data base of $\delta S_R^{\text{dens}}(\text{obs})$ from McDougall et al. (2010a).

### A.20.2 Including a source term in the evolution equation for Absolute Salinity

An equivalent procedure is to carry the following evolution equation (A.20.6) for Absolute Salinity, which more specifically, is called Density Salinity, $S_A = S_A^{\text{dens}}$. On inspection of Eqn. (A.20.2), $S_A^{\text{dens}} - S_r \approx (1 + \eta) \delta S_R^{\text{dens}}$, and recognizing that $S_r$ is a conservative variable, it is clear that the non-conservative production of $S_A^{\text{dens}}$ must occur at the rate $(1 + \eta)$ times the rate at which the same non-conservative processes affect the Absolute Salinity Anomaly $S_A^{\text{dens}}$. Since (from Eqn. (A.20.4)) the non-conservative source term for $\delta S_R^{\text{dens}}$ is $\tau^{-1}(\delta S_R^{\text{dens}}(\text{obs}) - \delta S_R^{\text{dens}})$, we find that the evolution equation for Density Salinity to be

$$\frac{dS_A^{\text{dens}}}{dr} = \frac{1}{\rho} \nabla \cdot \left( hK \nabla S_A^{\text{dens}} \right) + \left( D \frac{\partial S_A^{\text{dens}}}{\partial z} \right)_z + (1 + \eta) \tau^{-1}(\delta S_R^{\text{dens}}(\text{obs}) - \delta S_R^{\text{dens}})$$

Alternatively, this equation can be derived by summing Eqn. (A.20.3) plus $(1 + \eta)$ times Eqn. (A.20.4). Here the non-conservative source term in the evolution equation for Density Salinity has been given the label $\delta S_A^{\text{dens}}$ for later use.

In this approach the evolution equation (A.20.4) for $\delta S_R^{\text{dens}}$ is also carried and the model’s salinity variable, $S_A^{\text{dens}}$, is used directly as the argument of the equation of state and other thermodynamic functions in the model. The model would be initialized with values of Density Salinity using Eqn. (A.4.2) (namely $S_A^{\text{dens}} = \delta S_R + \delta S_R^{\text{dens}}$) based on
observations of Reference Salinity and on the global data base of $\delta S_R^\text{dens}(\text{obs})$ from McDougall et al. (2010a).

This approach should give identical results to that described in section A.20.1 using Preformed Salinity. One disadvantage of having Density Salinity as the model’s salinity variable is that its evolution equation (A.20.6) is not in the conservative form so that, for example, it is not possible to perform easy global budgets of salinity to test for the numerical integrity of the model code. Another disadvantage is that the air-sea flux of carbon dioxide and other gases may need to be taken into account as the surface boundary condition of Density Salinity. Such air-sea fluxes do not affect Preformed Salinity.

### A.20.3 Including a source term in the evolution equation for Reference Salinity

An equivalent procedure is to carry the following evolution equation (A.20.7) for Reference Salinity. On inspection of Eqn. (A.20.1), $S_R - S_* \approx \eta \delta S_R^\text{dens}$, and recognizing that $S_*$ is a conservative variable, it is clear that the non-conservative production of $S_R$ must occur at the rate $\eta$ times the rate at which the same non-conservative processes affect the Absolute Salinity Anomaly $\delta S_R^\text{dens}$. Since (from Eqn. (A.20.4)) the non-conservative source term for $\delta S_R^\text{dens}$ is $\tau^{-1}(\delta S_R^\text{dens}(\text{obs}) - \delta S_R^\text{dens})$, the evolution equation for Reference Salinity is

$$
\frac{d\hat{S}_R}{d \tau} = \frac{1}{\eta} \nabla \cdot \left( h K \nabla \hat{S}_R \right) + \left( D \frac{\partial \hat{S}_R}{\partial z} \right)_z + \eta \tau^{-1}(\delta S_R^\text{dens}(\text{obs}) - \delta S_R^\text{dens})
$$

(A.20.7)

where the non-conservative source term is $\eta/(1 + \eta)$ times the corresponding source term in the evolution equation for Density Salinity in Eqn. (A.20.6).

In this approach the evolution Eqsns. (A.20.7) and (A.20.4) for $\hat{S}_R$ and $\delta S_R^\text{dens}$ are carried by the ocean model, while $\hat{S}_R^\text{dens}$ is calculated by the model at each time step according to Eqn. (A.4.2), namely

$$
\hat{S}_R^\text{dens} = \hat{S}_R + \delta S_R^\text{dens}.
$$

(A.20.8)

This approach, like that of section A.20.2 should give identical results to that described in section A.20.1 using Preformed Salinity except for the more complicated air-sea flux boundary condition for Reference Salinity than for Preformed Salinity. It does seem that the conservative nature of Eqn. (A.20.3) for Preformed Salinity is a significant advantage, and so this approach is likely to be preferred by ocean modelers.

### A.20.4 Discussion of the consequences if remineralization is ignored

If an ocean model does not carry the evolution equation for Absolute Salinity Anomaly (Eqn. (A.20.4)) and the model’s salinity evolution equation does not contain the appropriate non-conservative source term, is there then any preference to initializing and interpreting the model’s salinity variable as either Preformed Salinity, Absolute Salinity or Reference Salinity? That is, the simplest method of dealing with these salinity issues is to continue the general approach that has been taken for the past several decades of simply taking one type of salinity in the model and that salinity is taken to be conservative. Under this approximation the salinity that is used in the equation of state to calculate density in the model is the same as the salinity that obeys a normal conservation equation of the form Eqn. (A.20.3). In this approach there is still a choice of how to initialize the salinity in a model, and here we discuss the relative virtues of these options.

If the model is initialized with a data set of estimated Preformed Salinity $S_*$, then $S_*$ should evolve correctly, since $S_*$ is a conservative variable and its evolution equation Eqn. (A.20.3) contains no non-conservative source terms. In this approach the equation of state
will be called with \( \hat{S} \), rather than \( \hat{S}_{\text{A}}^{\text{dens}} \), and these salinities differ by approximately \((1 + \eta) \delta S_{\text{R}}^{\text{dens}}\). The likely errors with this approach can be estimated using the simple example of Figure A.5.1. The vertical axis in this figure is the difference between the northward density gradient at constant pressure when the equation of state is called with \( \hat{S}_{\text{A}}^{\text{dens}} \) and with \( \hat{S}_{\text{R}} \). The figure shows that when using \( \hat{S}_{\text{R}} \) for all the data in the world ocean below a depth of 1000 m, 58% of this data is in error by more than 2%. If this graph were re-done with \( \hat{S} \) as the salinity argument rather than \( \hat{S}_{\text{R}} \), the errors would be larger in the ratio \((1 + \eta) \approx 1.35\). That is, for 58% of the data in the world ocean deeper than 1000 m, the “thermal wind” relation would be misestimated by \( \eta \approx 2.7\% \) if \( \hat{S} \) is used in place of \( \hat{S}_{\text{A}}^{\text{dens}} \) as the salinity argument to the equation of state. Also, these percentage errors in “thermal wind” are larger in the Pacific Ocean.

Another choice of the salinity data to initialize the model is \( \hat{S}_{\text{A}}^{\text{dens}} \). This choice has the advantage that for an initial period of time after initialization the equation of state is called with the correct salinity variable. However at later times, the neglect of the non-conservative source term in Eqn. (A.20.6) means that the model’s salinity variable will depart from reality and errors will creep in due to the lack of these legitimate non-conservative source terms. How long might it be acceptable to integrate such a model before the errors approached those described in the previous paragraph? One could imagine that in the upper ocean the influence of these different salinity variables is dwarfed by other physics such as air sea interaction and active gyral motions. If one considered a depth of 1000m as being a depth where the influence of the different salinities would be both apparent and would make a significant impact on the thermal wind equation, then one might guess that it would take several decades for the neglect of the non-conservative source terms in the evolution equation for Density Salinity to begin to be important. This is not to suggest that the relaxation time scale \( \tau \) should be chosen to be as long as this, rather this is an estimate of how long it would take for the neglect of the non-conservative source term \( \delta S_{\text{A}} \) in Eqn. (A.20.6) to become significant.

A third choice is to initialize the model with Reference Salinity, \( \hat{S}_{\text{R}} \). This choice incurs the errors displayed in Figure A.5.1 right from the start of any numerical simulation. Thereafter, on some unknown timescale, further errors will arise because the conservation equation for Reference Salinity is missing the legitimate non-conservative source terms that represent the effects of biogeochemistry on conductivity and \( \hat{S}_{\text{R}} \). Hence this choice is the least desired of the three considered in this subsection. Note that this choice is basically the approach that has been used to date in ocean modeling studies since we have routinely initialized models with observations of Practical Salinity and have treated it as though it were a conservative variable and have used it as the salinity argument for the equation of state.

In principle, there are other combinations of options where the evolution equation for Absolute Salinity Anomaly (A.20.4) is carried by an ocean model, but some option other than those discussed in subsections A.20.1 – A.20.3 is pursued. We do not consider these various options here, since if one goes to the trouble of carrying the evolution equation for Absolute Salinity Anomaly, then one should be sufficiently careful to implement one of the options discussed in subsections A.20.1 – A.20.3.

### A.20.5 Discussion of the options for including remineralization

The approaches of subsections A.20.1 – A.20.3 of this appendix can each account for the non-conservative effects of remineralization if \( \eta \) is a constant and so long as the appropriate boundary conditions are imposed. The advantage of using \( \hat{S} \) is that it obeys a standard conservative evolution equation (A.20.3) with no source term on the right-hand side. Since \( S \) is designed to be a conservative salinity variable, it would appear to be the most appropriate salinity variable for having as an axis of the traditional "\( S - \theta \) diagram",...
which would then become the $S_\ast - \Theta$ diagram. Similarly, $\dot{S}_\ast$ would also be the best choice for the salinity variable in an inverse study.

If an ocean model were to be run without carrying the evolution equation for Absolute Salinity Anomaly (A.20.4) and hence without the ability to incorporate the appropriate non-conservative source terms in either Eqns. (A.20.6) or (A.20.7), then the model must resort to carrying only one salinity variable, and this salinity variable must be treated as a conservative variable in the ocean model. In this circumstance, we advise that the ocean’s salinity variable be interpreted as Density Salinity, and initialized as such. In this way, the errors in the thermal wind equation will develop only slowly over a time scale of several decades or more in the deep ocean.

It should be noted that each of the modelling approaches described in subsections A.20.1 – A.20.3 are related to today’s estimate of the $\delta S_{\ast,\text{ens}}^\text{obs}$ field. This field will change not only as the observational data base improves but also as the ocean composition evolves with time.

### A.21 The material derivatives of $S_\ast$, $S_A$, $S_R$ and $\Theta$ in a turbulent ocean

Preformed Salinity $S_\ast$ is designed to be a conservative variable which obeys the following instantaneous conservation equation (based on Eqn. (A.8.1))

$$
\left( \rho S_\ast \right)_t + \nabla \cdot (\rho \mathbf{u} S_\ast) = \rho \frac{dS_\ast}{dt} = -\nabla \cdot \mathbf{F}^S.
$$

(A.21.1)

There are several different contributions to the molecular flux of salt $\mathbf{F}^S$, expressions for which can be seen at equation (58.11) of Landau and Lifshitz (1959) and in Eqn. (B.23) below. For completeness, we repeat the continuity equation (A.8.2) here as

$$
\rho_1 + \nabla \cdot (\rho \mathbf{u}) = 0.
$$

(A.21.2)

Temporally averaging this equation in Cartesian coordinates (i.e. at fixed $x, y, z$) gives

$$
\overline{\rho} + \nabla \cdot (\overline{\rho \mathbf{u}}) = 0,
$$

(A.21.3)

which we choose to write in the following form, after division by a constant density $\rho_0$ (usually taken to be 1035 kg m$^{-3}$, see Griffies (2004))

$$
\left( \frac{\overline{\rho}}{\rho_0} \right)_t + \nabla \cdot \overline{\mathbf{u}} = 0 \quad \text{where} \quad \overline{\mathbf{u}} = \frac{\overline{\rho \mathbf{u}}}{\rho_0}.
$$

(A.21.4)

This velocity $\overline{\mathbf{u}}$ is actually proportional to the average mass flux of seawater per unit area.

The conservation equation for Preformed Salinity (A.21.1) is now averaged in the corresponding manner obtaining (McDougall et al. 2002)

$$
\left( \frac{\overline{\rho}}{\rho_0} \overline{S_\ast^\rho} \right)_t + \nabla \left( \overline{\mathbf{u}} \overline{S_\ast^\rho} \right) = \frac{\overline{\rho}}{\rho_0} \frac{\partial \overline{S_\ast^\rho}}{\partial t} + \overline{\mathbf{u}} \cdot \nabla \overline{S_\ast^\rho} = -\frac{1}{\overline{\rho}} \nabla \cdot \overline{\mathbf{F}^S} - \frac{1}{\overline{\rho}} \nabla \cdot \left( \overline{\rho \mathbf{u} S_\ast^\rho} \right).
$$

(A.21.5)

Here the Preformed Salinity has been density-weighted averaged, that is, $\overline{S_\ast^\rho} = \overline{\rho S_\ast}/\overline{\rho}$, and the double primed quantities are deviations of the instantaneous quantity from its density-weighted average value. Since the turbulent fluxes are many orders of magnitude larger than molecular fluxes in the ocean, the molecular flux of salt is henceforth ignored.

The averaging process involved in Eqn. (A.21.5) has not invoked the traditional Boussinesq approximation. The above averaging process is best viewed as an average over many small-scale mixing processes over several hours, but not over mesoscale time and space scales. This later averaging over the energetic mesoscale eddies is not always necessary, depending on the scale of the piece of ocean or ocean model that is under investigation. The two-stage averaging processes, without invoking the Boussinesq approximation, over first small-scale mixing processes (several meters) followed by averaging over the mesoscale (of order 100 km) has been performed by Greatbatch and McDougall (2003), yielding the prognostic equation for Preformed Salinity.
Here the over-caret means that the variable (e.g. $\hat{S}_S$) has been averaged in a thickness-and-density-weighted manner between a pair of “neutral surfaces” a small distance $h$ apart in the vertical, $\hat{v}$ is the thickness-and-density-weighted horizontal velocity, $\hat{e}$ is the dianeutral velocity (the vertical velocity that penetrates through the neutral tangent plane) and $\hat{e}^*$ is the temporal average of $\hat{e}$ on the “neutral surface” (that is, $\hat{e}^*$ is not thickness-weighted). The turbulent fluxes are parameterized by the epineutral diffusivity $K$ and the dianeutral (or vertical) diffusivity $D$. The density value $\hat{\rho}$ is the density whose average height is the height at which the equation is evaluated. The issues of averaging involved in Eqns. (A.21.5) and (A.21.6) are subtle, and are not central to our purpose in this thermodynamic manual. Hence we proceed with the more standard Boussinesq approach, but retain the over-carets to remind the reader of the thickness-weighted nature of the variables.

Having derived this evolution equation (A.21.6) for Preformed Salinity without invoking the Boussinesq approximation, we now follow common practice and invoke this approximation, finding the simpler expression

$$\left(\frac{\partial \hat{S}_S}{\partial t}\right)_n + \hat{\nabla}_n \cdot \left(\frac{\partial \hat{S}_S}{\partial \hat{v}}\right)_z = \hat{\rho} \frac{\partial \hat{S}_S}{\partial t} + \hat{\rho} \hat{v} \cdot \nabla_n \hat{S}_S + \hat{\rho} \hat{e}^* \frac{\partial \hat{S}_S}{\partial \hat{e}}$$

\[= \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \hat{S}_S \right) + \left( D \frac{\partial \hat{S}_S}{\partial \hat{e}} \right)_z. \tag{A.21.6} \]

The left-hand side is the material derivative of the thickness-weighted Preformed Salinity with respect to the thickness-weighted horizontal velocity $\hat{v}$ and the temporally averaged dianeutral velocity $\hat{e}$ of density coordinates. The right-hand side is the divergence of the turbulent fluxes of Preformed Salinity; the fact that the lateral diffusion term is the divergence of a flux can be seen when it is transformed to Cartesian coordinates. The same conservation statement Eqn. (A.21.7) can be derived without making the Boussinesq approximation by a simple reinterpretation of the vertical coordinate as being pressure, and this interpretation is now becoming common in ocean modelling (see Bleck (1978), Huang et al. (2001), de Szoeke and Samelson (2002), Losch et al. (2004) and Griffies (2004)).

We now proceed to develop the corresponding evolution equation for Absolute Salinity $S_A$. Note that $S_A$ is the convenient generic symbol for Density Salinity $S_A^{\text{den}}$; unless there is room for confusion with the other measures of absolute salinity, $S_A^{\text{vol}}$ and $S_A^{\text{add}}$, it proves convenient to use the simpler symbol $S_A$ rather than $S_A^{\text{den}}$ and to use the description Absolute Salinity rather than Density Salinity.

Absolute Salinity obeys the instantaneous evolution equation (based on Eqn. (A.8.1))

$$\left( \rho S_A \right)_t + \nabla \cdot \left( \rho u S_A \right) = \rho \frac{dS_A}{dt} = -\nabla \cdot \mathbf{F}^S + \rho \mathcal{S}^{S_A}. \tag{A.21.8}$$

The source term $\mathcal{S}^{S_A}$ is described in appendix A.20 (see eqn. (A.20.6)). This non-conservative source term is due to biogeochemical processes, for example, the remineralization of biological material; the turning of particulate matter into dissolved seacoast. When this equation is density-weighted averaged, we find

$$\left( \frac{\rho}{\rho_0} \overline{S_A^\rho} \right)_t + \nabla \cdot \left( \overline{S_A^\rho} \overline{\mathbf{u}} \right) = \frac{\rho}{\rho_0} \frac{\partial \overline{S_A^\rho}}{\partial t} + \overline{\mathbf{u}} \cdot \nabla \overline{S_A^\rho}$$

\[= -\frac{1}{\rho_0} \nabla \cdot \mathbf{F}^S - \frac{1}{\rho_0} \nabla \cdot \left( \rho \overline{S_A^\rho} \mathbf{u} \right) + \frac{\rho}{\rho_0} \mathcal{S}^{S_A^\rho}, \tag{A.21.9} \]

which corresponds to Eqn. (A.21.5) above. When averaged over the mesoscale the prognostic equation for Absolute Salinity becomes
\[
\left( \frac{\partial}{\partial t} \hat{S}_A \right)_n + \nabla_n \cdot \left( \frac{\rho}{\rho_0} \hat{S}_A \hat{v} \right) + \left( \frac{\rho}{\rho_0} \hat{S}_A \right)_z = \frac{\rho}{\rho_0} \frac{\partial \hat{S}_A}{\partial t} \bigg|_n + \frac{\rho}{\rho_0} \hat{v} \cdot \nabla_n \bar{S}_A + \frac{\rho}{\rho_0} \hat{e} \frac{\partial \hat{S}_A}{\partial z}
\]
(A.21.10)

and when the Boussinesq approximation is made we find the simpler expression

\[
\frac{\partial \hat{S}_A}{\partial t} + \hat{v} \cdot \nabla_n \bar{S}_A + \hat{e} \frac{\partial \hat{S}_A}{\partial z} = \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \bar{S}_A \right) + \frac{D}{h} \frac{\partial \hat{S}_A}{\partial z} + \hat{\mathcal{S}}^{SA}.
\]
(A.21.11)

The left-hand side is the material derivative of the thickness-weighted Absolute Salinity with respect to the thickness-weighted horizontal velocity \( \hat{v} \) and the temporally averaged dianeutral velocity \( \hat{e} \) of density coordinates. Apart from the non-conservative source term \( \hat{\mathcal{S}}^{SA} \), the right-hand side is the divergence of the turbulent fluxes of Absolute Salinity.

The corresponding turbulent evolution equation for Reference Salinity is

\[
\frac{\partial \hat{S}_R}{\partial t} + \hat{v} \cdot \nabla_n \bar{S}_R + \hat{e} \frac{\partial \hat{S}_R}{\partial z} = \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \bar{S}_R \right) + \frac{D}{h} \frac{\partial \hat{S}_R}{\partial z} + \frac{\eta}{(1 + \eta)} \hat{\mathcal{S}}^{SA}.
\]
(A.21.12)

The non-conservative source term here is justified in subsection A.20.3 of appendix A.20. As discussed in appendices A.4 and A.20, given our rather elementary knowledge of the way variations in seawater composition affect conductivity, we recommend that \( \eta \) be taken to be the constant \( \eta = 0.35 \). Hence we see that Reference Salinity is affected by biogeochemical processes at about 0.26 \((\approx 0.35/1.35)\) of the corresponding influence of biogeochemistry on Density Salinity.

We turn now to consider the material derivative of Conservative Temperature in a turbulent ocean. From Eqns. (A.13.5) and (A.21.8) the instantaneous material derivative of \( \Theta \) is, without approximation,

\[
\rho c_p \frac{d \Theta}{dt} = \frac{T_0 + \Theta}{T_0 + t} \left( -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^0 + \rho c + h_{SA} \rho \hat{\mathcal{S}}^{SA} \right) - \left[ \frac{T_0 + \Theta}{T_0 + t} \right] \mu(p) - \mu(0) \left( -\nabla \cdot \mathbf{F} + \rho \hat{\mathcal{S}}^{SA} \right).
\]
(A.21.13)

The fact that the right-hand side of Eqn. (A.21.13) is not the divergence of a flux means that \( \Theta \) is not a 100% conservative variable. However, the finite-amplitude analysis of mixing pairs of seawater parcels in appendix A.18 has shown that the non constant coefficients of the divergences of the molecular fluxes of heat \( -\nabla \cdot \mathbf{F}^0 \) and salt \( -\nabla \cdot \mathbf{F}^S \) appearing on the right-hand side of Eqn. (A.21.13) are of no practical consequence as they cause an error in Conservative Temperature of no more than 1.2 mK (see Figure A.18.1). These non-ideal terms on the right-hand side of Eqn. (A.21.13) are no larger than the dissipation term \( \rho c \) which is also justifiably neglected in oceanography (McDougall (2003)). The source term \( \rho \hat{\mathcal{S}}^{SA} \) was not considered in the mixing of seawater parcels in appendix A.18, and we now show that these terms also make negligible contributions to Eqn. (A.21.13).

The partial derivative of enthalpy with respect to Absolute Salinity, \( h_{SA} \), that appears in Eqn. (A.21.13) is about \(-65 J g^{-1} \) (i.e. \(-65 J kg^{-1} (g kg^{-1})^{-1} \)) at a temperature of \(10^\circ C \). This value can be deduced from Figure A.17.1 and also from Figure 30(c) and Table 12 of Feistel (2003), albeit for the Gibbs function of seawater that immediately predated the TEOS-10 saline Gibbs function of Feistel (2008) and IAPWS (2008). The spatial integral of the source term \( \rho \hat{\mathcal{S}}^{SA} \) from the North Atlantic to the North Pacific is sufficient to cause a change in Absolute Salinity of 0.025 g kg^{-1}, so the maximum contribution to an error in \( \Theta \)
from the source term $h_3 \rho \mathcal{S}^{S_3} (T_0 + \Theta)/(T_0 + t)$ in Eqn. (A.21.13), when integrated over the whole ocean, is approximately $(\epsilon_p^0)^{-1} \left( 65 \text{ J g}^{-1} \right) \left( 0.025 \text{ g kg}^{-1} \right) \approx 0.4 \text{ mK}$. The other term in $\rho \mathcal{S}^{S_3}$ in Eqn. (A.21.13) is multiplied by the square bracket which from equation (27) of McDougall (2003) is equal to $(T_0 + \Theta)/(T_0 + t)$ times approximately $-\rho \beta \Theta \rho_0$, so that this square bracket is approximately $30 \text{ J g}^{-1}$ (i.e. $30 \text{ J kg}^{-1}(g \text{ kg}^{-1})$) at a pressure $p$ of 4000 dbar (40 MPa) so the contribution of this term is less than half that of the term in $\rho \mathcal{S}^{S_3}$ in the first line of Eqn. (A.21.13). This confirms that the presence of the two terms in $\rho \mathcal{S}^{S_3}$ in the First Law of Thermodynamics has less impact than even the non-ideal nature of the molecular flux divergence terms in Eqn. (A.21.13) and the dissipation of mechanical energy in this equation.

Hence with negligible error, the right-hand side of Eqn. (A.21.13) may be regarded as the sum of the ideal molecular flux of heat term $-\nabla \cdot \mathbf{F}^0$ and the term due to the boundary and radiative heat fluxes, $-(T_0 + \Theta) \nabla \cdot \mathbf{F}^R/(T_0 + t)$. At the sea surface the potential temperature $\Theta$ and in situ temperature $t$ are equal so that this term is simply $-\nabla \cdot \mathbf{F}^R$ so that there are no approximations with treating the air-sea sensible, latent and radiative heat fluxes as being fluxes of $\epsilon_p^0 \Theta$. There is an issue at the sea floor where the boundary heat flux (the geothermal heat flux) affects Conservative Temperature through the “heat capacity” $(T_0 + t) \epsilon_p^0/(T_0 + \Theta)$ rather than simply $\epsilon_p^0$. That is, the input of a certain amount of geothermal heat will cause a local change in $\Theta$ as though the seawater had the “specific heat capacity” $(T_0 + t) \epsilon_p^0/(T_0 + \Theta)$ rather than $\epsilon_p^0$. These two specific heat capacities differ from each other by no more than 0.15% at a pressure of 4000 dbar. If this small percentage change in the effective “specific heat capacity” was ever considered important, it could be corrected by artificially multiplying the geothermal heat flux at the sea floor by $(T_0 + \Theta)/(T_0 + t)$.

We conclude that it is sufficiently accurate to assume that Conservative Temperature is in fact conservative and that the instantaneous conservation equation is

$$\epsilon_p^0 (\rho \Theta) + \epsilon_p^0 \nabla \cdot (\rho \Theta \mathbf{u}) = \rho \epsilon_p^0 \frac{d \Theta}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^0. \quad (A.21.14)$$

Now we perform the same two-stage averaging procedure as outlined above in the case of Preformed Salinity. The Boussinesq form of the mesoscale-averaged equation is

$$(A.21.15)$$

As in the case of the $S$ equation (A.21.7), the molecular flux of heat has been ignored in comparison with the turbulent fluxes of Conservative Temperature. The air-sea fluxes of sensible and latent heat, the radiative and the geothermal heat fluxes remain in Eqn. (A.21.15) in the vertical heat flux $F^{\text{bound}}$ which is the sum of these boundary heat fluxes divided by $\rho_0 \epsilon_p^0$. Any conservative variable, $C$, obeys a conservation equation identical in form to Eqns. (A.21.7) and (A.21.15), with $\mathcal{C}$ simply replacing $\mathcal{S}$ or $\Theta$ in these equations, and of course with the boundary flux being the boundary flux of property $C$.

The errors incurred in ocean models by treating potential temperature $\Theta$ as being conservative have not yet been thoroughly investigated, but McDougall (2003) and Tailleux (2010) have made a start on this topic. McDougall (2003) found that typical errors in $\Theta$ are $\pm 0.1^\circ \text{C}$ while in isolated regions such as where the fresh Amazon water discharges into the ocean, the error can be as large as $1.4^\circ \text{C}$. The corresponding error in the meridional heat flux appears to be about 0.005 PW (or a relative error of 0.4%). The use of Conservative Temperature $\Theta$ in ocean models reduces these errors by two orders of magnitude.

It is possible to derive an evolution equation for potential temperature which resembles Eqn. (A.21.15) but which contains additional non-conservative source terms on
the right-hand side of the equation. However, there seems little point in doing so here, as it is much more convenient to instead adopt the Conservative Temperature variable. Note that the consequences for dynamical oceanography of ignoring the non-conservative source terms in the potential temperature evolution equation are as large as ignoring the variations in seawater composition; a $\theta$ range of 0.2°C corresponds to a density range of 0.04 kg m$^{-3}$ which is twice as large as the density error due to ignoring the maximum value of $S_h - S_r$ of 0.025 g kg$^{-1}$.

The evolution equations of Preformed Salinity (A.21.7) and Conservative Temperature (A.21.15) are the underpinning conservation equations for these variables in ocean models. An important issue for ocean models is how to relate $\mathbf{v}$ to the Eulerian-mean horizontal velocity $\mathbf{\hat{v}}$. This area of research involves temporal-residual-mean theory and the quasi-Stokes streamfunction (Gent and McWilliams (1990), Gent et al. (1995), McDougall and McIntosh (2001) and Griffies (2004)). We will not discuss this topic here. Suffice it to say that the mean advection can be expressed in Cartesian coordinates, with for example, Eqn. (A.21.15) becoming

$$\frac{d\Theta}{dt} = \hat{\Theta}|_e + \hat{\mathbf{v}} \cdot \nabla \hat{\Theta} + w^* \hat{\Theta}_z = \frac{1}{h} \nabla_n \cdot \left( h K \nabla_n \hat{\Theta} \right) + \left( D \hat{\Theta}_z - F^{\text{bound}} \right)_z, \quad (A.21.16)$$

where the vertical velocity $w^*$ is related to $\mathbf{\hat{v}}$ by

$$w^* = z|_n + \hat{\mathbf{v}} \cdot \nabla_n z + \mathbf{\hat{v}}. \quad (A.21.17)$$

### A.22 The material derivatives of density and of locally-referenced potential density; the dianeutral velocity $\mathbf{\hat{v}}$

Regarding density to be a function of Conservative Temperature (i.e. $\rho = \hat{\rho}(S_h, \Theta, \rho)$) and taking the material derivative of the natural logarithm of density following the mesoscale-thickness-weighted-averaged mean flow (as in Eqs. (A.21.15) or (A.21.16)), we have

$$\hat{\rho}^{-1} \frac{d\hat{\rho}}{dt} = \rho^\Theta \frac{d\hat{S}_\Theta}{dt} - \alpha^\Theta \frac{d\hat{\Theta}}{dt} + \kappa \frac{d\rho}{dt}, \quad (A.22.1)$$

where $\hat{\rho}$ is the thickness-weighted average value of density. One can continue to consider the material derivative of in situ density, and in so doing, one carries along the last term in Eqn. (A.22.1), $\kappa \frac{d\rho}{dt}$, but it is more relevant and more interesting to consider the material derivative of the logarithm of the locally-referenced potential density, $\hat{\rho}^l$, since this variable is locally constant in the neutral tangent plane. The material derivative of $\hat{\rho}^l$ is given by

$$\hat{\rho}^{-1} \frac{d\hat{\rho}^l}{dt} = \hat{\rho}^{-1} \frac{d\hat{\rho}}{dt} - \kappa \frac{d\rho}{dt} = \rho^\Theta \frac{d\hat{S}_\Theta}{dt} - \alpha^\Theta \frac{d\hat{\Theta}}{dt}. \quad (A.22.2)$$

Substituting from Eqs. (A.21.11) and (A.21.15) above, and noting that both the temporal and the lateral gradients of $\hat{\rho}^l$ vanish along the neutral tangent plane (that is, $\alpha^\Theta \nabla_n \hat{\Theta} - \beta^\Theta \nabla_n \hat{S}_\Theta = 0$ and $\alpha^\Theta \hat{S}_\Theta|_n - \beta^\Theta \hat{S}_\Theta|_l = 0$), the material derivative of $\hat{\rho}^l$ amounts to the following equation for the dianeutral velocity $\mathbf{\hat{v}}$ (note that the boundary heat flux $F^{\text{bound}}$ also needs to be included for fluid volumes that abut the sea surface)

$$\mathbf{\hat{v}} \left( \alpha^\Theta \hat{\Theta}_z - \beta^\Theta \hat{S}_\Theta z \right) = \alpha^\Theta h^{-1} \nabla_n \left( h K \nabla_n \hat{\Theta} \right) - \beta^\Theta h^{-1} \nabla_n \left( h K \nabla_n \hat{S}_\Theta \right) + \alpha^\Theta \left( D \hat{\Theta}_z \right)_z - \beta^\Theta \left( D \hat{S}_\Theta \right)_z - \beta^\Theta \hat{S}_\Theta. \quad (A.22.3)$$

The left-hand side is equal to $\mathbf{\hat{v}} g^{-1} \mathbf{N}^2$ and the first two terms on the right hand side would sum to zero if the equation of state were linear. This equation can be rewritten as the following equation for the temporally averaged vertical velocity through the neutral
tangent plane at a given longitude and latitude (from McDougall (1987b), and see Eqns. (3.8.2) and (3.9.2) for the definitions of $C_b^\Theta$ and $T_b^\Theta$)

$$\bar{e} g^{-1}N^2 = -K\left(C_b^\Theta \dot{\Theta}_n \cdot \nabla_n \dot{\Theta} + T_b^\Theta \dot{\Theta}_n \cdot \nabla_n \rho\right) + \alpha^\Theta \left(D\dot{\Theta}_z\right)_z - \beta^\Theta \left(D\dot{S}_\lambda\right)_z - \beta^\Theta \dot{S}^{\lambda\lambda}.$$ (A.22.4)

The cabling nonlinearity (the $C_b^\Theta$ term) always causes “densification”, that is, it always causes a negative dianeutral velocity, $\bar{e}$, while the thermobaric nonlinearity (the $T_b^\Theta$ term) can cause either diapycnal upwelling or downwelling.

To summarize this appendix A.22; we have found that the material derivative of in situ density Eqn. (A.22.1), when adjusted for the dynamically passive compressibility term, becomes the material derivative of locally-referenced potential density Eqn. (A.22.2) which can be interpreted as an expression Eqn. (A.22.4) for $\bar{e}$, the temporally-averaged vertical velocity through the local neutral tangent plane. This dianeutral velocity $\bar{e}$ is not a separate mixing process, but rather is a direct result of mixing processes such as (i) small-scale turbulent mixing as parameterized by the diffusivity $D$, and (ii) lateral turbulent mixing of heat and salt along the neutral tangent plane (as parameterized by the lateral turbulent diffusivity $K$) acting in conjunction with the cabling and thermobaric nonlinearities of the equation of state. Note that a common diapycnal mixing mechanism, double-diffusive convection (which actually occurs in two separate flavours, a salt-fingering type and a “diffusive” type of double-diffusive convection) is omitted from the conservation equations (A.21.11) and (A.21.15) and also from the mean dianeutral velocity equation (A.22.4). It is however straightforward to include these processes in these conservation equations (see for example McDougall (1994, 1997b)).

### A.23 The water-mass transformation equation

It is instructive to substitute Eqn. (A.22.4) for $\bar{e}$ into the expression (A.21.15) for the material derivative of $\dot{\Theta}$, thus eliminating $\bar{e}$ and obtaining the following equation for the temporal and spatial evolution of $\dot{\Theta}$ along the neutral tangent plane (McDougall (1984))

$$\begin{align*}
\frac{\dot{\Theta}}{\partial t} + \nabla \cdot \dot{\Theta}_n &= \frac{1}{h} \nabla \cdot \left(hK\nabla_n \dot{\Theta}\right) + KgN^{-2}\dot{\Theta}_z \left(C_b^\Theta \dot{\Theta}_n \cdot \nabla_n \dot{\Theta} + T_b^\Theta \dot{\Theta}_n \cdot \nabla_n \rho\right) \\
\end{align*}$$

$$+ D\beta^\Theta gN^{-2}\dot{\Theta}_z \frac{d^2S\lambda}{d\Theta^2} + \frac{\beta^\Theta}{\alpha^\Theta \left(R_p-1\right)} \dot{S}^{\lambda\lambda},$$ (A.23.1)

where $R_p$ is the stability ratio of the water column, $R_p = \alpha^\Theta \dot{\Theta}_z / \beta^\Theta S\lambda$. The term involving $D$ has been written as proportional to the curvature of the $S\lambda - \dot{\Theta}$ diagram of a vertical cast; this term can also be written as $D\beta^\Theta gN^{-2} \left(\dot{\Theta}_z S\lambda - \dot{\Theta}_z S\lambda\right)$. The form of Eqn. (A.23.1) illustrates that when analyzed in density coordinates, Conservative Temperature (and Absolute Salinity) (i) are affected not only by the expected lateral diffusion process along density surfaces but also by the nonlinear dianeutral advection processes, cabling and thermobaricity, (ii) are affected by diapycnal turbulent mixing only to the extent that the vertical $S\lambda - \dot{\Theta}$ diagram is not locally straight, and (iii) are not influenced by the vertical variation of $D$ since $D_z$ does not appear in this equation.

Equations (A.21.11) and (A.21.15) are the fundamental conservation equations of salinity and Conservative Temperature in a turbulent ocean, and the pair of equations (A.22.4) and (A.23.1) are simply derived as linear combinations of Eqns. (A.21.11) and (A.21.15). The “density” conservation equation (A.22.4) and the “water-mass transformation” equation (A.23.1) are in some sense the “normal modes” of Eqns. (A.21.11) and (A.21.15). That is, Eqn. (A.22.4) expresses how mixing processes contribute to the mean vertical velocity $\bar{e}$ through the neutral tangent plane, while (A.23.1) expresses
how the tracer called “Conservative Temperature measured along the neutral direction” is affected by mixing processes; this equation does not contain $\tilde{e}$.

For completeness, the water-mass conservation equation for Absolute Salinity that corresponds to Eqn. (A.23.1) is

$$\frac{\partial \hat{S}_A}{\partial t} + \nabla \cdot \hat{v} \hat{S}_A = \frac{1}{h} \nabla \cdot \left( hK \nabla \hat{S}_A \right) + K gN^{-2} \hat{S}_A \left( C^\Theta \nabla \hat{S} + \nabla \hat{S} \right) + T^\Theta \nabla \hat{S} \cdot \nabla p \right)$$

$$+ Da^\Theta gN^{-2} \hat{S}^2 \frac{d^2 \hat{S}}{d\Theta^2} + \frac{R_p}{(R_p-1)} \hat{e}^S \hat{S}_A,$$

and it easy to show that $a^\Theta$ times the right-hand side of Eqn. (A.23.1) is equal to $\beta^\Theta$ times the right-hand side of Eqn. (A.23.2).

To construct the water-mass transformation equation of a conservative tracer $C$, the mean dianeutral velocity $\tilde{e}$ is eliminated from the $\hat{C}$ conservation equation (A.24.1) using Eqn. (A.22.4) giving (from McDougall (1984))

$$\frac{\partial \hat{C}}{\partial t} + \nabla \cdot \hat{v} \hat{C} = \frac{1}{h} \nabla \cdot \left( hK \nabla \hat{C} \right) + K gN^{-2} \hat{C} \left( C^\Theta \nabla \hat{S} + \nabla \hat{S} \right) + T^\Theta \nabla \hat{S} \cdot \nabla p \right)$$

$$+ D \left( \hat{S}_A \right)^2 \frac{d^2 \hat{C}}{d\hat{S}_A^2} + \frac{\hat{C}}{\hat{S}_A} Da^\Theta gN^{-2} \hat{S}^2 \frac{d^2 \hat{S}}{d\Theta^2} =$$

$$D \left( \hat{S}_A \hat{C}_z - \hat{S}_A \hat{C}_z \right)/\hat{S}_A + D \hat{C}_z a^\Theta gN^{-2} \left( \hat{S}_A \hat{C}_z - \hat{S}_A \hat{C}_z \right)/\hat{S}_A.$$

**A.24 Conservation equations written in potential density coordinates**

The material derivative of a quantity $C$ can be expressed with respect to the Cartesian reference frame, the neutral tangent plane, or a potential density reference frame so that the conservation equation of a conservative variable can be written as (see Eqn. (A.21.16),

$$\frac{\partial \hat{C}}{\partial t} + \nabla \cdot \hat{v} \hat{C} = \frac{\partial \hat{C}}{\partial t} + \nabla \cdot \hat{v} \hat{C} + \epsilon^d \hat{C} =$$

$$\frac{1}{h} \nabla \cdot \left( hK \nabla \hat{C} \right) + \left( D \hat{C}_z \right)_z,$$

where $\epsilon^d$ is the mean vertical component of the total transport velocity that moves through the potential density surface. Any flux of $C$ across the ocean boundaries $F_{\text{bound}}$ (e.g., the sea surface) would need to be added as the extra term $-F_{\text{bound}}$ on the last line of Eqn. (A.24.1). Notice that the lateral diffusion occurs along the neutral tangent plane. In this section we consider what terms are neglected if this lateral mixing term is instead regarded as diffusion occurring along potential density surfaces.

The temporal and lateral gradients of Absolute Salinity and Conservative Temperature in a potential density surface are related by (McDougall (1991))

$$\alpha^\Theta (p) \hat{S} - \beta^\Theta (p) \hat{S}_A = 0 \quad \text{and} \quad \alpha^\Theta (p) \nabla \hat{S} - \beta^\Theta (p) \nabla \hat{S}_A = 0,$$

where $\alpha^\Theta (p)$ and $\beta^\Theta (p)$ are shorthand notations for $\alpha^\Theta (\hat{S}_A, \hat{S}, p)$ and $\beta^\Theta (\hat{S}_A, \hat{S}, p)$ respectively, and $p$ is the reference pressure of the potential density. Using Eqns. (3.17.1)
to (3.17.5) which relate the gradients of properties in a potential density surface to those in a neutral tangent plane, the following form of the conservation equation (A.21.15) for Conservative Temperature can be derived (see equation (26) of McDougall (1991))

\[
\frac{\partial \Theta}{\partial t} + \mathbf{v} \cdot \nabla \Theta + \mathbf{e} \cdot \nabla \Theta = \frac{1}{\kappa} \nabla (h^\sigma \nabla) + \left( D \nabla \right)_{z} \\
- \frac{1}{\kappa} \nabla \cdot \left( \frac{G^\Theta r}{\kappa} \right) [k \nabla \cdot \nabla \Theta]_{z} \\
- \left( G^\Theta \left[ G^\Theta r - 1 \right] K \frac{\nabla \Theta \cdot \nabla p}{\Theta z} \right)_{z} 
\]

(A.24.3)

where the “isopycnal temperature gradient ratio” \( G^\Theta \) is defined as (from Eqn. (3.17.4)) \( G^\Theta = r [P_p r] R_p - 1 \) and \( r \) is defined in Eqn. (3.17.2) as the ratio of \( \alpha^\Theta / \beta^\Theta \) at the \textit{in situ} pressure \( p \) to that evaluated at the reference pressure \( p_r \). The corresponding equation for Absolute Salinity is

\[
\frac{\partial \hat{S}}{\partial t} + \mathbf{v} \cdot \nabla \hat{S} + \mathbf{e} \cdot \nabla \hat{S} = \frac{1}{\kappa} \nabla (h^\sigma \nabla \hat{S}) + \left( D \hat{S}_{\lambda} \right)_{z} + \mathbf{S} \hat{S}_{\lambda} \\
- \frac{1}{\kappa} \nabla \cdot \left( \frac{G^\Theta r}{\kappa} \right) [k \nabla \cdot \nabla \hat{S}]_{z} \\
- \left( G^\Theta \left[ G^\Theta r - 1 \right] K \frac{\nabla \hat{S} \cdot \nabla p}{\Theta z} \right)_{z} 
\]

(A.24.4)

The terms in the second and third lines of Eqns. (A.24.3) and (A.24.4) arise because in the first line of these equations, the lateral diffusion is written as being along potential density surfaces rather than along neutral tangent planes. As explained in McDougall (1991), these terms are non zero even at the reference pressure of the potential density variable.

Multiplying Eqn. (A.24.4) by \( \beta^\Theta (p_r) \) and subtracting \( \alpha^\Theta (p_r) \) times Eqn. (A.24.3) we find the corresponding expression for the diapycnal velocity \( \mathbf{e} \) (following McDougall (1991))

\[
\mathbf{e} \cdot \frac{1}{\rho^\Theta} \frac{\partial \hat{p}_\Theta}{\partial z} = \beta^\Theta (p_r) \left( \frac{1}{h^\sigma} \nabla (h^\sigma \nabla \hat{S}) - \alpha^\Theta (p_r) \frac{1}{h^\sigma} \nabla (h^\sigma \nabla \hat{p}_\Theta) \right) \\
+ \beta^\Theta (p_r) \left( D \hat{S}_{\lambda} \right)_{z} - \alpha^\Theta (p_r) \left( D \hat{p}_\Theta \right)_{z} + \beta^\Theta (p_r) \mathbf{S} \hat{S}_{\lambda} \\
+ \alpha^\Theta (p_r) (r-1) \frac{1}{\kappa} \nabla \cdot \left( h^\sigma \nabla \hat{p}_\Theta \right) + \alpha^\Theta (p_r) \frac{G^\Theta}{r} k \nabla \hat{p}_\Theta \nabla \hat{p}_\Theta \\
- \beta^\Theta (p_r) \left( \frac{G^\Theta}{r} \right) \left[ G^\Theta \left[ G^\Theta r - 1 \right] K \frac{\nabla \hat{S} \cdot \nabla \hat{p}_\Theta}{\Theta z} \right] \\
- \beta^\Theta (p_r) \left( \frac{G^\Theta}{r} \right) \left[ G^\Theta \left[ G^\Theta r - 1 \right] K \left( C_b \nabla \hat{p}_\Theta \cdot \nabla \hat{p}_\Theta + T_b \nabla \hat{p}_\Theta \cdot \nabla \hat{p}_\Theta \right) \right]. 
\]

(A.24.5)

All the terms in the last three lines of this equation occur because the first line has lateral mixing along potential density surfaces rather than along neutral tangent planes. Even at the reference pressure where \( G^\Theta = r = 1 \) these last three lines do not reduce to zero but rather to \( T_b K \nabla \hat{p}_\Theta \cdot \nabla \hat{p}_\Theta \) showing that the thermobaric effect remains.

In summary, this section has written down the expressions for the material derivatives of Conservative Temperature, Absolute Salinity and potential density in a form where one can identify the many rather nasty terms that are neglected if one assumes that the ocean mixes laterally along potential density surfaces instead of the physically correct neutral tangent planes. It is noted in passing that the first line of the right-hand side of Eqn. (A.24.5) can also be written as \( C_b (p_r) K \nabla \hat{p}_\Theta \cdot \nabla \hat{p}_\Theta \) (c.f. the last line of Eqn. (A.27.2) below).
A.25 The vertical velocity through a general surface

Consider a general surface which we identify with the label “a” (for example, this could stand for “approximately neutral surface”). The material derivative on the left-hand sides of the conservation equations (A.21.11) and (A.21.15) for Absolute Salinity and Conservative Temperature are now written with respect to this general “a” coordinate as

\[
\frac{\partial \bar{S}_h}{\partial t} + \hat{\mathbf{v}} \cdot \nabla_{a} \bar{S}_h + \bar{e}^a \frac{\partial \bar{S}_h}{\partial z} = \frac{1}{h} \nabla_{a} \cdot \left(hK \nabla_{a} \bar{S}_h\right) + \left(D \frac{\partial \bar{S}_h}{\partial z}\right)_{z} + \mathbf{F}^{\bar{S}_h}, \tag{A.25.1}\]

and

\[
\frac{\partial \Theta}{\partial t} + \hat{\mathbf{v}} \cdot \nabla_{a} \Theta + \bar{e}^a \frac{\partial \Theta}{\partial z} = \frac{1}{h} \nabla_{a} \cdot \left(hK \nabla_{a} \Theta\right) + \left(D \frac{\partial \Theta}{\partial z}\right)_{z}. \tag{A.25.2}\]

Cross-multiplying these equations by \(\beta^\Theta = \beta^\Theta \left(\bar{S}_h, \Theta, p\right)\) and \(\alpha^\Theta = \alpha^\Theta \left(\bar{S}_h, \Theta, p\right)\) and subtracting gives the following equation for the vertical velocity through the approximately neutral surface,

\[
\bar{e}^a = -g N^{-2} K \left(C_k \nabla_{a} \Theta \cdot \nabla_{a} \Theta + T_k \nabla_{a} \Theta \cdot \nabla_{a} p\right) + g N^{-2} \left(\alpha^\Theta \left(D \Theta\right)_{z} - \beta^\Theta \left(D \bar{S}_h\right)_{z}\right) - g N^{-2} \beta^\Theta \mathbf{F}^{\bar{S}_h} \tag{A.25.3}\]

\[
+ g N^{-2} \hat{\mathbf{v}} \left[\beta^\Theta \nabla_{a} \bar{S}_h \alpha^\Theta \nabla_{a} \Theta - \alpha^\Theta \nabla_{a} \bar{S}_h \beta^\Theta \nabla_{a} \Theta\right] + g N^{-2} \left[\beta^\Theta \frac{\partial \bar{S}_h}{\partial t} \alpha^\Theta \frac{\partial \Theta}{\partial t} - \alpha^\Theta \frac{\partial \bar{S}_h}{\partial t} \beta^\Theta \frac{\partial \Theta}{\partial t}\right]_{a}. \tag{A.25.4}\]

The terms in the third line of this equation represent the deviation of the “a” coordinate from neutrality and these terms can be shown to be (from Klocker and McDougall (2010b) and from Eqn. (3.14.1) above, assuming the surfaces are not vertical)

\[
g N^{-2} \hat{\mathbf{v}} \left[\beta^\Theta \nabla_{a} \bar{S}_h - \alpha^\Theta \nabla_{a} \Theta\right] = -\hat{\mathbf{v}} \cdot \frac{\nabla_{a} \rho^j}{\rho^j} = \hat{\mathbf{v}} \cdot \left(\nabla_{a} z - \nabla_{a} z\right) = \hat{\mathbf{v}} \cdot \mathbf{s} \tag{A.25.5}\]

and

\[
g N^{-2} \left[\beta^\Theta \frac{\partial \bar{S}_h}{\partial t} \alpha^\Theta \frac{\partial \Theta}{\partial t} - \alpha^\Theta \frac{\partial \bar{S}_h}{\partial t} \beta^\Theta \frac{\partial \Theta}{\partial t}\right]_{a} = -\frac{\left|\hat{\mathbf{r}}\right|_{a}}{\rho^j_{a}} = \left|z_{i_{a}} \right| = \left|z_{i_{a}} \right|_{a}. \tag{A.25.6}\]

where \(\hat{\mathbf{r}}^j\) is the (thickness-weighted) locally-referenced potential density.

Combining these results with Eqn. (A.22.4) we have the rather simple kinematic result that

\[
\bar{e}^a = \bar{e} + \hat{\mathbf{v}} \cdot \mathbf{s} + z_{i_{a}} - z_{i_{a}}. \tag{A.25.7}\]

showing that the vertical velocity through a general “a” surface, \(\bar{e}^a\), is that through the neutral tangent plane \(\bar{e}\) plus that due to the “a” surface having a different slope in space to the neutral tangent plane, \(\hat{\mathbf{v}} \cdot \mathbf{s}\), plus that due to the “a” surface moving vertically in time (at fixed latitude and longitude) at a different rate than the neutral tangent plane, \(z_{i_{a}} - z_{i_{a}}\).

A.26 The material derivative of potential density

The material derivative of the natural logarithm of potential density is \(\beta^\Theta (p_i)\) times the material derivative Eqn. (A.21.11) of Absolute salinity minus \(\alpha^\Theta (p_i)\) times the material derivative Eqn. (A.21.15) of Conservative Temperature. Using the relationships Eqn. (A.24.2) that relate the gradients of Absolute Salinity and Conservative Temperature in potential density surfaces, and taking the material derivative of potential density with
respect to potential density surfaces, one finds that the temporal and isopycnal gradient terms cancel leaving only the term in the mean diapycnal velocity \( \bar{v}^d \) as follows

\[
\bar{v}^d \frac{1}{\rho^0} \frac{\partial \rho^0}{\partial z} = \beta^\theta (p_r) \frac{1}{\nu} \nabla \cdot \left( hK^n \nabla \hat{S}_\lambda \right) - \alpha^\theta (p_r) \frac{1}{\nu} \nabla \cdot \left( hK^n \hat{\Theta} \right) \\
+ \beta^\theta (p_r) \left(D \hat{S}_\lambda \right)_z - \alpha^\theta (p_r) \left(D \hat{\Theta} \right)_z + \beta^\theta (p_r) \hat{\mathbf{S}}^\lambda,
\]

where the following exact expression for the vertical gradient of potential density has been used,

\[
\frac{1}{\rho^0} \frac{\partial \rho^0}{\partial z} = \beta^\theta (p_r) \hat{S}_\lambda - \alpha^\theta (p_r) \hat{\Theta}.
\]

Equation (A.26.1) can be written more informatively as (following McDougall, 1991)

\[
\bar{v}^d \frac{1}{\rho^0} \frac{\partial \rho^0}{\partial z} = \left( \frac{D}{\rho^0} \frac{\partial \rho^0}{\partial z} \right)_z + \beta^\theta (p_r) \hat{\mathbf{S}}^\lambda \\
+ D \left[ \alpha^\theta (p_r) \hat{\Theta}^2 + 2 \alpha^\theta (p_r) \hat{\Theta} \hat{S}_\lambda - \beta^\theta (p_r) \hat{S}_\lambda^2 \right] \\
+ \alpha^\theta (p_r) [\nu - \left( hK^n \hat{\Theta} \right)] \\
+ \frac{\beta^\theta (p_r)}{\beta^\theta (p_r)} K \left( \hat{c}^\sigma \nabla \hat{\Theta} \cdot \nabla \hat{\Theta} + \hat{r}^\sigma \nabla \hat{\Theta} \cdot \nabla \hat{p} \right),
\]

where \( r \) is defined as the ratio of \( \alpha^\theta / \beta^\theta \) at the in situ pressure \( p \) to that evaluated at the reference pressure \( p_r \). If the equation of state were linear, only the first two terms would be present on the right of Eqn. (A.26.3).

**A.27 The diapycnal velocity of layered ocean models (without rotation of the mixing tensor)**

Layered models of the ocean circulation have a potential density variable (usually with a reference pressure \( p_r \) of 2000 dbar) as their vertical coordinate. To date these models have not rotated the direction of lateral mixing to align with the neutral tangent plane but rather have mixed laterally along the potential density coordinate direction. The diapycnal velocity \( \hat{v}^d, \text{model} \) in this class of model obeys the equation (c.f. Eqn. (A.26.1) above)

\[
\hat{v}^d, \text{model} \frac{1}{\rho^0} \frac{\partial \rho^0}{\partial z} = \beta^\theta (p_r) \frac{1}{\nu} \nabla \cdot \left( hK^\sigma \nabla \hat{S}_\lambda \right) - \alpha^\theta (p_r) \frac{1}{\nu} \nabla \cdot \left( hK^\sigma \nabla \hat{\Theta} \right) \\
+ \beta^\theta (p_r) \left(D \hat{S}_\lambda \right)_z - \alpha^\theta (p_r) \left(D \hat{\Theta} \right)_z + \beta^\theta (p_r) \hat{\mathbf{S}}^\lambda,
\]

where \( \nabla \sigma \) is the gradient operator along the potential density coordinate, \( K^\sigma \) is the lateral diffusivity along the layers and \( h^\sigma \) is the thickness between a pair of potential density surfaces in the vertical. This equation can be rewritten as

\[
\hat{v}^d, \text{model} \frac{1}{\rho^0} \frac{\partial \rho^0}{\partial z} = \left( \frac{D}{\rho^0} \frac{\partial \rho^0}{\partial z} \right)_z + \beta^\theta (p_r) \hat{\mathbf{S}}^\lambda \\
+ D \left[ \alpha^\theta (p_r) \hat{\Theta}^2 + 2 \alpha^\theta (p_r) \hat{\Theta} \hat{S}_\lambda - \beta^\theta (p_r) \hat{S}_\lambda^2 \right] \\
+ K^\sigma C_b (p_r) \nabla \hat{\Theta} \cdot \nabla \hat{\Theta}.
\]

The terms in the vertical turbulent diffusivity \( D \) are identical to those in the correct equation (A.26.3) while the diapycnal velocity due to cabbeling is quite similar to that in the correct expression Eqn. (A.26.3); the difference mostly being that the cabbeling coefficient is here evaluated at the reference pressure instead of at the in situ pressure, and
that the lateral temperature gradient is here evaluated along the potential density surface rather than along the neutral tangent plane (these gradients are proportional to each other via the relation (3.17.3)). Another difference is that the term \( \alpha (p, r)[r - 1]h^3 \nabla _n \cdot (h \nabla _n \dot{\Theta}) \) in Eqn. (A.26.3) is missing from Eqn. (A.27.2). This type of difference is to be expected since the direction of the lateral mixing is different.

Notice the absence of the thermobaric diapycnal advection from Eqn. (A.27.2); that is, the term proportional to \( K T_n \nabla _n \Theta \cdot \nabla _n p \) in Eqn. (A.26.3) is absent from Eqn. (A.27.2), as first remarked on by Ludicone et al. (2008). The thermobaric diapycnal advection is probably significant in the Southern Ocean (Klocker and McDougall (2010a)) and this would argue for the rotation of the lateral mixing tensor in layered models to the local direction of the neutral tangent plane, as is done in height-coordinate ocean models. Also missing from layered ocean models is the mean vertical advection \( \hat{v} \cdot \mathbf{s} \) due to the helical nature of neutral trajectories in the ocean (see section 3.13, Eqn. (A.25.4) and Klocker and McDougall (2010b)).

### A.28 The material derivative of orthobaric density

Orthobaric density \( \rho _o (p, \rho) \) has been defined by de Szoeke et al. (2000) as a pressure corrected form of in situ density. The construction of orthobaric density requires the isentropic compressibility to be approximated as a function of pressure and in situ density. While orthobaric density has the advantage of being a thermodynamic variable, orthobaric density surfaces are often not particularly good approximations to neutral tangent planes (see McDougall and Jackett (2005a) and Klocker et al. (2009a,b)). The material derivative of \( \rho _o \) can be expressed with respect to orthobaric density surfaces as

\[
\frac{\partial \rho _o}{\partial t} + \hat{v} \cdot \nabla _n \rho _o + \hat{v}^\rho \frac{\partial \rho _o}{\partial z} = \hat{v}^\rho \frac{\partial \rho _o}{\partial z},
\]

where the temporally averaged vertical velocity through the \( \rho _o \) surface is given by (from McDougall and Jackett (2005a))

\[
\hat{v}^\rho = g N^{-2} \left( \alpha (p, \rho) + \left( \psi - 1 \right) \left( \rho _e |_{\rho _o} + \hat{v} \cdot \nabla _n p \right) / p_z \right),
\]

where (from de Szoeke et al. (2000))

\[
(\psi - 1) \approx 2 g^2 N^{-2} c_0^3 \Delta c \approx - \rho g^2 \nabla ^2 N^{-2} \left[ \hat{\Theta} \Theta _b (p, \rho) \right].
\]

and \( \Delta c \) is the difference between the reference sound speed function \( c_0 (p, \rho) \) and the sound speed of seawater which can be expressed in the functional form \( c (p, \rho, \Theta) \). This difference in the sound speed is equivalent to the difference between the actual Conservative Temperature of a water parcel and the reference value \( \Theta _b (p, \rho) \). Here \( \hat{S} \) is shorthand for the material derivative of \( \hat{S} \) and is expressed in terms of mixing processes by the right-hand side of Eqn. (A.21.11); \( \hat{\Theta} \Theta _b \) is similarly shorthand for the material derivative of \( \hat{\Theta} \) and is given by the right-hand side of Eqn. (A.21.15).

The first term on the right of Eqn. (A.28.2) represents the effects of irreversible mixing processes on the flow through orthobaric density surfaces, and this contribution to \( \hat{v}^\rho \) is exactly the same as the flow through neutral tangent planes, \( \hat{v} \) (Eqn. (A.22.4)). The second term in Eqn. (A.28.2) arises from the non-quasi-material (non-potential) nature of orthobaric density. This vertical advection arises from the seemingly innocuous sliding motion along the sloping orthobaric density surface and from the vertical heaving of these surfaces.
A.29 The material derivative of Neutral Density

Neutral Density \( \gamma^n \) is not a thermodynamic function since it depends on latitude and longitude. The Neutral Density algorithm finds the data point in a pre-labeled reference data set that has the same potential density as the data point that is being labeled; the reference pressure of this potential density is the average of the pressures of the two parcels. The material derivative of \( \gamma^n \) can be expressed as

\[
\frac{\partial \gamma^n}{\partial t} + \mathbf{v} \cdot \nabla \gamma^n + \mathbf{\tilde{v}} \cdot \gamma^n = \mathbf{\tilde{v}} \cdot \gamma^n,
\]

(A.29.1)

where the temporally averaged vertical velocity through the \( \gamma^n \) surface is given by (from McDougall and JACKETT (2005b))

\[
\mathbf{\tilde{v}} \approx \frac{\alpha^0 (\overline{\rho}) \Theta - \beta^0 (\overline{\rho}) \overline{S}_\Lambda}{\alpha^0 (\overline{\rho}) \Theta^\text{ref} - \beta^0 (\overline{\rho}) \overline{S}_\Lambda^\text{ref}} + \mathbf{v} \cdot \mathbf{s}^\text{ref} \\
+ (\psi^n - 1) \left( p_{L} + \mathbf{v} \cdot \nabla \rho \right) (p_z)^{-1} \\
+ (\psi^n - 1) \left( \mathbf{\tilde{v}} \cdot \nabla \rho^\text{ref} - \frac{(p - p^\text{ref})}{(\Theta - \Theta^\text{ref})} \mathbf{\tilde{v}} \cdot \nabla \Theta^\text{ref} \right) (p_z)^{-1} \\
+ 2(\psi^n - 1) \left( \alpha^0 (\overline{\rho}) \Theta - \beta^0 (\overline{\rho}) \overline{S}_\Lambda \right) \\
+ (\psi^n - 1) \tilde{\mathbf{v}} \cdot \mathbf{s}^\text{ref}.
\]

(A.29.2)

Here \( \overline{S}_\Lambda \) is shorthand for the material derivative of \( \overline{S}_\Lambda \) following the appropriate mean velocity and is expressed in terms of mixing processes by the right-hand side of Eqn. (A.21.11), \( \Theta \) is similarly shorthand for the material derivative of \( \Theta \) and is given by Eqn. (A.21.15), and \( (\psi^n - 1) \) is defined by

\[
(\psi^n - 1) = \frac{-\frac{1}{2} \rho g^2 T_b^0 (\Theta - \Theta^\text{ref})}{N_e^2 + \rho g^2 T_b^0 (\Theta - \Theta^\text{ref}) + \frac{1}{2} g T_b^0 (p - p^\text{ref}) \Theta^\text{ref}}.
\]

(A.29.3)

Here \( N_e^2 \) is the square of the buoyancy frequency of the pre-labeled reference data set. Equation (A.29.3) shows that \( (\psi^n - 1) \) is nonzero to the extent that there is a water mass contrast \( (\Theta - \Theta^\text{ref}) \) between the seawater parcel that is being labeled and the data on the pre-labeled reference data set that communicates neutrally with the seawater sample. For reasonable values of \( (\Theta - \Theta^\text{ref}) \) and \( (p - p^\text{ref}) \) the denominator in Eqn. (A.29.3) is close to \( N_e^2 \) and \( (\psi^n - 1) \) is small. In these expressions the thermal expansion coefficient \( \alpha^0 (\overline{\rho}) \) and saline contraction coefficient \( \beta^0 (\overline{\rho}) \) are evaluated at the average of the properties of the parcel being labeled and the parcel in the reference data set to which it is neutrally related, that is, \( \alpha^0 (\overline{\rho}) \) and \( \beta^0 (\overline{\rho}) \) are shorthand for \( \alpha^0 (\overline{S}_\Lambda, \overline{\rho}) \) and \( \beta^0 (\overline{S}_\Lambda, \overline{\rho}) \).

The first term in Eqn. (A.29.2) is expected as Neutral Density changes in response to the irreversible mixing processes \( \Theta \) and \( \overline{S}_\Lambda \). The next term in Eqn. (A.29.2), \( \mathbf{v} \cdot \mathbf{s}^\text{ref} \), is also expected; it is the mean vertical motion through the \( \gamma^n \) surface due to the helical motion of neutral trajectories in the reference data set, caused in turn by the non-zero neutral helicity of the reference data set. The remaining terms in the last four lines of Eqn. (A.29.2) arise because of the non-quasi-material (non-potential) nature of Neutral Density. The second line of Eqn. (A.29.2) represents the contribution to \( \mathbf{\tilde{v}} \) arising from the seemingly innocuous sliding motion along the sloping \( \gamma^n \) surface and from the vertical heaving of these surfaces. The lateral gradients of properties in the reference data set also affect the mean flow \( \mathbf{\tilde{v}} \) through the \( \gamma^n \) surface. Note that as \( (\Theta - \Theta^\text{ref}) \) tends to zero, \( (\psi^n - 1) \) also tends to zero so that the third line of Eqn. (A.29.2) is well-behaved and becomes proportional to \( p_z^{-1} (p - p^\text{ref}) \mathbf{\tilde{v}} \cdot \nabla \Theta^\text{ref} \).
A.30 Computationally efficient 25-term expressions for the density of seawater in terms of Θ and θ

Ocean models to date have treated their salinity and temperature variables as being Practical Salinity $S_p$ and potential temperature $θ$. As the full implications of TEOS-10 are incorporated into ocean models they will need to carry Preformed Salinity $S_A$ and Conservative Temperature $Θ$ as conservative variables (as discussed in appendices A.20 and A.21), and a computationally efficient expression for density in terms of Absolute Salinity $S_A$ and Conservative Temperature $Θ$ will be needed.

Following the work of McDougall et al. (2003) and Jackett et al. (2006), the TEOS-10 density $ρ$ has been approximated by a rational function of the same form as in those papers. The fitted expression is the ratio of two polynomials of $(S_A, Θ, p)$

$$ρ ≈ ρ^{25} = \frac{P_{num}^{25}}{P_{denom}^{25}}.$$  \hspace{1cm} (A.30.1)

The density data has been fitted in a “funnel” of data points in $(S_A, t, p)$ space which is described in more detail in McDougall et al. (2010b). The “funnel” extends to a pressure of 8000 dbar. At the sea surface the “funnel” covers the full range of temperature and salinity while for pressures greater than 5500 dbar, the maximum temperature of the fitted data is 12°C and the minimum Absolute Salinity is $u_{ps} 30$ g kg$^{-1}$. That is, the fit has been performed over a region of parameter space which includes water that is approximately 10°C warmer and 5 g kg$^{-1}$ fresher in the deep ocean than exists in the present ocean (see Figure 1 of Jackett et al. (2006)). Table K.1 of appendix K contains the 25 coefficients of the expression (A.30.1) for density in terms of $(S_A, Θ, p)$.

As outlined in appendix K, this 25-term rational-function expression for $ρ$ yields the thermal expansion and haline contraction coefficients, $α^Θ$ and $β^Θ$, that are essentially as accurate as those derived from the full TEOS-10 Gibbs function for data in the “oceanographic funnel”. The same cannot be claimed for the sound speed derived by differentiating Eqn. (A.30.1) with respect to pressure; this sound speed has an rms error in the “funnel” of almost 0.25 m s$^{-1}$ whereas TEOS-10 fits the available sound speed data with an rms error of only 0.035 m s$^{-1}$.

In dynamical oceanography it is the thermal expansion and haline contraction coefficients $α^Θ$ and $β^Θ$ which are the most important aspects of the equation of state since the “thermal wind” is proportional to $α^Θ \nabla \rho Θ − β^Θ \nabla \rho S_A$ and the vertical static stability is given in terms of the buoyancy frequency $N$ by $g^{-1}N^2 = α^Θ Θ_z − β^Θ (S_A)_z$. Hence for dynamical oceanography we may take the 25-term rational function expression for density, Eqn. (A.30.1), as essentially reflecting the full accuracy of TEOS-10. This is confirmed in Fig. A.30.1 where the error in using the 25-term expression for density to calculate the isobaric northward density gradient is shown. The vertical axis on this figure is the magnitude of the difference in the northward isobaric density gradient in the world ocean below 1000 m when evaluated using Eqn. (A.30.1) versus using the full TEOS-10 Gibbs function. The scales of the axes of this figure have been chosen to be the same as those of Fig. A.5.1 of appendix A.5 so that the smallness of the errors associated with using the 25-term density expression can be appreciated. The errors represented in Fig. A.30.1 represent perhaps half of the remaining uncertainty in our knowledge of seawater properties, and by comparing Figs. A.30.1 and A.5.1 it is clear that the much more important issue is to properly represent the effects of seawater composition on seawater density. The rms value of the vertical axis in Fig. A.30.1 is 11.4% of that of Fig. A.5.1.

McDougall et al. (2010b) have also provided a 25-term rational-function expression for density in terms of $(S_A, θ, p)$. The 25 coefficients can be found in Table K.2 of appendix K. As an approximation to density, this 25-term rational function is approximately as accurate as the one described above in terms of $(S_A, Θ, p)$. It must be emphasized though
that an ocean model that treated potential temperature as a conservative variable would make errors in its treatment of heat fluxes, as described in appendices A.13, A.14 and A.17, and as illustrated in Figures A.13.1, A.14.1 and A.17.1.

**Figure A.30.1.** The northward density gradient at constant pressure (the horizontal axis) for data in the world ocean atlas of Gouretski and Koltermann (2004) for \( p > 1000 \) dbar. The vertical axis is the magnitude of the difference between evaluating the density gradient using the 25-term expression Eqn. (A.30.1) instead of using the full TEOS-10 expression, using Absolute Salinity \( S_A \) as the salinity argument in both cases.

Appendix P describes how an expression for the enthalpy of seawater in terms of Conservative Temperature, specifically the functional form \( h(S_A, \Theta, p) \), together with an expression for entropy in the form \( \eta(S_A, \Theta) \), can be used as an alternative thermodynamic potential to the Gibbs function \( g(S_A, t, p) \). The need for the functional form \( h(S_A, \Theta, p) \) also arises in section 3.32 and in Eqns. (3.26.3) and (3.29.1). The 25-term expression, Eqn. (A.30.1), for \( \rho^{25} = \rho^{25}(S_A, \Theta, p) \) can be used to find a closed expression for \( h(S_A, \Theta, p) \) by integrating the reciprocal of \( \rho^{25}(S_A, \Theta, p) \) with respect to pressure (in Pa), since \( \dot{h}_p = v = \rho^{-1} \) (see Eqn. (2.8.3)).

The 25-term expression for specific volume, Eqn. (A.30.1), is first written explicitly as the ratio of two polynomials in sea pressure \( p \) (in dbar) as

\[
\dot{\nu}^{25} = \frac{1}{\rho^{25}} = \frac{a_0 + a_1 p + a_2 p^2 + a_3 p^3}{b_0 + 2b_1 p + b_2 p^2},
\]

(A.30.2)

where the coefficients \( a_0 \) to \( a_3 \) and \( b_0 \) to \( b_2 \) are the following functions of \( S_A \) and \( \Theta \):

\[
a_0 = 1 + c_{14} \Theta + c_{15} \Theta^2 + c_{16} \Theta^3 + c_{17} \Theta^4 + c_{18} S_A + c_{19} S_A \Theta + c_{20} S_A \Theta^2 + c_{21} (S_A)^{1.5} + c_{22} (S_A)^{1.5} \Theta^2,
\]

\[
a_1 = c_{23},
\]

\[
a_2 = c_{24} \Theta^3,
\]

\[
a_3 = c_{25} \Theta,
\]

\[
b_0 = c_1 + c_2 \Theta + c_3 \Theta^2 + c_4 \Theta^3 + c_5 S_A + c_6 S_A \Theta + c_7 (S_A)^2,
\]

\[
b_1 = 0.5 \left( c_8 + c_9 \Theta^2 + c_{10} S_A \right),
\]

\[
b_2 = c_{11} + c_{12} \Theta^2,
\]

and the numbered coefficients \( c_1 \) to \( c_{25} \) are so identified in Table K.1 (note that \( c_{13} = 1 \)).

It is not difficult to rearrange Eqn. (A.30.2) into the form
\[
\hat{v}^{25} = \hat{v}^{25}(S_A, \Theta, p) = \left( \frac{a_2}{b_2} - \frac{2a_1b_1}{b_2^2} \right) + \frac{a_2}{b_2} p + \frac{N + Mp}{b_0 + 2h_2p + b_2p^2},
\]

(A.30.3)

where \( N \) and \( M \) are given by

\[
N = a_0 + \frac{2a_1b_1}{b_2} - \frac{a_2b_1}{b_2}, \quad \text{and} \quad M = a_1 + \frac{4a_1b_1^2}{b_2^2} - \frac{a_2b_1}{b_2} - \frac{2a_2b_1}{b_2}.
\]

(A.30.4)

The pressure integral of the last term in Eqn. (A.30.3) is well known (see for example section 2.103 of Gradshteyn and Ryzhik (1980)) and is dependent on the sign of the discriminant of the denominator. In our case it can be shown that \( b_1 > b_2 \) over the domain of the “funnel” and also that both \( b_0 \) and \( b_1 \) are positive, while \( b_2 \) is negative and bounded away from zero. The indefinite integral, with respect to sea pressure measured in Pa, of the last term in Eqn. (A.30.3) is

\[
\int \frac{N + Mp}{b_0 + 2h_2p + b_2p^2} \, dp' = \frac{M^*}{2b_2} \ln \left| \frac{b_0 + 2h_1p + b_2p^2}{b_0 + 2h_1p + b_2p^2} \right| + \frac{N^*b_2 - M^*b_1}{2b_2\sqrt{b_1^2 - b_2^2}} \ln \left| \frac{b_0 + 2h_1p + \sqrt{b_1^2 - b_2^2}}{b_0 + 2h_1p - \sqrt{b_1^2 - b_2^2}} \right|
\]

(A.30.5)

where \( N^* = 10^4N \) and \( M^* = 10^4M \). The enthalpy \( \hat{h}^{25}(S_A, \Theta, p) \) is the definite integral of Eqn. (A.30.3) from \( p = 0 \) dbar to \( p \), plus the value of enthalpy at \( p = 0 \) dbar, namely \( c_p^0\Theta \).

Hence the full expression for \( \hat{h}^{25}(S_A, \Theta, p) \) is

\[
\hat{h}^{25}(S_A, \Theta, p) = c_p^0\Theta + 10^4 \left( \frac{a_2}{b_2} - \frac{2a_1b_1}{b_2^2} \right) p + 10^4 \frac{a_2}{b_2} p^2
\]

\[
+ \frac{M^*}{2b_2} \ln \left| \frac{b_0 + 2h_1p + b_2p^2}{b_0 + 2h_1p + b_2p^2} \right| + \frac{N^*b_2 - M^*b_1}{2b_2\sqrt{b_1^2 - b_2^2}} \ln \left| \frac{b_0 + 2h_1p + \sqrt{b_1^2 - b_2^2}}{b_0 + 2h_1p - \sqrt{b_1^2 - b_2^2}} \right|
\]

(A.30.6)

\[
- \frac{M^*}{2b_2} \ln \left| b_0 \right| - \frac{N^*b_2 - M^*b_1}{2b_2\sqrt{b_1^2 - b_2^2}} \ln \left| \frac{b_0 - \sqrt{b_1^2 - b_2^2}}{b_0 + \sqrt{b_1^2 - b_2^2}} \right|
\]

The factor of \( 10^4 \) that appears here and in \( N^* \) and \( M^* \) effectively serves to convert the pressure of the integration variable from dbar to Pa so that \( \hat{h}^{25}(S_A, \Theta, p) \) has units of J kg\(^{-1}\). In these equations \( S_A \) is in g kg\(^{-1}\), \( \Theta \) in °C and \( p \) is in dbar.

The four terms involving natural logarithms in the last two lines of this equation are readily combined so that only two natural logarithms need to be evaluated. The same computational efficiency occurs when the enthalpy difference (at the same values of \( S_A \) and \( \Theta \) but at different pressures) of Eqn. (3.32.2) is evaluated using Eqn. (A.30.6).

Following Young (2010), the difference between specific enthalpy and \( c_p^0\Theta \) may be called “dynamic enthalpy” and can be readily calculated from Eqn. (A.30.6), recognizing that this equation is based on the 25-term expression for density of McDougall et al. (2010b) rather than being evaluated from the full TEOS-10 Gibbs function. Similarly, the partial derivatives of \( \hat{h}^{25}(S_A, \Theta, p) \) with respect to Absolute Salinity \( S_A \) and with respect to Conservative Temperature \( \Theta \) can be calculated either by algebraic differentiation of Eqn. (A.30.6) or by first algebraically differentiating Eqn. (A.30.1) and then numerically integrating this expression with respect to pressure (this second procedure is motivated by taking the appropriate \( S_A \) or \( \Theta \) derivatives of Eqn. (3.2.1); see Eqns. (A.18.4) and (A.18.5)). These partial derivatives, the 25-term expression (A.30.1), and the expression (A.30.6) for \( \hat{h}^{25}(S_A, \Theta, p) \) are available as part of the GSW software library.

An expression \( \hat{h}^{25}(S_A, \theta, p) \) for enthalpy as a function of potential temperature \( \theta \) can be found in a similar manner to that outlined above, but with the coefficients of the 25-term rational-function expression for density now being taken from Table K.2, and with the first term being expressed as the exact polynomial expression for \( \hat{h}(S_A, \theta, 0) \) instead of as \( c_p^0\Theta \).
Appendix B:
Derivation of the First Law of Thermodynamics

Motivation
For a pure fluid in which there is no dissolved material (such as pure water with zero Absolute Salinity) the derivation of the First Law of Thermodynamics usually starts with a discussion of how the internal energy $U$ of a fixed mass of fluid is changed under the influence of it being “heated” by the amount $\delta Q$ and its volume $V$ being changed. The infinitesimal change in the internal energy of the parcel is written as $dU = \delta Q - (p + P_0) dV$ where $-(p + P_0) dV$ is the mechanical work done on the fluid by the pressure at the moving boundaries of the fluid parcel. This relationship can be written in terms of the specific (i.e. per unit mass) enthalpy $h$, the density $\rho$, and $\delta Q$ per unit volume, $\delta q$, as

$$\rho \left( \frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} \right) = \frac{\delta q}{dt}. \quad \text{for pure water (B.1)}$$

It is recognized that the right-hand side of (B.1) is not the divergence of a “heat” flux, and the term that causes this complication is the dissipation of mechanical energy into “heat”, which contributes $\rho \varepsilon$ to the right-hand side of (B.1). Apart from this familiar dissipation term, the right-hand side is minus the divergence of the sum of the boundary and radiative heat fluxes, $\mathbf{F}^R$, and minus the divergence of the molecular flux of heat $\mathbf{F}^S = -kT \nabla T$ (where $k_T$ is the molecular diffusivity of heat), so that the First Law of Thermodynamics for pure water is

$$\rho \left( \frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} \right) = \frac{\delta q}{dt} = -\nabla \cdot \mathbf{F}^R + \nabla \cdot (k_T \nabla T) + \rho \varepsilon. \quad \text{for pure water (B.2)}$$

Now consider seawater in which the Absolute Salinity and its gradients are non-zero. The same traditional discussion of the First Law of Thermodynamics involving the “heating”, the application of compression work and the change of salinity to a fluid parcel shows that the change of enthalpy of the fluid parcel is given by (see equations 6b and 17b of Warren (2006))

$$dH - V dP = \delta Q + (\mu - [T_0 + t] \mu_T) M dS_A,$$ \hspace{1cm} (B.3)

where $M$ is the mass of the fluid parcel. When written in terms of the specific enthalpy $h$, and $\delta Q$ per unit volume, $\delta q$, this equation becomes (using $\rho dS_A / dt = -\nabla \cdot \mathbf{F}^S$)

$$\rho \left( \frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} \right) = \frac{\delta q}{dt} - (\mu - [T_0 + t] \mu_T) \nabla \cdot \mathbf{F}^S. \quad \text{(B.4)}$$

Does this help with the task of constructing an expression for the right-hand side of (B.4) in terms of the dissipation of mechanical energy and the molecular, radiative and boundary fluxes of “heat” and salt? If the “heating” term $\delta q / dt$ in (B.4) were the same as in the pure water case (B.2) then we would have successfully derived the First Law of Thermodynamics in a saline ocean via this route. However, we will now show that $\delta q / dt$ in (B.4) is not the same as that in the pure water case, (B.2).

Substituting the expression for $\delta q / dt$ from (B.2) into the right-hand side of (B.4) we find that the right-hand side is not the same as the First Law of Thermodynamics (B.19) which we derive below (this comparison involves using the correct expression (B.24)) for
the molecular flux $F^0$). The two versions of the First Law of Thermodynamics are different by

$$- (\mu - [T_0 + t] \mu_T) \nabla \cdot F^S + \nabla \cdot \left[ \mu + b \frac{[T_0 + t] \mu_S}{\rho k^S} \right] F^S \right]. \tag{B.5}$$

This inconsistency means that the rather poorly defined “rate of heating” $\delta q/\delta t$ must be different in the saline case than in the pure water situation by this amount. We know of no way of justifying this difference and in the absence of new inspiration which we have not found in the literature, we tentatively conclude that any attempt to derive the First Law of Thermodynamics via this route involving the loosely defined “rate of heating” $\delta q/\delta t$ is doomed to failure.

Since there appears to be no way of deriving the First Law of Thermodynamics that involves the “heating” term $\delta q/\delta t$, we follow Landau and Lifshitz (1959) and derive the First Law via the following circuitous route. Rather than attempting to guess the form of the molecular forcing terms in this equation directly, we first construct a conservation equation for the total energy, being the sum of the kinetic, gravitational potential and internal energies. It is in this equation that we insert the molecular fluxes of heat and momentum and the radiative and boundary fluxes of heat. We know that the evolution equation for total energy must have the conservative form, and so we insist that the forcing terms in this equation appear as the divergence of fluxes.

Having formed the conservation equation for total energy, the known evolution equations for two of the types of energy, namely the kinetic and gravitational potential energies, are subtracted, leaving a prognostic equation for the internal energy, that is, the First Law of Thermodynamics.

We start by developing the evolution equations for gravitational potential energy and for kinetic energy (via the momentum equation). The sum of these two evolution equations is noted. We then step back a little and consider the simplified situation where there are no molecular fluxes of heat and salt and no effects of viscosity and no radiative or boundary heat fluxes. In this “adiabatic” limit we are able to develop the conservation equation for total energy, being the sum of internal energy, kinetic energy and gravitational potential energy. To this equation we introduce the molecular, radiative and boundary flux divergences. Finally the First Law of Thermodynamics is found by subtracting from this total energy equation the conservation statement for the sum of the kinetic and gravitational potential energies.

**The fundamental thermodynamic relation**

Recall the fundamental thermodynamic relation (A.7.1) repeated here in the form (A.7.2) in terms of material derivatives following the instantaneous motion of a fluid parcel $d / dt = \partial / \partial t + \mathbf{v} \cdot \nabla$,

$$\frac{dh}{dt} - \frac{1}{\rho} \frac{dP}{dt} = \frac{du}{dt} + (P + P_0) \frac{dv}{dt} = (T_0 + t) \frac{d\eta}{dt} + \mu \frac{d\Sigma_A}{dt}. \tag{B.6}$$

The use of the same symbol $t$ for time and for in situ temperature in °C is noted but should not cause confusion. The middle expression in (B.6) uses the fact that specific enthalpy $h$ and specific internal energy $u$ are related by $h = u + P v = u + (P + P_0) v$ where $v$ is the specific volume.
Gravitational potential energy

If the gravitational acceleration is taken to be constant the gravitational potential energy per unit mass with respect to the height \( z = 0 \) is simply \( gz \). Allowing the gravitational acceleration to be a function of height means that the gravitational potential energy per unit mass \( \Phi \) with respect to some fixed height \( z_0 \) is defined by

\[
\Phi = \int_{z_0}^{z} g(z') \, dz'. \tag{B.7}
\]

At a fixed location in space \( \Phi \) is independent of time while its spatial gradient is given by \( \nabla \Phi = g \mathbf{k} \) where \( \mathbf{k} \) is the unit vector pointing upwards in the vertical direction. The evolution equation for \( \Phi \) is then readily constructed as

\[
(\rho \dot{\Phi}) + \nabla \cdot (\rho \Phi \mathbf{u}) = \rho \frac{d\Phi}{dt} = \rho gw, \tag{B.8}
\]

Where \( w \) is the vertical component of the three-dimensional velocity, that is \( w = \mathbf{u} \cdot \mathbf{k} \). (Clearly in this section \( g \) is the gravitational acceleration, not the Gibbs function). Note that this local balance equation for gravitational potential energy is not in the form (A.8.1) required of a conservative variable since the right-hand side of (B.8) is not minus the divergence of a flux.

Momentum evolution equation

The momentum evolution equation is derived in many textbooks including Landau and Lifshitz (1959), Batchelor (1970), Gill (1982) and Griffies (2004). The molecular viscosity appears in the exact momentum evolution equation in the rather complicated expressions appearing in equations (3.3.11) and (3.3.12) of Batchelor (1970). We ignore the term that depends on the product of the so called dynamic viscosity \( \nu_{\text{visc}} \) and the velocity divergence \( \nabla \cdot \mathbf{u} \) (following Gill (1982)), so arriving at

\[
\rho \frac{d\mathbf{u}}{dt} + f \times \rho \mathbf{u} = -\nabla P - \rho g \mathbf{k} + \nabla \cdot \left( \rho \nu_{\text{visc}} \nabla \mathbf{u} \right), \tag{B.9}
\]

Where \( f \) is the Coriolis frequency, \( \nu_{\text{visc}} \) is the viscosity and \( \nabla \mathbf{u} \) is twice the symmetrized velocity shear, \( \nabla \mathbf{u} = \left( \partial u_i / \partial x_j + \partial u_j / \partial x_i \right) \). Under the same assumption as above of ignoring the velocity divergence, the pressure \( P \) that enters (B.9) can be shown to be equivalent to the equilibrium pressure that is rightly the pressure argument of the equation of state (Batchelor 1970). The centripetal acceleration associated with the coordinate system being on a rotating planet can be taken into account by an addition to the gravitational acceleration in (B.9) (Griffies 2004)).

Kinetic energy evolution equation

The kinetic energy evolution equation is found by taking the scalar product of Eqn. (B.9) with \( \mathbf{u} \) giving

\[
(\rho \frac{1}{2} \mathbf{u} \cdot \mathbf{u})_{,t} + \nabla \cdot \left( \rho \frac{1}{2} [\mathbf{u} \cdot \mathbf{u}] \right) = \rho \frac{d}{dt} \left( \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) = \mathbf{u} \cdot \nabla P - \rho gw + \nabla \cdot \left( \rho \nu_{\text{visc}} \nabla \frac{1}{2} [\mathbf{u} \cdot \mathbf{u}] \right) - \rho \varepsilon, \tag{B.10}
\]

where the dissipation of mechanical energy \( \varepsilon \) is the positive definite quantity

\[
\varepsilon = \frac{1}{2} \nu_{\text{visc}} \left( \nabla \mathbf{u} \cdot \nabla \mathbf{u} \right). \tag{B.11}
\]
**Evolution equation for the sum of kinetic and gravitational potential energies**

The evolution equation for total mechanical energy \(0.5u \cdot u + \Phi\) is found by adding Eqns. (B8) and (B10) giving

\[
\left( \rho \left[ \frac{1}{2}u \cdot u + \Phi \right] \right)_t + \nabla \cdot \left( \rho u \left[ \frac{1}{2}u \cdot u + \Phi \right] \right) = \rho d \left( \frac{1}{2}u \cdot u + \Phi \right)/dt = -u \cdot \nabla P + \nabla \cdot \left( \rho v_{\text{visc}} \nabla \frac{1}{2} \left[ u \cdot u \right] \right) - \rho \varepsilon. \tag{B.12}
\]

Notice that the term \(\rho gw\) which has the role of exchanging energy between the kinetic and gravitational potential forms has cancelled when these two evolution equations were added.

**Conservation equation for total energy \(\mathcal{E}\) in the absence of molecular fluxes**

In the absence of molecular or other irreversible processes (such as radiation of heat), and in the absence of the non-conservative source term for Absolute Salinity that is associated with remineralization, both the specific entropy \(\eta\) and the Absolute salinity \(S_A\) of each fluid parcel is constant following the fluid motion so that the right-hand side of (B.6) is zero and the material derivative of internal energy satisfies \(du/dt = (p + P_0)dv/dt\) so that the internal energy changes only as a result of the work done in compressing the fluid parcel. Realizing that \(v = \rho^{-1}\) and using the continuity Eqn. (A.8.1) in the form \(d\rho/dt + \rho \nabla \cdot u = 0\), \(du/dt\) can be expressed in this situation of no molecular, radiative or boundary fluxes as \(du/dt = -\rho^{-1}(p + P_0)\nabla \cdot u\). Adding this equation to the inviscid, non-dissipative version of (B.12) gives

\[
\left( \rho \mathcal{E} \right)_t + \nabla \cdot \left( \rho u \mathcal{E} \right) = \rho d \mathcal{E}/dt = -\nabla \cdot \left( [p + P_0]u \right), \quad \text{no molecular fluxes (B.13)}
\]

where the total energy

\[
\mathcal{E} = u + \frac{1}{2}u \cdot u + \Phi \tag{B.14}
\]

is defined as the sum of the internal, kinetic and gravitational potential energies.

**Conservation equation for total energy in the presence of molecular fluxes and remineralization**

Now, following section 49 Landau and Lifshitz (1959) we need to consider how molecular fluxes of heat and salt and the radiation of heat will alter the simplified conservation equation of total energy (B.14). The molecular viscosity gives rise to a stress in the fluid represented by the tensor \(\mathbf{\sigma}\), and the interior flux of energy due to this stress tensor is \(u \cdot \mathbf{\sigma}\) so that there needs to be the additional term \(-\nabla \cdot (u \cdot \mathbf{\sigma})\) added to the right-hand side of the total energy conservation equation. Consistent with Eqn. (B.9) above we take the stress tensor to be \(\mathbf{\sigma} = -\rho v_{\text{visc}} \mathbf{\nabla} u\) so that the extra term is \(-\nabla \cdot \left( \rho v_{\text{visc}} \mathbf{\nabla} \frac{1}{2} \left[ u \cdot u \right] \right)\). Also heat fluxes at the ocean boundaries and by radiation \(\mathbf{F}^R\) and molecular diffusion \(\mathbf{F}^D\) necessitate the additional terms \(-\nabla \cdot \mathbf{F}^R - \mathbf{\nabla} \cdot \mathbf{F}^D\). At this stage we have not specified the form of the molecular diffusive flux of heat \(\mathbf{F}^D\) in terms of gradients of temperature and Absolute Salinity; this is done below in eq. (B.24). The non-conservative production of Absolute Salinity by the remineralization of sinking particulate matter, \(\rho \mathcal{S}^{\lambda}\), introduces a source of energy because the specific internal energy and the specific enthalpy of seawall are not the same as for pure water. The total energy conservation equation in the presence of molecular, radiative and boundary fluxes, as well as the interior source of salinity is

\[
\left( \rho \mathcal{E} \right)_t + \nabla \cdot \left( \rho u \mathcal{E} \right) = \rho d \mathcal{E}/dt = -\nabla \cdot \left( [p + P_0]u \right) - \nabla \cdot \mathbf{F}^R - \mathbf{\nabla} \cdot \mathbf{F}^D
\]

\[
+ \nabla \cdot \left( \rho v_{\text{visc}} \mathbf{\nabla} \frac{1}{2} \left[ u \cdot u \right] \right) + h_{\mathcal{S}} \rho \mathcal{S}^{\lambda}. \tag{B.15}
\]
where \( h_{SA} = \mu - (T_0 + t) \mu_T \) (see Eqn. (A.11.1)) is the partial derivative of specific enthalpy with respect to Absolute Salinity at fixed temperature and pressure. This last term in Eqn. (B.15) is more readily justified in Eqn. (B.17) below, which is a rearranged form of Eqn. (B.15).

If it were not for the remineralization source term, \( h_{SA} \rho \mathcal{S}^{SA} \), the right-hand side of the \( \mathcal{E} \) conservation equation (B.15) would be the divergence of a flux, ensuring that total energy \( \mathcal{E} \) would be both a “conservative” variable and an “isobaric conservative” variable (see appendix A.8 for the definition of these characteristics).

**Two alternative forms of the conservation equation for total energy**

Another way of expressing the total energy equation (B.15) is to write it in a quasi-divergence form, with the temporal derivative being of \( \rho \mathcal{E} = \rho (\dot{u} + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi) \) while the divergence part of the left-hand side is based on a different quantity, namely the Bernoulli function \( \mathbf{B} = h + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi \). This form of the total energy equation is

\[
(\rho \mathcal{E})_i + \nabla \cdot (\rho \mathbf{u} \mathbf{B}) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^G + \nabla \cdot \left( \rho \nu \text{visc} \nabla \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + h_{SA} \rho \mathcal{S}^{SA}.
\]

(B.16)

In an ocean modelling context, it is rather strange to contemplate the energy variable that is advected through the face of a model grid, \( \mathbf{B} \), to be different to the energy variable that is changed in the grid cell, \( \mathcal{E} \). Hence this form of the total energy equation has not proved popular.

A third way of expressing the total energy equation (B.15) is to write the left-hand side in terms of only the Bernoulli function \( \mathbf{B} = h + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi \) so that the prognostic equation for the Bernoulli function is

\[
\frac{d}{dt} (\rho \mathbf{B}) + \nabla \cdot (\rho \mathbf{u} \mathbf{B}) = \rho \mathbf{B}_i = P_i - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^G + \nabla \cdot \left( \rho \nu \text{visc} \nabla \frac{1}{2} \mathbf{u} \cdot \mathbf{u} \right) + h_{SA} \rho \mathcal{S}^{SA}.
\]

(B.17)

The source term \( \rho \mathcal{S}^{SA} \) of Absolute Salinity caused by the remineralization of particulate matter affects enthalpy at the rate \( h_{SA} = \mu - (T_0 + t) \mu_T \) and can be thought of as replacing some seasalt in place of water molecules, occurring at fixed pressure and temperature, as might occur through two syringes in the interior of a seawater parcel, one supplying pure salt and the other extracting pure water, at the same temperature and pressure. The influence of the salinity increment caused by this source term on enthalpy (and therefore on the Bernoulli function \( \mathbf{B} \)) is similar to the way an increment of Absolute Salinity enters Eqn. (B.3). When the flow is steady, and in particular, when the pressure field is time invariant at every point in space, this Bernoulli form of the total energy equation has the desirable property that \( \mathbf{B} \) is conserved following the fluid motion in the absence of radiative, boundary and molecular fluxes and in the absence of non-conservative salinity production. Subject to this steady-state assumption, and in the absence of \( \rho \mathcal{S}^{SA} \) the Bernoulli function \( \mathbf{B} \) possesses the “potential” property. The negative aspect of this \( \mathbf{B} \) evolution equation (B.17) is that in the more general situation where the flow is unsteady, the presence of the \( P_i \) term means that the Bernoulli function does not behave as a conservative variable because the right-hand side of (B.17) is not the divergence of a flux. In this general non-steady situation \( \mathbf{B} \) is “isobaric conservative” but is not a “conservative” variable nor does it posses the “potential” property.

Noting that the total energy \( \mathcal{E} \) is related to the Bernoulli function by \( \mathcal{E} = \mathbf{B} - (P_i + P_0)/\rho \) and continuing to take the whole ocean to be in a steady state and with \( \rho \mathcal{S}^{SA} = 0 \), so that \( \mathbf{B} \) has the “potential” property, it is clear that \( \mathcal{E} \) does not have the “potential” property in this situation. That is, if a seawater parcel moves from say 2000 dbar to 0 dbar without exchange of material or heat with its surroundings and with \( P_i = 0 \) everywhere, then \( \mathbf{B} \) remains constant while the parcel’s total energy \( \mathcal{E} \) changes by the difference in the quantity \( -(P_i + P_0)/\rho \) between the two locations. Hence we conclude that even in a steady ocean \( \mathcal{E} \) does not posses the “potential” property.
Obtaining the First Law of Thermodynamics by subtraction

The evolution equation (B.12) for the sum of kinetic and gravitational potential energies is now subtracted from the total energy conservation equation (B.15) giving

\[
(\rho u) + \nabla \cdot (\rho u u) = \rho \frac{du}{dt} = - (p + P_0) \frac{d\theta}{dt} + \nabla \cdot F^R - \nabla \cdot F^Q + \rho \varepsilon + h_{S_A} \rho S^{S_A}. \tag{B.18}
\]

Using the continuity equation in the form \( \rho \frac{dv}{dt} = \nabla \cdot u \) and the fundamental thermodynamic relation (A.7.2), this equation can be written as

\[
\rho \left( \frac{dh}{dt} - \frac{1}{\rho} \frac{d\rho}{dt} \right) = \rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left( (p + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) = - \nabla \cdot F^R - \nabla \cdot F^Q + \rho \varepsilon + h_{S_A} \rho S^{S_A}, \tag{B.19}
\]

which is the First Law of Thermodynamics. The corresponding evolution equation for Absolute Salinity is (Eqn. (A.21.8))

\[
\rho \frac{dS_A}{dt} = (\rho S_A)_t + \nabla \cdot (\rho u S_A) = - \nabla \cdot F^S + \rho S^{S_A}, \tag{B.20}
\]

where \( F^S \) is the molecular flux of salt and \( \rho S^{S_A} \) is the non-conservative source of Absolute Salinity due to the remineralization of particulate matter. For many purposes in oceanography the exact dependence of the molecular fluxes of heat and salt on the gradients of Absolute Salinity, temperature and pressure is unimportant, nevertheless, Eqns. (B.23) and (B.24) below list these molecular fluxes in terms of the spatial gradients of these quantities.

At first sight Eqn. (B.19) has little to recommend it; there are two non-conservative source terms \( \rho \varepsilon \) and \( h_{S_A} \rho S^{S_A} \) on the right-hand side and the left-hand side is not \( \rho \) times the material derivative of any quantity as is required of a conservation equation of a conservative variable. Equation (B.19) corresponds to equation (57.6) of Landau and Lifshitz (1959) and is repeated at Eqns. (A.13.1) and (A.13.3) above.

The approach used here to develop the First Law of Thermodynamics seems rather convoluted in that the conservation equation for total energy is first formed, and then the evolution equations for kinetic and gravitational potential energies are subtracted. Moreover, the molecular, radiative and boundary fluxes were included into the total energy conservation equation as separate deliberate flux divergences, rather than coming from an underlying basic conservation equation. This is the approach of Landau and Lifshitz (1959) and it is adopted for the following reasons. First this approach ensures that the molecular, radiative and boundary fluxes do enter the total energy conservation equation (B.15) as the divergence of fluxes so that the total energy is guaranteed to be a conservative variable (apart from the salinity source term). This is essential; total energy can only be allowed to spontaneously appear or disappear when there is a \textit{bona fide} interior source term such as \( h_{S_A} \rho S^{S_A} \). Second, it is rather unclear how one would otherwise arrive at the molecular fluxes of heat and salt on the right-hand side of the First Law of Thermodynamics since the direct approach which was attempted at the beginning of this appendix involved the poorly defined “rate of heating” \( \frac{\Delta q}{\Delta t} \) and did not lead us to the First Law. For completeness, the molecular fluxes \( F^Q \) and \( F^S \) are now written in terms of the spatial gradients of Absolute Salinity, temperature and pressure.

Landau and Lifshitz (1959) (their section 58) show that the molecular fluxes \( F^Q \) and \( F^S \) are given in terms of the chemical potential \( \mu \) and the gradients of temperature and of chemical potential by
\[ \mathbf{F}^S = -a \nabla \mu - b \nabla T, \]  
(B.21)

and

\[ \mathbf{F}^Q = -b(T_0 + t) \nabla \mu - \gamma \nabla T + \mu \mathbf{F}^S, \]  
(B.22)

where \( a, b \) and \( \gamma \) are three independent coefficients. Note the symmetry between some of the cross-diffusion terms in that the same coefficient \( b \) appears in both equations. When written in terms of the gradients of Absolute Salinity, temperature and pressure these expressions for the molecular fluxes \( \mathbf{F}^Q \) and \( \mathbf{F}^S \) become

\[ \mathbf{F}^S = -\rho k^S \nabla S_A - \left( \frac{\rho k^S \mu_T}{\mu_{S_A}} + b \right) \nabla T + \frac{k^S \beta^S}{\mu_{S_A}} \nabla P, \]  
(B.23)

(using the relation \( \beta^S = -\rho \mu_p \) that follows from the definition of both \( \beta^i \) and \( \mu \) in terms of the Gibb’s function) and

\[ \mathbf{F}^Q = \left( \mu + b \frac{(T_0 + t) \mu_{S_A}}{\rho k^S} \right) \mathbf{F}^S - k^T \nabla T. \]  
(B.24)

These expressions involve the pure molecular diffusivities of temperature and salinity (\( k^T \) and \( k^S \)) and the single parameter \( b \) that appears in part of both the cross-diffusion of salt down the temperature gradient and part of the cross-diffusion of “heat” down the gradient of Absolute Salinity. The other parameters in these equations follow directly from the Gibb’s function of seawater. The last term in (B.23) represents “barodiffusion” as it causes a flux of salt down the gradient of pressure. The middle term in (B.23) is a flux of salt due to the gradient of in situ temperature and is called the Soret effect while the first term in (B.24) is a flux of “heat” caused by the molecular flux of salt, \( \mathbf{F}^S \), and this is called the Dufour effect.

The molecular flux of salt is independent of the four arbitrary constants (Fofonoff (1962)) that appear in the Gibb’s function of seawater (see Eqn. (2.6.2)). Since \( \mu_T \) contains the arbitrary additional constant \( a_4 \), the fact that \( \mathbf{F}^S \) contains no arbitrary constants implies that the cross-diffusion coefficient \( b \) in Eqns. (B.21)–(B.24) is arbitrary to the extent \(- a_4 \rho k^S / \mu_{S_A}\).

The molecular flux of “heat” \( \mathbf{F}^Q \) is unknowable to the extent \( a_3 \mathbf{F}^S \) (since \( \mu \) is arbitrary to the extent \( a_3 + a_4 (T_0 + t) \) and the presence of \( b \) in Eqn. (B.24) cancels the influence of \( a_4 \)). This means that the \(- \nabla \cdot \mathbf{F}^Q\) term on the right of the First Law Eqn. (B.19) is unknowable to the extent \(- a_3 \nabla \cdot \mathbf{F}^S\). The left-hand side of Eqn. (B.19) is unknowable to the extent \( a_3 \rho dS_{S_A}/dt \) (since specific enthalpy \( h \) contains the arbitrary component \( a_1 + a_2 S_A \)). The last term in Eqn. (B.19) contains the arbitrary term \( a_3 \rho S_{S_A} \) (since \( h_{S_A} \) is arbitrary by the amount \( a_3 \)). These three arbitrary, unknowable contributions to the First Law of Thermodynamics Eqn. (B.19) sum to \( a_3 \) times the evolution equation (B.20) for Absolute Salinity. This allows these arbitrary terms to be subtracted from Eqn. (B.19), confirming that the four arbitrary unknowable constants of Eqn. (2.6.2) have no measurable consequences on the First Law of Thermodynamics.

Regarding Eqns. (B.21)–(B.24), it is noted that strictly speaking the gradient of the chemical potential \( \mu \) must be replaced by the gradients of the chemical potentials of the individual constituents of sea salt, and the diffusion coefficients in front of these many gradients are different for each constituent, since there is no uniform molecular diffusion of the mixture "sea salt". When additional processes act to keep the composition approximately fixed, the use of only one chemical potential for sea salt is permitted in non-equilibrium situations. These processes are mainly ion relaxation by Coulomb forces, which in the form of ambipolar diffusion prevent any local electrical charge separation, and secondly, turbulent mixing which has the same transport coefficient for each species and whose fluxes are proportional to the concentration gradients of “potential” quantities (see appendix A.9) rather than to the gradients of the individual chemical potentials.
Appendix C:
Publications describing the TEOS-10 thermodynamic
descriptions of seawater, ice and moist air

Primary standard documents


Hyland, R. W. and A. Wexler, 1983: Formulations for the thermodynamic properties of dry air
from 173.15 to 473.15 K, and of saturated moist air from 173.15 to 372.15 K, at pressures
up to 5MPa. *ASHRAE Transact.* 89, 520–535.

IAPWS, 2008a: Release on the IAPWS Formulation 2008 for the Thermodynamic Properties of
Seawater. The International Association for the Properties of Water and Steam. Berlin,
Germany, September 2008, available from [http://www.iapws.org](http://www.iapws.org). This Release is referred to
in the text as IAPWS-08.

IAPWS, 2009b: Revised Release on the IAPWS Formulation 1995 for the Thermodynamic
Properties of Ordinary Water Substance for General and Scientific Use. The International
Association for the Properties of Water and Steam. Doorwerth, The Netherlands,
September 2009, available from [http://www.iapws.org](http://www.iapws.org). This revised Release is referred to
in the text as IAPWS-95.

IAPWS, 2009c: Supplementary Release on a Computationally Efficient Thermodynamic
Formulation for Liquid Water for Oceanographic Use. The International Association for
the Properties of Water and Steam. Doorwerth, The Netherlands, September 2009,
available from [http://www.iapws.org](http://www.iapws.org). This Release is referred to in the text as IAPWS-09.

IAPWS, 2009a: Revised Release on the Equation of State 2006 for H₂O Ice Ih. The International
Association for the Properties of Water and Steam. Doorwerth, The Netherlands,
September 2009, available from [http://www.iapws.org](http://www.iapws.org). This revised Release is referred to
in the text as IAPWS-06.

IAPWS, 2010: Guideline on an Equation of State for Humid Air in Contact with Seawater and
Ice, Consistent with the IAPWS Formulation 2008 for the Thermodynamic Properties of
Seawater. The International Association for the Properties of Water and Steam. Niagara
Falls, Canada, July 2010, available from [http://www.iapws.org](http://www.iapws.org). This Guideline is referred to
in the text as IAPWS-10.

properties of air and mixtures of nitrogen, argon and oxygen from 60 to 2000 K at

Seawater and the definition of the Reference-Composition Salinity Scale, *Deep-Sea Res. I*,
55, 50-72.

Secondary standard documents

IOC, SCOR and IAPSO, 2010a: The international thermodynamic equation of seawater – 2010:
Calculation and use of thermodynamic properties. Intergovernmental Oceanographic

Tertiary standard documents


Background papers to the declared standards


Feistel, R., 2008: A Gibbs function for seawater thermodynamics for −6 to 80 °C and salinity up to 120 g kg⁻¹. Deep-Sea Res. I, 55, 1639-1671.


Papers describing computer software


TEOS-10 web site

SCOR/IAPSO Working Group 127 has created and is maintaining the web site [www.TEOS-10.org](http://www.TEOS-10.org) which serves many of the TEOS-10 papers, this TEOS-10 manual as well as the SIA and GSW libraries of oceanographic computer software.

Note that several of the papers listed in this appendix are appearing in *Ocean Science* in the special issue “Thermophysical Properties of Seawater” in 2010.
Appendix D: Fundamental constants

Following the recommendation of IAPWS (2005), the values of the fundamental constants were taken from CODATA 2006 (Mohr et al. (2008)), as listed in Table D.1. Selected properties of pure water were taken from IAPWS (1996, 1997, 2005, 2006) as listed in Table D.2. The chemical Reference Composition of seawater from Millero et al. (2008a) is given in Table D.3. Selected seawater constants derived from the Reference Composition are listed in Table D.4. The exact value of the isobaric “heat capacity” \( c_p^0 \) is given in Table D.5.

### Table D.1. Fundamental constants from CODATA 2006 (Mohr et al. (2008)) and ISO (1993).

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<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
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<td>Pa</td>
<td>normal pressure</td>
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<tr>
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<td>K</td>
<td>Celsius zero point</td>
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</table>


<table>
<thead>
<tr>
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<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
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<td>0.000 84</td>
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<td>0.001</td>
<td>kg m(^{-3})</td>
<td>density at ( T_0 ) and ( P_0 ), ( \rho^0 = 1 / \nu^0 )</td>
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<td>( (\partial \rho^0 / \partial T)_{T} )</td>
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<td>0.06 \times 10(^{-2})</td>
<td>kg m(^{-3}) K(^{-1})</td>
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<tr>
<td>( \rho_t )</td>
<td>999.793</td>
<td>0.01</td>
<td>kg m(^{-3})</td>
<td>triple point density</td>
</tr>
<tr>
<td>( \eta_t )</td>
<td>0</td>
<td>exact</td>
<td>J kg(^{-1}) K(^{-1})</td>
<td>triple point entropy</td>
</tr>
<tr>
<td>( u_t )</td>
<td>0</td>
<td>exact</td>
<td>J kg(^{-1})</td>
<td>triple point internal energy</td>
</tr>
<tr>
<td>( T_{f}^0 )</td>
<td>273.152 519</td>
<td>0.000 002</td>
<td>K</td>
<td>freezing point at ( P_0 )</td>
</tr>
</tbody>
</table>
Table D.3. The sea salt composition definition for reference salinity of the standard ocean.


<table>
<thead>
<tr>
<th>Solute $j$</th>
<th>$Z_j$</th>
<th>$M_j$ <em>g mol⁻¹</em></th>
<th>$X_j$ <em>10⁻⁷</em></th>
<th>$X_j \times Z_j$ <em>10⁻⁷</em></th>
<th>$W_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>+1</td>
<td>22.989 769 28(2)</td>
<td>4188071</td>
<td>4188071</td>
<td>0.3065958</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>+2</td>
<td>24.305 0(6)</td>
<td>471678</td>
<td>943356</td>
<td>0.0365055</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>+2</td>
<td>40.078(4)</td>
<td>91823</td>
<td>183646</td>
<td>0.0117186</td>
</tr>
<tr>
<td>K⁺</td>
<td>+1</td>
<td>39.098 3(1)</td>
<td>91159</td>
<td>91159</td>
<td>0.0113495</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>+2</td>
<td>87.62(1)</td>
<td>810</td>
<td>1620</td>
<td>0.0002260</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>−1</td>
<td>35.453(2)</td>
<td>4874839</td>
<td>−4874839</td>
<td>0.5503396</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>−2</td>
<td>96.062 6(50)</td>
<td>252152</td>
<td>−504304</td>
<td>0.0771319</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>−1</td>
<td>61.016 84(96)</td>
<td>15340</td>
<td>−15340</td>
<td>0.0029805</td>
</tr>
<tr>
<td>Br⁻</td>
<td>−1</td>
<td>79.904(1)</td>
<td>7520</td>
<td>−7520</td>
<td>0.0019134</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>−2</td>
<td>60.008 9(10)</td>
<td>2134</td>
<td>−4268</td>
<td>0.0004078</td>
</tr>
<tr>
<td>B(OH)₄⁻</td>
<td>−1</td>
<td>78.840 4(70)</td>
<td>900</td>
<td>−900</td>
<td>0.0002259</td>
</tr>
<tr>
<td>F⁻</td>
<td>−1</td>
<td>18.998 403 2(5)</td>
<td>610</td>
<td>−610</td>
<td>0.0000369</td>
</tr>
<tr>
<td>OH⁻</td>
<td>−1</td>
<td>17.007 33(7)</td>
<td>71</td>
<td>−71</td>
<td>0.0000038</td>
</tr>
<tr>
<td>B(OH)₃⁻</td>
<td>0</td>
<td>61.833 0(70)</td>
<td>2807</td>
<td>0</td>
<td>0.0005527</td>
</tr>
<tr>
<td>CO₂</td>
<td>0</td>
<td>44.009 5(9)</td>
<td>86</td>
<td>0</td>
<td>0.0000121</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td></td>
<td>1 000 000 0</td>
<td>0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Table D.4. Selected properties of the KCl-normalised reference seawater (Millero et al. 2008a), and proposals of WG127 (2006).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_S$</td>
<td>31.403 8218</td>
<td>0.001</td>
<td>g mol$^{-1}$</td>
<td>reference salinity molar mass $M_S = \sum_j X_j M_j$</td>
</tr>
<tr>
<td>$Z^2$</td>
<td>1.245 2898</td>
<td>exact$^a$</td>
<td></td>
<td>reference salinity valence factor $Z^2 = \sum_j X_j Z_j^2$</td>
</tr>
<tr>
<td>$N_A$</td>
<td>6.022 141 79 x 10$^{23}$</td>
<td>3 x 10$^{16}$</td>
<td>mol$^{-1}$</td>
<td>Avogadro constant</td>
</tr>
<tr>
<td>$N_S$</td>
<td>1.917 6461 x 10$^{22}$</td>
<td>6 x 10$^{17}$</td>
<td>g$^{-1}$</td>
<td>reference salinity particle number $N_S = N_A / M_S$</td>
</tr>
<tr>
<td>$u_{ps}$</td>
<td>1.004 715…</td>
<td>exact$^a$</td>
<td>g kg$^{-1}$</td>
<td>unit conversion factor, $u_{ps} = 35.165 04$ g kg$^{-1}$ / 35</td>
</tr>
<tr>
<td>$S_{SO}$</td>
<td>35.165 04</td>
<td>exact$^a$</td>
<td>g kg$^{-1}$</td>
<td>standard ocean reference salinity, 35 $u_{ps}$</td>
</tr>
<tr>
<td>$T_{SO}$</td>
<td>273.15</td>
<td>exact</td>
<td>K</td>
<td>standard ocean temperature $T_{SO} = T_0$</td>
</tr>
<tr>
<td>$t_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>°C</td>
<td>standard ocean temperature $t_{SO} = T_{SO} - T_0$</td>
</tr>
<tr>
<td>$P_{SO}$</td>
<td>101 325</td>
<td>exact</td>
<td>Pa</td>
<td>standard ocean surface pressure $P_{SO} = P_0$</td>
</tr>
<tr>
<td>$p_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>Pa</td>
<td>standard ocean surface sea pressure $p_{SO} = P_{SO} - P_0$</td>
</tr>
<tr>
<td>$h_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>J kg$^{-1}$</td>
<td>standard ocean surface enthalpy $h_{SO} = u_t$</td>
</tr>
<tr>
<td>$\eta_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>standard ocean surface entropy $\eta_{SO} = \eta_t$</td>
</tr>
<tr>
<td>$S_u$</td>
<td>40.188 617…</td>
<td>exact$^a$</td>
<td>g kg$^{-1}$</td>
<td>unit-related scaling constant, 40 $u_{ps}$</td>
</tr>
<tr>
<td>$t_u$</td>
<td>40</td>
<td>exact</td>
<td>°C</td>
<td>unit-related scaling constant</td>
</tr>
<tr>
<td>$p_u$</td>
<td>10$^8$</td>
<td>exact</td>
<td>Pa</td>
<td>unit-related scaling constant</td>
</tr>
<tr>
<td>$g_u$</td>
<td>1</td>
<td>exact</td>
<td>J kg$^{-1}$</td>
<td>unit-related scaling constant</td>
</tr>
</tbody>
</table>

$^a$ by definition of Reference Salinity and reference composition

Table D.5. The exact definition of the isobaric “heat capacity” that relates potential enthalpy to Conservative Temperature $\Theta$.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p^0$</td>
<td>3991.867 957 119 63</td>
<td>exact</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>See Eqn. (3.3.3)</td>
</tr>
</tbody>
</table>
Table D.6. Chemical composition of dry air with a fixed CO₂ level.

Mole fractions are from Picard et al. (2008) except for N₂ which was adjusted by subtracting all other mole fractions from 1 (Picard et al. (2008)). Uncertainties of the molar masses (Wieser (2006)) are given in brackets.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Mole fraction</th>
<th>Mass fraction</th>
<th>Molar mass g mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>0.780 847 9</td>
<td>0.755 184 73</td>
<td>28.013 4(3)</td>
</tr>
<tr>
<td>O₂</td>
<td>0.209 390 0</td>
<td>0.231 318 60</td>
<td>31.998 8(4)</td>
</tr>
<tr>
<td>Ar</td>
<td>0.009 332 0</td>
<td>0.012 870 36</td>
<td>39.948 (1)</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.000 400 0</td>
<td>0.000 660 75</td>
<td>44.009 5(9)</td>
</tr>
<tr>
<td>Ne</td>
<td>0.000 018 2</td>
<td>0.000 012 68</td>
<td>20.179 7(6)</td>
</tr>
<tr>
<td>Ne</td>
<td>0.000 005 2</td>
<td>0.000 000 72</td>
<td>4.002 602(2)</td>
</tr>
<tr>
<td>CH₄</td>
<td>0.000 001 5</td>
<td>0.000 000 83</td>
<td>16.042 46(81)</td>
</tr>
<tr>
<td>Kr</td>
<td>0.000 001 1</td>
<td>0.000 003 18</td>
<td>83.798 (2)</td>
</tr>
<tr>
<td>H₂</td>
<td>0.000 000 5</td>
<td>0.000 000 03</td>
<td>2.015 88(10)</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.000 000 3</td>
<td>0.000 000 46</td>
<td>44.012 8(4)</td>
</tr>
<tr>
<td>CO</td>
<td>0.000 000 2</td>
<td>0.000 000 19</td>
<td>28.010 1(9)</td>
</tr>
<tr>
<td>Xe</td>
<td>0.000 000 1</td>
<td>0.000 000 45</td>
<td>131.293 (6)</td>
</tr>
<tr>
<td>Air</td>
<td>1.000 000 0</td>
<td>0.999 999 98</td>
<td>28.965 46(33)</td>
</tr>
</tbody>
</table>

Coriolis Parameter
The rotation rate of the earth Ω is (in radians per second)

Ω = 7.292 1150 x 10⁻⁵ s⁻¹,  \hspace{1cm} (D.1)

(Groten (2004)) and the Coriolis parameter f is (in radians per second)

f = 2Ω sin φ = 1.458 423 00 x 10⁻⁴ sin φ s⁻¹, \hspace{1cm} (D.2)

where φ is latitude (φ has opposite signs in the two hemispheres).

Gravitational Acceleration
The gravitational acceleration g in the ocean can be taken to be the following function of latitude φ and sea pressure p, or height z relative to the geoid,

\[ g = 9.780 327 \left(1 + 5.3024 x 10^{-3} \sin^2 \phi - 5.8 x 10^{-6} \sin^2 2\phi \right) \left(1 - 2.26 x 10^{-7} z/(m) \right) \]

\[ = 9.780 327 \left(1 + 5.2792 x 10^{-3} \sin^2 \phi + 2.32 x 10^{-5} \sin^4 \phi \right) \left(1 - 2.26 x 10^{-7} z/(m) \right) \]  \hspace{1cm} (D.3)

\[ \approx 9.780 327 \left(1 + 5.2792 x 10^{-3} \sin^2 \phi + 2.32 x 10^{-5} \sin^4 \phi \right) \left(1 + 2.22 x 10^{-7} p/(dbar) \right). \]

The dependence on latitude in Eqn. (D.3) is from Moritz (2000) and is the gravitational acceleration on the surface of an ellipsoid which approximates the geoid. The variation of g with z and p in the ocean in Eqn. (D.3) is derived in McDougall et al. (2010b). The height z above the geoid is negative in the ocean. Note that g increases with depth in the ocean at about 71.85% of the rate at which it decreases with height in the atmosphere.

At a latitude of 45°N and at \( p = 0 \), \( g = 9.8062 \text{ m s}^{-2} \), which is a value commonly used in ocean models. The value of g averaged over the earth’s surface is \( g = 9.7976 \text{ m s}^{-2} \), while the value averaged over the surface of the ocean is \( g = 9.7963 \text{ m s}^{-2} \) (Griffies (2004)).
Appendix E:
Algorithm for calculating Practical Salinity

E.1 Calculation of Practical Salinity in terms of \( K_{15} \)

Practical salinity \( S_p \) is defined on the Practical Salinity Scale of 1978 (Unesco (1981, 1983)) in terms of the conductivity ratio \( K_{15} \) which is the electrical conductivity of the sample at temperature \( t_{68} = 15 \, \text{°C} \) and pressure equal to one standard atmosphere \( (p = 0 \, \text{dbar and absolute pressure } P = 101325 \, \text{Pa}) \), divided by the conductivity of a standard potassium chloride (KCl) solution at the same temperature and pressure. The mass fraction of KCl in the standard solution is \( 32.4356 \times 10^{-3} \) (mass of KCl per mass of solution).

When \( K_{15} = 1 \), the Practical Salinity \( S_p \) is by definition 35. Note that Practical Salinity is a unit-less quantity. Though sometimes convenient, it is technically incorrect to quote Practical Salinity in “psu”; rather it should be quoted as a certain Practical Salinity “on the Practical Salinity Scale PSS-78”.

When \( K_{15} \) is not unity, \( S_p \) and \( K_{15} \) are related by (Unesco, 1981, 1983) the PSS-78 equation

\[
S_p = \sum_{i=0}^{5} a_i (K_{15})^{i/2} \quad \text{where} \quad K_{15} = \frac{C(S_p, t_{68}=15\,\text{°C},0)}{C(35,t_{68}=15\,\text{°C},0)},
\]

(E.1.1)

and the coefficients \( a_i \) are given in the following table. Note that the sum of the six \( a_i \) coefficients is precisely 35, while the sum of the six \( b_i \) coefficients is precisely zero. Equation (E.1.1) is valid in the range \( 2 < S_p < 42 \).

<table>
<thead>
<tr>
<th>( i )</th>
<th>( a_i )</th>
<th>( b_i )</th>
<th>( c_i )</th>
<th>( d_i )</th>
<th>( e_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0080</td>
<td>0.0005</td>
<td>6.766097 x 10^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.1692</td>
<td>-0.0056</td>
<td>2.00564 x 10^{-2}</td>
<td>3.426 x 10^{-2}</td>
<td>2.070 x 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>25.3851</td>
<td>-0.0066</td>
<td>1.104259 x 10^{-4}</td>
<td>4.464 x 10^{-4}</td>
<td>-6.370 x 10^{-10}</td>
</tr>
<tr>
<td>3</td>
<td>14.0941</td>
<td>-0.0375</td>
<td>-6.9698 x 10^{-7}</td>
<td>4.215 x 10^{-1}</td>
<td>3.989 x 10^{-15}</td>
</tr>
<tr>
<td>4</td>
<td>-7.0261</td>
<td>0.0636</td>
<td>1.0031 x 10^{-9}</td>
<td>-3.107 x 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.7081</td>
<td>-0.0144</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E.2 Calculation of Practical Salinity at oceanographic temperature and pressure

The following formulae from Unesco (1983) are valid over the range \(-2 \, \text{°C} \leq t \leq 35 \, \text{°C} \) and \( 0 \leq p \leq 10 \, 000 \, \text{dbar} \). Measurements of salinity in the field generally measure the conductivity ratio \( R \)

\[
R = \frac{C(S_P, t_{68}, p)}{C(35, t_{68} = 15 \, \text{°C}, 0)} = \frac{C(S_P, t_{68}, p)}{C(S_P, t_{68}, 0)} \frac{C(S_P, t_{68}, 0)}{C(35, t_{68}, 0)} \frac{C(35, t_{68})}{C(35, t_{68} = 15 \, \text{°C}, 0)}
\]

(E.2.1)

which has been expressed in (E.2.1) as the product of three factors, which are labeled \( R_p, R_t \), and \( r_t \) as follows

\[
R = \frac{C(S_P, t_{68}, p)}{C(35, t_{68} = 15 \, \text{°C}, 0)} = R_p R_t r_t.
\]

(E.2.2)
The last factor \( r_i \) has been fitted to experimental data as the polynomial in temperature \( (t_{68}) \)

\[
    r_i = \sum_{i=0}^{4} c_i \left( \frac{t_{68}}{\circ C} \right)^i
\]

(E.2.3)

and the factor \( R_p \) has been fitted to experimental data as a function of \( p \), \( t_{68} \) and \( R \) as

\[
    R_p = 1 + \frac{\sum_{i=1}^{3} e_i p^i}{1+d_1(t_{68} / \circ C) + d_2(t_{68} / \circ C)^2 + R \left[ d_3 + d_4(t_{68} / \circ C) \right]}
\]

(E.2.4)

Thus for any sample measurement of \( R \) it is possible to evaluate \( r_i \) and \( R_p \) and hence calculate

\[
    R_i = \frac{R}{R_p r_i}
\]

(E.2.5)

At a temperature of \( t_{68} = 15 \circ C \), \( R_i \) is simply \( K_{15} \) and Practical Salinity \( S_p \) can be determined form (E.1.1). For temperatures other than \( t_{68} = 15 \circ C \), Practical Salinity \( S_p \) is given by the following function of \( R_i \) with \( k = 0.0162 \),

\[
    S_p = \sum_{i=0}^{5} a_i \left( R_1 \right)^{i/2} + \frac{(t_{68}/\circ C - 15)}{[1 + k(t_{68}/\circ C - 15)]} \sum_{i=0}^{5} b_i \left( R_1 \right)^{i/2}
\]

(E.2.6)

Equations (E.1.1) and (E.2.6) are valid only in the range \( 2 < S_p < 42 \). Outside this range \( S_p \) can be determined by dilution with pure water or evaporation of a seawater sample. Practical Salinity \( S_p \) can also be estimated from the extensions of the Practical Salinity Scale proposed by Hill et al. (1986) for \( 0 < S_p < 2 \) and by Poisson and Gadhoumi (1993) for \( 42 < S_p < 50 \). The values of Practical Salinity \( S_p \) estimated in this manner may then be used in Eqn. (2.4.1), namely \( S_R \approx u_{PS} S_p \) to estimate Reference Salinity \( S_R \).

The temperatures in Eqns. (E.2.1) to (E.2.6) are all on the IPTS-68 scale. The functions and coefficients have not been refitted to ITS-90 temperatures. Therefore in order to calculate Practical Salinity from conductivity ratio at a measured pressure and \( t_{90} \) temperature, it is necessary first to convert the temperature to \( t_{68} \) using \( t_{68} = 1.00024 t_{90} \) as described Eqn. (A.1.3) of appendix A.1. This is done as the first line of the computer code described in the GSW software library (appendix N). Further remarks on the implications of the different temperature scales on the definition and calculation of Practical Salinity can be found in appendix E.4 below.

### E.3 Calculation of conductivity ratio \( R \) for a given Practical Salinity

When Practical Salinity is known and one wants to deduce the conductivity ratio \( R \) associated with this value of Practical Salinity at a given temperature, a Newton-Raphson iterative inversion of Eqn. (E.2.6) is first performed to evaluate \( R_i \). Because \( r_i \) is a function only of temperature, at this stage both \( R_i \) and \( r_i \) are known so that Eqn. (E.2.4) can be written as a quadratic in \( R \) with known coefficients which is solved to yield \( R \). This procedure is outlined in more detail in Unesco (1983) and is also available in the SIA and GSW algorithm libraries. Note that this inverse procedure is done in terms of \( t_{68} \), the code in the GSW library accepts \( t_{90} \) as the input and immediately converts this to a \( t_{68} \) temperature before performing the above procedure.
E.4 Evaluating Practical Salinity using ITS-90 temperatures

We first consider the consequence of the change from IPTS-68 to ITS-90 for the definition of Practical Salinity as a function of $K_{15}$ and the defining mass fraction of KCl. Suppose Practical Salinity $S_p$ were to be evaluated using the polynomial (E.1.1) but using $K_{15\text{–}90}$ instead of $K_{15}$, where $K_{15\text{–}90}$ is defined

$$K_{15\text{–}90} = \frac{C(S_p,t_{90} = 15^\circ\text{C},0)}{C(35,t_{90} = 15^\circ\text{C},0)}.$$  

(E.4.1)

The magnitude of the difference $K_{15\text{–}90} - K_{15}$ can be calculated and is found to be less than $6.8 \times 10^{-7}$ everywhere in the range $2 < S_p < 42$. Further calculation shows that $\partial S_p/\partial K_{15} < 41$ everywhere in the valid range of Practical Salinity, so that the consequence of using $K_{15\text{–}90}$ in (E.1.1) instead of $K_{15}$ incurs a change in Practical Salinity of less than $3 \times 10^{-5}$. This is nearly two orders of magnitude below the measurement accuracy of a sample, and an order of magnitude smaller than the error caused by the uncertainty in the definition of the mass fraction of KCl. If all the original measurements that form the basis of the Practical Salinity Scale were converted to ITS-90, and the analysis repeated to determine the appropriate mass fraction to give the required conductivity at $t_{90} = 15^\circ\text{C}$, the same mass fraction $32.4356 \times 10^{-3}$ would be derived.

Not withstanding the insensitivity of this conductivity ratio to such a small temperature difference, following Millero et al. (2008a) the definition of Practical Salinity can be restated with reference to the ITS-90 scale by noting that the $K_{15}$ ratio in Eqn. (E.1.1) can equivalently refer to a ratio of conductivities at $t_{90} = 14.996^\circ\text{C}$.

The fact that the conductivity ratio $R_t$ is rather weakly dependent on the temperature at which the ratio is determined is important for the practical use of bench salinometers. It is important that samples and seawater standards should be run at the same temperature, stable at order 1 mK. This is achieved by the use of a large water bath in the instrument. However, it is not critical to know the stable bath temperature to any better than 10 or 20 mK.

The ratios $R_p$, $R_t$ and $R_t$ that underlie the temperature-dependent expression (E.2.6) for Practical Salinity are more sensitive to the difference between IPTS-68 and ITS-90 temperatures and this is the reason why we recommend retaining the original computer algorithms for these ratios, and to simply convert the input temperature (which these days is on the ITS-90 temperature scale) in to the corresponding IPTS-68 temperature using $t_{68} = 1.00024t_{90}$ as the first operation in the software. Thereafter the software proceeds according to (E.2.1) – (E.2.6).

E.5 Towards SI-traceability of the measurement procedure for Practical Salinity and Absolute Salinity

The observation of climate change taking place in the world ocean on a global scale over decades or centuries requires measurement techniques that permit the highest accuracy currently available, long-term stability and world-wide comparability of the measured values. The highest reliability for this purpose can be ensured only by traceability of these measurement results to the primary standards of the International System of Units (SI), supported by the National Metrological Institutes such as the NIST (National Institute of Standards and Technology) in the US, the NPL (National Physical Laboratory) in the UK, or the PTB (Physikalisch-Technische Bundesanstalt) in Germany.

In order to compute the thermodynamic properties of a seawater sample with standard composition, three independent parameters must be measured. Since the introduction of the Practical Salinity Scale of 1978 as an international standard for oceanography, these three properties have been electrolytic conductivity, temperature
and pressure, from which salinity, density and other properties are computed in turn by standard algorithms. The traceability of temperature and pressure measurement results, for example by CTD sensors, is ensured due to established calibration procedures carried out by the manufacturer or other laboratories and will not be considered here any further.

The observation of the ocean’s salinity is a more complicated task (Millero et al. (2008a)). Even though over the last century different and permanently improved methods were developed and introduced in oceanography, traceability of salinity measurement results to SI units has not yet been achieved (Seitz et al. 2008 and Seitz et al. (2010b)). This implies the risk that readings taken today may possess an enlarged uncertainty when being compared with observations taken a hundred years from now, a circumstance that will reduce the accuracy of long-term trend analyses performed in the future.

A quantity, quite generally, is a “property of a phenomenon, body or substance, where the property has a magnitude that can be expressed as a number” (ISO/IEC, 2007). The process to obtain this number is called measurement. The value of the indicated number (the quantity value) is determined by a calibration of the measuring system with a reference having a known quantity value of the same kind. In turn, the quantity value of the reference is assigned in a superior measurement procedure, which is likewise calibrated with a reference and so on. This calibration hierarchy ends in a primary reference procedure used to assign a quantity value and a unit to a primary standard for that kind of quantity. Thus, the unit of a measured quantity value expresses its link (its metrological traceability) to the quantity value of the corresponding primary standard. Obviously, quantity values measured at different times or locations, by different persons with different devices or methods can be compared with each other only if they are linked to the same reference standard, whose corresponding quantity value must be reproducible with a high degree of reliability.

Concerning comparability of measured quantity values a second aspect is of importance. The quantity value of a primary standard can only be realised with an inevitable uncertainty. The same holds for every measurement and calibration. A measurement result therefore always has to indicate the measured quantity value and its uncertainty. Obviously, the latter increases with every calibration step down the calibration hierarchy. Measured quantity values can evidently only be assumed equivalent if their difference is smaller than their measurement uncertainty (compatibility). On the other hand they can only be assumed reliably different, if the difference is larger than the uncertainty.

To ensure comparability in practice, the International System of Units (SI) was established. National Metrological Institutes (NMIs) have developed primary reference procedures to realise the SI units in the form of primary standards. Extensive (ongoing) efforts are made to link these units to fundamental and physical constants in order to achieve the highest degree of reproducibility. Moreover, the NMIs periodically conduct international comparison measurements under the umbrella of the International Bureau of Weights and Measures, in order to ensure the compatibility of the quantity values of national standards.

PSS-78, and similarly the new Reference-Composition Salinity Scale (Millero et al. (2008a)), compute the salinity value from a measured conductivity ratio with respect to the $K_{15}$ conductivity ratio of IAPSO Standard Seawater (SSW, Culkin and Ridout (1998) and Bacon et al. (2007)), which plays the role of a primary standard. The production procedure if IAPSO Standard Seawater, and in particular the adjustment of its conductivity to that of a potassium chloride (KCl) solution of definite purity and the corresponding assignment of the $K_{15}$ ratio, can be seen as a primary reference procedure. However both of these solutions are artefacts lying outside the SI system; they are not subject to regular international inter-comparisons; their sufficiently precise replicability
by arbitrary independent laboratories is neither known nor even granted. A slow drift of artefact properties cannot rigorously be excluded, similar in principle to the “evaporation” of mass from the kilogram prototype stored in Paris. It is impossible to foresee effects that might affect the conductivity of SSW solution one day. Thus, with respect to decadal or century time scales, there is an uncertainty of its $K_{14}$ ratio, which a priori can not be quantified and puts long term comparability of salinity measurement results at risk.

This fundamental problem, which is related to any artificial reference standard, can, at least in principle, be avoided if the conductivity of seawater is measured traceable to primary SI standards (“absolute” conductivity) rather than relying on a conductivity ratio. Unfortunately the related uncertainty of absolute conductivity measurements with present-day state-of-the-art technology is one order of magnitude larger than that of the relative measurements presently used for the ocean observation system (Seitz et al. (2008)).

A way out of this practical dilemma is the measurement of a different seawater quantity that is traceable to SI standards and possesses the demanded small uncertainty, and from which the salinity can be computed via an empirical relation that is very precisely known (Seitz et al. (2010b)). Among the potential candidates for this purpose are the sound speed, the refractive index, chemical analysis (e.g. by mass spectroscopy) of the sea-salt constituents, in particular chlorine, and direct density measurements. The latter has three important advantages, i) SI-traceable density measurements of seawater can be carried out with a relative uncertainty of 1 ppm (Wolf (2008)), which perfectly meets the needs of ocean observation, ii) a relation exists between density and the Absolute Salinity of seawater is available with a relative uncertainty of 4 ppm in the form of the TEOS-10 Gibbs function, iii) the measurand, density, is of immediate relevance for oceanography, in contrast to other options.

It is important to note that the actual measuring procedure for a quantity value is irrelevant for its traceability. To measure the weight of a person, a mass balance can be used, a spring or a magnetic coil; it is the quantity value that is traceable, not the method to achieve this value. The method in use is not intrinsically important except in so far as it is responsible for the uncertainty of the quantity value. Hence, we may measure the density of seawater with a CTD conductivity sensor, provided this sensor is properly calibrated with respect to an SI-traceable density reference standard. In practice, this will mean that the sensor calibration in oceanographic labs must be done with standard seawater samples of certified density rather than certified Practical Salinity. The density value returned from the CTD reading at sea is then converted into an Absolute Salinity value by means of the equation of state of seawater, and eventually into a Practical Salinity number for storage in data centres. The latter step may include some modification regarding local sea salt composition anomalies. Storing a salinity value rather than the related density reading has the advantage of conservativity with respect to dilution or changes of temperature or pressure.

This conceptual proposal of WG127 is still immature and needs to be worked out in more detail in the following years. Although it may imply only minor changes in the practical use of a CTD or similar devices, the new concept is very promising regarding the long-term reliability of observations made in the near future for climatic trend analyses to be performed by the coming generations. An immediate consequence of this proposal is to have the density (at a given temperature and pressure) of several samples of each batch of IAPSO Standard Seawater measured when they are produced and have these densities made available as reference values for each batch.
Appendix F:
Coefficients of the IAPWS-95 Helmholtz function of fluid water (with extension down to 50 K)

The specific Helmholtz energy for fluid (gaseous and liquid) water is given by the revised IAPWS Release, IAPWS (2009b), which is based mainly on the work of Wagner and Pruß (2002). This revised release is still referred to as IAPWS-95. The specific Helmholtz energy of IAPWS-95 is defined by

\[
 f^{\text{fla}}(T, \rho) = f^{V, \text{id}}(T, \rho) + R_W T \varphi^\text{res}(\tau, \delta),
\]

where \( f^{V, \text{id}}(T, \rho) \) is the ideal-gas part, (F.2), \( R_W = 461.518 \) 05 J kg\(^{-1}\) K\(^{-1}\) is the specific gas constant of water used in IAPWS-95, and \( \varphi^\text{res}(\tau, \delta) \) is the dimensionless residual part consisting of 56 terms, available from (F.5) and Tables F.2 - F.4. Note that the gas constant used here differs from the most recent value, \( R_W = R/M^W = 461.523 \) 64 J kg\(^{-1}\) K\(^{-1}\), where \( M^W = 18.015 \) 268 g mol\(^{-1}\) is the molar mass of water (IAPWS (2005)).

The ideal-gas part, \( f^{V, \text{id}}(T, \rho) \), of the specific Helmholtz energy for water vapour is (from IAPWS (2009b), Wagner and Pruß (2002), Feistel et al. (2010a))

\[
 f^{V, \text{id}}(T, \rho) = R_W T \left[ \varphi^0(\tau, \delta) + \varphi^{\text{ex}}(\tau) \right].
\]

Note that the term \( \varphi^{\text{ex}}(\tau) \) has been added by Feistel et al. (2010a) in order to extend the formulation to extraterrestrial applications, and because sublimation pressure values are now available down to 50 K from Feistel and Wagner (2007) and IAPWS (2008b); an extreme range where no related experiments have been performed. This term is additional to the specific Helmholtz energy of IAPWS (2009b) and Wagner and Pruß (2002). The function \( \varphi^0(\tau, \delta) \) was obtained from an equation for the specific isobaric heat capacity of vapour and reads

\[
 \varphi^0(\tau, \delta) = \ln \delta + n_1^0 + n_2^0 \tau + n_3^0 \ln \tau + \sum_{i=4}^8 n_i^0 \ln \left( 1 - e^{-\delta^0_i} \right).
\]

The “reduced density” \( \delta = \rho / \rho_c \) and “reduced temperature” \( \tau = T_c / T \) are specified by \( \rho_c = 322 \) kg m\(^{-3}\), \( T_c = 647.096 \) K. The coefficients of (F.3) are available from Table F.1. The IAPWS-95 reference state conditions define the internal energy and the entropy of liquid water to be zero at the triple point. A highly accurate numerical implementation of these conditions gives the following values rounded to 16 digits for the adjustable coefficients \( n_1^0 = -8.320 \) 446 483 749 693 and \( n_2^0 = 6.683 \) 210 527 593 226. These are the values used in TEOS-10 (IAPWS (2009b), Feistel et al. (2008a)).

The temperature \( T \) is measured on the ITS-90 scale. The range of validity is 130 – 2000 K without the extension (F.4), that is with \( \varphi^{\text{ex}}(\tau) = 0 \). The range can be extended to include the region 50 – 130 K with the following correction function \( \varphi^{\text{ex}}(\tau) \) added to (F.2) in this temperature range,

\[
 \varphi^{\text{ex}}(\tau) = E \times \left( -\frac{1}{2\tau} - \frac{3}{e^\tau} (\tau + e) \ln \frac{\tau}{e} - \frac{9}{2e^\tau} + \frac{9\tau}{2e^\tau} + \frac{\tau^2}{2e^\tau} \right), \quad \text{for } 50 \text{ K} \leq T \leq 130 \text{ K},
\]

where \( T_c = 130 \) K, \( E = 0.278 \) 296 458 178 592, and \( e = T_c / T \). At \( \tau = e \), \( \varphi^{\text{ex}}(\tau) \) is zero, as well as its first, second, third and fourth temperature derivatives. This correction has been determined such that when applied to the formula used in IAPWS-95, it results in a fit to the heat capacity data of Woolley (1980) between 50 and 130 K with an r.m.s.
deviation of $6 \times 10^{-4}$ in $c_p/R_w$. This extension formula has been developed particularly for implementation in TEOS-10 (Feistel et al. (2010a)), it is consistent with the correlation function given in IAPWS (2008b), but it has not yet been endorsed by IAPWS.

The residual part of (F.1) has the form

$$
\phi^{\text{res}} = \sum_{i=1}^{7} n_i \delta^{d_i} \tau^{\epsilon_i} + \sum_{i=8}^{51} n_i \delta^{d_i} \tau^{\epsilon_i} \exp\left(-\delta^{\gamma_i}\right)
$$

$$
+ \sum_{i=52}^{54} n_i \delta^{d_i} \tau^{\epsilon_i} \exp\left(-\alpha_i \left(\delta - \epsilon_i\right)^2 - \beta_i \left(\tau - \gamma_i\right)^2\right) + \sum_{i=55}^{56} n_i \Delta^{i_i} \delta \psi
$$

with the abbreviations

$$
\Delta = \theta^2 + B_i \delta - 1^{2i_i}, \quad \theta = 1 - \tau + A_i \delta - 1^1_i, \quad \psi = \exp\left(-C_i \left(\delta - 1\right)^2 - D_i \left(\tau - 1\right)^2\right).
$$

The coefficients of (F.5) are available from Tables F.2 – F.4.

**Table F.1. Coefficients appearing in Eqn. (F.3).** Note that the originally published values (Wagner and Pruss (2002)) of the adjustable coefficients $n_1^i$ and $n_2^i$ are slightly different from those of TEOS-10 given here (Feistel et al. (2008a)).

<table>
<thead>
<tr>
<th>$i$</th>
<th>$n_1^i$</th>
<th>$n_2^i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-8.32044648374969</td>
<td>0.012533547935523</td>
</tr>
<tr>
<td>2</td>
<td>6.68321052759323</td>
<td>3.89734222</td>
</tr>
<tr>
<td>3</td>
<td>3.00632</td>
<td>7.74073708</td>
</tr>
<tr>
<td>4</td>
<td>0.012436</td>
<td>9.24437796</td>
</tr>
<tr>
<td>5</td>
<td>0.97315</td>
<td>27.5075105</td>
</tr>
</tbody>
</table>

**Table F.2. Coefficients of the residual part (F.5).**

<table>
<thead>
<tr>
<th>$i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
<th>$l_i$</th>
<th>$n_i$</th>
</tr>
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<tr>
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</tr>
<tr>
<td>2</td>
<td>0</td>
<td>1</td>
<td>0.875</td>
<td>7.8957634722828</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>1</td>
<td>-8.7803203303561</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>2</td>
<td>0.5</td>
<td>0.31802509345418</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>2</td>
<td>0.75</td>
<td>-0.26145533859358</td>
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<tr>
<td>6</td>
<td>0</td>
<td>3</td>
<td>0.375</td>
<td>-7.8199751687981×10^{-3}</td>
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<tr>
<td>7</td>
<td>0</td>
<td>4</td>
<td>1</td>
<td>8.8089493102134×10^{-3}</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>-0.66856572307965</td>
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<tr>
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<td>1</td>
<td>1</td>
<td>6</td>
<td>0.20433810950965</td>
</tr>
<tr>
<td>10</td>
<td>1</td>
<td>1</td>
<td>12</td>
<td>-6.6212605039687×10^{-5}</td>
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<td>1</td>
<td>-0.19232721156002</td>
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<td>2</td>
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<td>2</td>
<td>-0.040092828925807</td>
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<td>13</td>
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<tr>
<td>20</td>
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<td>4</td>
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<td>1</td>
<td>13</td>
<td>13</td>
<td>-1.3251180074668×10^{-12}</td>
</tr>
<tr>
<td>22</td>
<td>1</td>
<td>15</td>
<td>1</td>
<td>-6.2639586912454×10^{-10}</td>
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Table F.3. Coefficients of the residual part (F.5).

<table>
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<th>(d_i)</th>
<th>(t_i)</th>
<th>(n_i)</th>
<th>(\alpha_i)</th>
<th>(\beta_i)</th>
<th>(\gamma_i)</th>
<th>(\epsilon_i)</th>
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<td>1.21</td>
<td>1</td>
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<tr>
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<td>31.546140237781</td>
<td>20</td>
<td>150</td>
<td>1.21</td>
<td>1</td>
</tr>
<tr>
<td>54</td>
<td>3</td>
<td>4</td>
<td>-2521.3154341695</td>
<td>20</td>
<td>250</td>
<td>1.25</td>
<td>1</td>
</tr>
</tbody>
</table>

Table F.4. Coefficients of the residual part (F.5).

<table>
<thead>
<tr>
<th>(i)</th>
<th>(a_i)</th>
<th>(b_i)</th>
<th>(B_i)</th>
<th>(n_i)</th>
<th>(C_i)</th>
<th>(D_i)</th>
<th>(A_i)</th>
<th>(\beta_i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
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<td>0.85</td>
<td>0.2</td>
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<td>28</td>
<td>700</td>
<td>0.32</td>
<td>0.3</td>
</tr>
<tr>
<td>56</td>
<td>3.5</td>
<td>0.95</td>
<td>0.2</td>
<td>0.318061108784444</td>
<td>32</td>
<td>800</td>
<td>0.32</td>
<td>0.3</td>
</tr>
</tbody>
</table>

Equation (F.1) is valid between 50 and 1273 K and for pressures up to 1000 MPa in the stable single-phase region of fluid water. Uncertainty estimates are available from IAPWS (2009b) and Wagner and Prüß (2002).
Appendix G: Coefficients of the pure liquid water Gibbs function of IAPWS-09

The pure liquid water part of the Gibbs function of Feistel (2003) has been approved by IAPWS (IAPWS (2009c)) as an alternative thermodynamic description of pure water to IAPWS-95 in the oceanographic ranges of temperature and pressure. The pure water specific Gibbs energy \( g^W(t, p) \) is the following function of the independent variables ITS-90 Celsius temperature, \( t = t_0 \times y \), and sea pressure, \( p = p_u \times z \)

\[
g^W(t, p) = g_a \sum_{j=0}^{6} \sum_{k=0}^{6} g_{jk} y^j z^k, \tag{G.1}
\]

with the reduced temperature \( y = t/t_0 \) and the reduced (dimensionless) pressure \( z = p/p_u \). The unit-related constants \( t_0, p_u \) and \( g_a \) are given in Table D4 of appendix D (e.g., \( p_u = 10^8 \text{ Pa} = 10^4 \text{ dbar} \)). Coefficients not contained in the table below have the value \( g_{jk} = 0 \). Two of these 41 parameters \( (g_{00} \text{ and } g_{10}) \) are arbitrary and are computed from the reference-state conditions of vanishing specific entropy, \( \eta \), and specific internal energy, \( u \), of liquid H2O at the triple point,

\[
\eta(T_p, p_i) = 0, \quad \text{and} \quad u(T_p, p_i) = 0. \tag{G.2}
\]

Note that the values of \( g_{00} \) and \( g_{10} \) in the table below are taken from Feistel et al. (2008a) and IAPWS (2009), and are not identical to the values in Feistel (2003). The modified values have been chosen to most accurately achieve the triple-point conditions (G.2) (see Feistel et al. (2008a) for a discussion of this point).

\[
\begin{array}{cccccc}
  j & k & g_{jk} & j & k & g_{jk} \\
  0 & 0 & 0.101342743139674 \times 10^5 & 3 & 2 & 0.499360390819152 \times 10^4 \\
  0 & 1 & 0.100015695367145 \times 10^5 & 3 & 3 & -0.239545330654412 \times 10^4 \\
  0 & 2 & -0.254457654203630 \times 10^5 & 3 & 4 & 0.488012518593872 \times 10^3 \\
  0 & 3 & 0.284517788446287 \times 10^5 & 3 & 5 & -0.166307106208905 \times 10^3 \\
  0 & 4 & -0.333146754253611 \times 10^5 & 4 & 0 & -0.148185936433658 \times 10^3 \\
  0 & 5 & 0.420263108803084 \times 10^5 & 4 & 1 & 0.397968445406972 \times 10^3 \\
  0 & 6 & -0.546428511471039 & 4 & 2 & -0.301815380621876 \times 10^3 \\
  1 & 0 & 0.590578347909402 \times 10^5 & 4 & 3 & 0.152196371733841 \times 10^4 \\
  1 & 1 & -0.270983805184062 \times 10^4 & 4 & 4 & -0.263748377232802 \times 10^4 \\
  1 & 2 & 0.776153611613101 \times 10^4 & 5 & 0 & 0.580259125842571 \times 10^4 \\
  1 & 3 & -0.196512550881220 \times 10^4 & 5 & 1 & -0.194618316061759 \times 10^4 \\
  1 & 4 & 0.289796529267157 \times 10^4 & 5 & 2 & 0.120520654902025 \times 10^4 \\
  1 & 5 & -0.213290083518327 \times 10^4 & 5 & 3 & -0.552723052340152 \times 10^4 \\
  2 & 0 & -0.123577859330390 \times 10^4 & 5 & 4 & 0.648190668077221 \times 10^3 \\
  2 & 1 & 0.145503645404680 \times 10^4 & 6 & 0 & -0.189843846514172 \times 10^3 \\
  2 & 2 & -0.756558385769359 \times 10^3 & 6 & 1 & 0.635113936641785 \times 10^3 \\
  2 & 3 & 0.273497662323528 \times 10^3 & 6 & 2 & -0.222897317140459 \times 10^3 \\
  2 & 4 & -0.55560463817218 \times 10^3 & 6 & 3 & 0.81706054181112 \times 10^3 \\
  2 & 5 & 0.434420671917197 \times 10^3 & 7 & 0 & 0.305081646487967 \times 10^3 \\
  3 & 0 & 0.736741204151612 \times 10^3 & 7 & 1 & -0.963108119393062 \times 10^3 \\
  3 & 1 & -0.672507783145070 \times 10^3 &
\end{array}
\]
Appendix H: Coefficients of the saline Gibbs function for seawater of IAPWS-08

Non-zero coefficients $g_{ijk}$ of the saline specific Gibbs energy $g^S(S_A,t,p)$ as a function of the independent variables absolute salinity, $S_A = S_u \times x^2$, ITS-90 Celsius temperature, $t = t_u \times y$, and sea pressure, $p = p_u \times z$:

$$g^S(S_A,t,p) = g_u \sum_{j,k} \left( g_{1jk} x^2 \ln x + \sum_{i=1}^{10} g_{ijk} x^i \right) y^j z^k. \quad (H.1)$$

The unit-related constants $S_u$, $t_u$, $p_u$ and $g_u$ are given in Table D4 of appendix D (e.g. $p_u = 10^9$ Pa = 10 dbar). Coefficients with $k > 0$ are adopted from Feistel (2003). Pure-water coefficients with $i = 0$ do not occur in the saline contribution. The coefficients $g_{200}$ and $g_{210}$ were determined to exactly achieve Eqns. (2.6.7) and (2.6.8) when the pure water Gibbs function was that of IAPWS-95.

<table>
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Appendix I: Coefficients of the Gibbs function of ice Ih of IAPWS-06

The Gibbs energy of ice Ih, the naturally abundant form of ice, having hexagonal crystals, is a function of temperature (ITS-90) and sea pressure, \( g^{\text{Ih}}(t, p) \). This Gibbs function has been derived by Feistel and Wagner (2006) and was adopted as an IAPWS Release in 2006 and revised in 2009 (IAPWS (2009a)), here referred to as IAPWS-06. This equation of state for ice Ih is given by Eqn. (I.1) as a function of temperature, with two of its coefficients being polynomial functions of sea pressure \( p \) \( (p = P - P_0) \):

\[
g^{\text{Ih}}(t, p) = g_0 - s_0 T_i \cdot \tau + T_i \cdot \text{Re} \sum_{k=1}^{2} r_k \left[ (t_k - \tau) \ln(t_k - \tau) + (t_k + \tau) \ln(t_k + \tau) - 2t_k \ln(t_k - \frac{\tau^2}{t_k}) \right]
\]

\[
g_0(p) = \sum_{k=0}^{4} g_{0k} \cdot \left( \frac{p}{P_i} \right)^k
\]

\[
r_2(p) = \sum_{k=0}^{2} r_{2k} \cdot \left( \frac{p}{P_i} \right)^k,
\]

with the reduced temperature \( \tau = (T_0 + t)/T_i \) and \( T_i \) and \( P_i \) are given in Table I.1. If the sea pressure \( p \) is expressed in dbar then \( P_i \) must also be given in these units as \( P_i = 0.0611657 \) dbar. The real constants \( g_{00} \) to \( g_{04} \) and \( s_0 \), the complex constants \( t_1, r_1, t_2, \) and \( r_{20} \) to \( r_{22} \) are listed in Table I.2.

### Table I.1: Special constants and values used in the ice Ih Gibbs function.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental triple-point pressure</td>
<td>( P_i )</td>
<td>611.657</td>
<td>Pa</td>
</tr>
<tr>
<td>Numerical triple-point pressure</td>
<td>( P_i^{\text{num}} )</td>
<td>611,654 771 007 894</td>
<td>Pa</td>
</tr>
<tr>
<td>Normal pressure</td>
<td>( P_0 )</td>
<td>101325</td>
<td>Pa</td>
</tr>
<tr>
<td>Triple-point temperature</td>
<td>( T_i )</td>
<td>273.16</td>
<td>K</td>
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TABLE I.2 Coefficients of the equation of state (Gibbs potential function) of ice Ih as given by Eqn. (I.1).

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<th>Coefficient</th>
<th>Real part</th>
<th>Imaginary part</th>
<th>Unit</th>
</tr>
</thead>
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<tr>
<td>$g_{00}$</td>
<td>$-0.632 020 233 335 886 \times 10^6$</td>
<td></td>
<td>$\text{J kg}^{-1}$</td>
</tr>
<tr>
<td>$g_{01}$</td>
<td>$0.655 022 213 658 955$</td>
<td></td>
<td>$\text{J kg}^{-1}$</td>
</tr>
<tr>
<td>$g_{02}$</td>
<td>$-0.189 369 929 326 131 \times 10^{-7}$</td>
<td></td>
<td>$\text{J kg}^{-1}$</td>
</tr>
<tr>
<td>$g_{03}$</td>
<td>$0.339 746 123 271 053 \times 10^{-14}$</td>
<td></td>
<td>$\text{J kg}^{-1}$</td>
</tr>
<tr>
<td>$g_{04}$</td>
<td>$-0.556 464 869 058 991 \times 10^{-21}$</td>
<td></td>
<td>$\text{J kg}^{-1}$</td>
</tr>
<tr>
<td>$s_0$ (absolute)</td>
<td>$0.189 13 \times 10^3$</td>
<td></td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
</tr>
<tr>
<td>$s_0$ (IAPWS-95)</td>
<td>$-0.332 733 756 492 168 \times 10^4$</td>
<td></td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
</tr>
<tr>
<td>$t_1$</td>
<td>$0.368 017 112 855 051 \times 10^{-1}$</td>
<td>$0.510 878 114 959 572 \times 10^{-1}$</td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
</tr>
<tr>
<td>$r_1$</td>
<td>$0.447 050 716 285 388 \times 10^{-2}$</td>
<td>$0.656 876 847 463 481 \times 10^{-2}$</td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
</tr>
<tr>
<td>$r_2$</td>
<td>$0.337 315 741 065 416$</td>
<td>$0.335 449 415 919 309$</td>
<td></td>
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<tr>
<td>$r_20$</td>
<td>$-0.725 974 574 329 220 \times 10^{-2}$</td>
<td>$-0.781 008 427 112 870 \times 10^{-2}$</td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
</tr>
<tr>
<td>$r_21$</td>
<td>$-0.557 107 698 030 123 \times 10^{-4}$</td>
<td>$0.464 578 634 580 806 \times 10^{-4}$</td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
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<tr>
<td>$r_22$</td>
<td>$0.234 801 409 215 913 \times 10^{-10}$</td>
<td>$-0.285 651 142 904 972 \times 10^{-10}$</td>
<td>$\text{J kg}^{-1} \text{K}^{-1}$</td>
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</table>

The numerical triple point pressure $P_{t,\text{num}}$ listed in Table I.1 was derived in Feistel et al. (2008a) as the absolute pressure at which the three phases of water were in thermodynamic equilibrium at the triple point temperature, using the mathematical descriptions of the three phases as given by IAPWS-95 and IAPWS-06. The complex logarithm $\ln(z)$ is meant as the principal value, i.e. it evaluates to imaginary parts in the interval $-\pi < \Im\left[\ln(z)\right] \leq +\pi$. The complex notation used here has no direct physical basis but serves for convenience of analytical partial derivatives and for compactness of the resulting formulae, especially in program code. Complex data types are supported by scientific computer languages like Fortran (as COMPLEX*16) or C++ (as complex <double>), thus allowing an immediate implementation of the formulae given, without the need for prior conversion to much more complicated real functions, or for experience in complex calculus.

The residual entropy coefficient $s_0$ is given in Table I.2 in the form of two alternative values. Its ‘IAPWS-95’ version is required for phase equilibria studies between ice and fluid water and seawater. This is the value of $s_0$ used in the TEOS-10 algorithms. In the 'absolute' version, $s_0$ is the statistical non-zero entropy ice possesses at the zero point (0 K) resulting from the multiplicity of its energetically equivalent crystal configurations (for details, see Feistel and Wagner (2005)).

The value of $g_{00}$ listed in Table I.2 is the value in the revised IAPWS-2006 Ice Ih Release (IAPWS (2009a)) which improves the numerical consistency (Feistel et al. (2008a)) with the IAPWS-1995 Release for the fluid phase of water.
Appendix J: Coefficients of the Helmholtz function of moist air of IAPWS-10

The equation of state of humid air described here (Feistel et al. (2010a), IAPWS (2010) [an IAPWS Guideline, in preparation]) is represented in terms of a Helmholtz function which expresses the specific Helmholtz energy as a function of dry-air mass fraction \( A \), absolute temperature \( T \) and humid-air mass density, \( \rho \), and takes the form

\[
f^{\Lambda V}(A,T,\rho) = (1-A)f^{V}(T,\rho^{V}) + Af^{\Lambda}(T,\rho^{\Lambda}) + f^{\text{mix}}(A,T,\rho).
\] (J.1)

The vapour part is given by the IAPWS-95 Helmholtz function for fluid water (IAPWS (2009b)),

\[
f^{V}(T,\rho^{V}) = f^{\text{flu}}(T,\rho^{V}),
\] (J.2)

is computed at the vapour density, \( \rho^{V} = (1-A)\rho \), and is defined in Eqn. (F.1) of appendix F. The dry-air part, \( f^{\Lambda}(T,\rho^{\Lambda}) \), is computed at the dry-air density, \( \rho^{\Lambda} = A\rho \), and is defined by Eqn. (J.3). The air-water cross-over part \( f^{\text{mix}} \) is defined by Eqn. (J.8).

### Table J.1. Special constants and values used in this appendix.

Note that the molar gas constant used here differs from the most recent value (IAPWS (2005)), and the molar mass of dry air used here differs from the most recent value (Picard et al. (2008)), Table D6.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
<th>Reference</th>
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<td>Molar gas constant</td>
<td>( R^L )</td>
<td>8.31451</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td>Lemmon et al. (2000)</td>
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<td>Molar gas constant</td>
<td>( R )</td>
<td>8.314472</td>
<td>J mol(^{-1}) K(^{-1})</td>
<td>IAPWS (2005)</td>
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<tr>
<td>Molar mass of dry air</td>
<td>( M_{A} )</td>
<td>28.9586</td>
<td>g mol(^{-1})</td>
<td>Lemmon et al. (2000)</td>
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<tr>
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<td>28.96546</td>
<td>g mol(^{-1})</td>
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<td>18.015268</td>
<td>g mol(^{-1})</td>
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<td>Celsius zero point</td>
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<td>K</td>
<td>Preston-Thomas (1990)</td>
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<tr>
<td>Normal pressure</td>
<td>( P_{0} )</td>
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<td>Pa</td>
<td>ISO(1993)</td>
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</table>

The specific Helmholtz energy for dry air is (Lemmon et al. (2000)),

\[
f^{\Lambda}(T,\rho^{\Lambda}) = \frac{R^L}{M_{A}} \left[ \alpha^{\text{id}}(\tau,\delta) + \alpha^{\text{res}}(\tau,\delta) \right].
\] (J.3)

The values to be used for molar mass \( M_{A} \) of dry air, and for the molar gas constant \( R^L \) are given in Table J.1. The function \( \alpha^{\text{id}}(\tau,\delta) \) is the ideal-gas part,
\[
\alpha^\text{id}(\tau, \delta) = \ln \delta + \sum_{i=1}^{5} n_i^0 \tau^{i-4} + n_6^0 \tau^{1.5} + n_7^0 \ln \tau + n_8^0 \ln \left[ 1 - \exp \left( -n_9^0 \tau \right) \right] + n_{10}^0 \ln \left[ 1 - \exp \left( -n_{11}^0 \tau \right) \right] + n_{12}^0 \ln \left[ 2/3 + \exp \left( n_{13}^0 \tau \right) \right]
\]  
\text{(J.4)}

and \( \alpha^\text{res}(\tau, \delta) \) is the residual part,
\[
\alpha^\text{res}(\tau, \delta) = \sum_{k=1}^{10} n_k \delta^k \tau^k + \sum_{k=11}^{19} n_k \delta^k \tau^k \exp \left( -\delta^k \right).
\]  
\text{(J.5)}

The “reduced variables” in Eqns. (J.3) - (J.5) are \( \tau = T^*_A / T \) with the reducing temperature \( T^*_A = 132.6312 \text{ K} \), and \( \delta = \rho^A / \rho^*_A \) with the reducing density \( \rho^*_A = 10.4477 \text{ mol dm}^{-3} \times M_A \). \( M_A \) is given in Table J.1. The coefficients of Eqns. (J.4) and (J.6) are given in Tables J.2 and J.3.

Two of the parameters \( (n_0^0 \text{ and } n_0^0) \) listed in Table J.2 are arbitrary and are computed here from the reference-state conditions of vanishing specific entropy, \( \eta^A \), and specific enthalpy, \( h^A \), of dry air at the temperature \( T_0 \) and the normal pressure \( P_0 \), as given in Table J.1,
\[
\eta^A(T_0, P_0) = 0, \quad \text{(J.6)}
\]
\[
h^A(T_0, P_0) = 0. \quad \text{(J.7)}
\]

The Helmholtz function \( f^\text{mix} \) in Eqn. (J.1) describes the water-air interaction and is defined by
\[
f^\text{mix}(A, T, \rho) = \frac{A(1-A)}{M_A M_W} \rho RT \left[ 2B^{AW}(T) + \frac{3}{2} \rho \left( \frac{A}{M_A} C^{A\text{AW}}(T) + \frac{(1-A)}{M_W} C^{A\text{WW}}(T) \right) \right]. \quad \text{(J.8)}
\]

The values used for the molar gas constant \( R \), the molar mass of dry air, \( M_A \), and the molar mass of water, \( M_W \), are given in Table J.1.

The second cross-virial coefficient, \( B^{AW}(T) \), is given by Harvey and Huang (2007) as
\[
B^{AW}(T) = b^* \sum_{i=1}^{3} c_i \tau^{d_i}. \quad \text{(J.9)}
\]

The coefficients of Eqn. (J.9) are given in Table J.4.

The third cross-virial coefficients \( C^{A\text{AW}}(T) \) and \( C^{A\text{WW}}(T) \) are defined in Hyland and Wexler (1983), in the form
\[
C^{A\text{AW}}(T) = c^* \sum_{i=0}^{4} a_i \tau^{-i}, \quad \text{(J.10)}
\]
and
\[
C^{A\text{WW}}(T) = -c^* \exp \left( \sum_{i=0}^{3} b_i \tau^{-i} \right). \quad \text{(J.11)}
\]
The coefficients \( a_i \) and \( b_i \) of Eqns. (J.10) and (J.11) are given in Table J.4.
Table J.2. Dimensionless coefficients and exponents for the ideal-gas part, Eqn. (J.4), for dry air (Lemmon et al. (2000)). In TEOS-10, the coefficients \( n_4^i \) and \( n_5^i \) are re-adjusted to the reference state conditions, Eqns. (J.6, J.7), and deviate from the originally published values of Lemmon et al. (2000).

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<th>( n_4^i )</th>
<th>( i )</th>
<th>( n_5^i )</th>
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<td>0.791 309 509 000 000</td>
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<td>–0.210 274 769 000 000 ( \times 10^{-4} )</td>
<td>9</td>
<td>0.212 236 768 000 000</td>
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<tr>
<td>3</td>
<td>–0.158 860 716 000 000 ( \times 10^{-3} )</td>
<td>10</td>
<td>–0.197 938 904 000 000</td>
</tr>
<tr>
<td>4</td>
<td>0.974 502 517 439 480 ( \times 10^{-10} )</td>
<td>11</td>
<td>0.253 636 500 000 000 ( \times 10^{2} )</td>
</tr>
<tr>
<td>5</td>
<td>0.100 986 147 428 912 ( \times 10^{-2} )</td>
<td>12</td>
<td>0.169 074 100 000 000 ( \times 10^{2} )</td>
</tr>
<tr>
<td>6</td>
<td>–0.195 363 420 000 000 ( \times 10^{-3} )</td>
<td>13</td>
<td>0.873 127 900 000 000 ( \times 10^{2} )</td>
</tr>
<tr>
<td>7</td>
<td>0.249 088 803 200 000 ( \times 10^{-10} )</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table J.3. Coefficients and exponents for the residual part, Eqn. (J.5), for dry air (Lemmon et al. (2000)).

<table>
<thead>
<tr>
<th>( k )</th>
<th>( i_k )</th>
<th>( j_k )</th>
<th>( l_k )</th>
<th>( n_k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0.118 160 747 229</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.33</td>
<td>0</td>
<td>0.713 116 392 079</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>1.01</td>
<td>0</td>
<td>–0.161 824 192 067 ( \times 10^{-10} )</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0.714 140 178 971 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>–0.865 421 396 646 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>0.15</td>
<td>0</td>
<td>0.134 211 176 704</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0.112 626 704 218 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>0.2</td>
<td>0</td>
<td>–0.420 533 228 842 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>0.35</td>
<td>0</td>
<td>0.349 008 431 982 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>1.35</td>
<td>0</td>
<td>0.164 957 183 186 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>11</td>
<td>1</td>
<td>1.6</td>
<td>1</td>
<td>–0.101 365 037 912</td>
</tr>
<tr>
<td>12</td>
<td>3</td>
<td>0.8</td>
<td>1</td>
<td>–0.173 813 690 970</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>0.95</td>
<td>1</td>
<td>–0.472 103 183 731 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>14</td>
<td>6</td>
<td>1.25</td>
<td>1</td>
<td>–0.122 523 554 253 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>15</td>
<td>1</td>
<td>3.6</td>
<td>2</td>
<td>–0.146 629 609 713</td>
</tr>
<tr>
<td>16</td>
<td>3</td>
<td>6</td>
<td>2</td>
<td>–0.316 055 879 821 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>17</td>
<td>11</td>
<td>3.25</td>
<td>2</td>
<td>0.233 594 806 142 ( \times 10^{-3} )</td>
</tr>
<tr>
<td>18</td>
<td>1</td>
<td>3.5</td>
<td>3</td>
<td>0.148 287 891 978 ( \times 10^{-1} )</td>
</tr>
<tr>
<td>19</td>
<td>3</td>
<td>15</td>
<td>3</td>
<td>–0.938 782 884 667 ( \times 10^{-2} )</td>
</tr>
</tbody>
</table>
Table J.4. Coefficients of the cross-virial coefficients $B^{AW}(T)$, $C^{AAW}(T)$ and $C^{AWW}(T)$, Eqns. (J.9) - (J.11). The reducing factors are $b^* = 10^{-6}$ m$^3$ mol$^{-1}$ and $c^* = 10^{-6}$ m$^6$ mol$^{-2}$, the “reduced temperature” is $\tau = T / (100\, \text{K})$.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.482737 $\times 10^{-1}$</td>
<td>-0.10728876 $\times 10^{2}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.105678 $\times 10^{-2}$</td>
<td>0.34780200 $\times 10^{2}$</td>
<td>0.665687 $\times 10^{2}$</td>
<td>-0.237</td>
</tr>
<tr>
<td>2</td>
<td>-0.656394 $\times 10^{-2}$</td>
<td>-0.38338300 $\times 10^{2}$</td>
<td>-0.238834 $\times 10^{3}$</td>
<td>-1.048</td>
</tr>
<tr>
<td>3</td>
<td>0.294442 $\times 10^{-1}$</td>
<td>0.33406000 $\times 10^{2}$</td>
<td>-0.176755 $\times 10^{3}$</td>
<td>-3.183</td>
</tr>
<tr>
<td>4</td>
<td>-0.319317 $\times 10^{-1}$</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The equation of state, Eqn. (J.1), is valid for humid air within the temperature and pressure range

$$193 \, \text{K} \leq T \leq 473 \, \text{K} \quad \text{and} \quad 10 \, \text{nPa} \leq P \leq 5 \, \text{MPa}.$$  \hspace{1cm} (J.12)

The pressure is computed from $P = \rho^2 f_{AV}^\rho$. All validity regions of the formulas combined in Eqn. (J.1), including the Helmholtz functions of water vapour and of dry air, as well as the cross-virial coefficients, overlap only in this range. The separate ranges of validity of the individual components are wider; some of them significantly wider. Therefore, Eqn. (J.1) will provide reasonable results outside of the $T-P$ range given above under the condition that a certain component dominates numerically in Eqn. (J.1) and is evaluated within its particular range of validity.

The air fraction $A$ can take any value between 0 and 1 provided that the partial vapour pressure, $P_{\text{vap}} = x_V P$, ($x_V$ is the mole fraction of vapour, Eqn. (3.35.3)) does not exceed its saturation value, i.e.,

$$0 \leq A \leq 1 \quad \text{and} \quad A_{\text{sat}}(T,P) \leq A.$$  \hspace{1cm} (J.13)

The exact value of the air fraction $A_{\text{sat}}(T,P)$ of saturated humid air is given by equal chemical potentials of water vapour in humid air and of either liquid water, Eqn. (3.37.5), if the temperature is above the freezing point, or of ice, Eqn. (3.35.4), if the temperature is below the freezing point. At low density, the saturation vapour pressure $P_{\text{sat}}$ of humid air can be estimated by the correlation function for either the vapour pressure, $P_{\text{vap}}^\rho(T)$, of pure water (IAPWS (2007)), or for the sublimation pressure, $P_{\text{subl}}(T)$, of ice (IAPWS (2008b)), to obtain $A_{\text{sat}}(T,P) = \left(P - P_{\text{sat}}\right) / \left[P - P_{\text{sat}} (1 - M_w / M_A)\right]$, from Eqn. (3.35.3) as a practically sufficient approximation.
Appendix K: Coefficients of 25-term expressions for the density of seawater in terms of $\Theta$ and of $\theta$

The TEOS-10 Gibbs function of seawater $g(S_\lambda, t, p)$ is written as a polynomial in terms of its in situ temperature $t$, while for ocean models, density needs to be expressed as a computationally efficient expression in terms of either Conservative Temperature $\Theta$ or potential temperature $\theta$ (referenced to $p_\text{i} = 0$ dbar). McDougall et al. (2010b) have fitted the TEOS-10 values of density $\rho$ to $S_\lambda$, $\Theta$ and $p$ in a “funnel” of data points in $(S_\lambda, t, p)$ space. The fitted expression is in the form of a rational function, being the ratio of two polynomials of $(S_\lambda, \Theta, p)$

$$\rho = \frac{P_{\text{num}}}{P_{\text{denom}}}. \quad (K.1)$$

The “funnel” of data points in $(S_\lambda, t, p)$ space is described in more detail in McDougall et al. (2010b); at the sea surface it covers the full range of temperature and salinity while for pressure greater than 5500 dbar, the maximum temperature of the fitted data is 12°C and the minimum Absolute Salinity is $u_{kg} 30$ g kg$^{-1}$. The maximum pressure of the “funnel” is 8000 dbar. Table K.1 contains the 25 coefficients of the expression (K.1) for density in terms of $(S_\lambda, \Theta, p)$. The coefficients $c_1 - c_{12}$ in this table have units of kg m$^{-3}$ and the coefficients $c_{13} - c_{25}$ are dimensionless, and the normalizing values of $S_\lambda$, $\Theta$ and $p$ are taken to be 1 g kg$^{-1}$, 1 K and 1 dbar respectively.

The rms error of this 25-term approximation to the TEOS-10 density is less than 0.0015 kg m$^{-3}$ over the “funnel”; this can be compared with the rms uncertainty of 0.004 kg m$^{-3}$ of the underlying laboratory density data to which the TEOS-10 Gibbs function was fitted (see the first two rows of Table O.1 of appendix O). Similarly, the appropriate thermal expansion coefficient,

$$\alpha^\Theta = -\frac{1}{\rho} \left. \frac{\partial \rho}{\partial \Theta} \right|_{S_\lambda, p} \quad (K.2)$$

of the 25-term equation of state is different from the same thermal expansion coefficient evaluated from TEOS-10 with an rms error in the “funnel” of less than $0.3 \times 10^{-6}$ K$^{-1}$, compared with the rms error of the thermal expansion coefficient of the laboratory data to which the Feistel (2008) Gibbs function was fitted of $0.6 \times 10^{-6}$ K$^{-1}$ (see row six of Table O.1 of appendix O). In terms of the evaluation of density gradients, the haline contraction coefficient evaluated from Eqn. (K.1) is more accurate than the thermal expansion coefficient. Hence we may consider the 25-term rational function expression for density, Eqn. (K.1), to be equally as accurate as the full TEOS-10 expressions for density, the thermal expansion coefficient and the saline contraction coefficient for data that reside inside the “oceanographic funnel”.

The sound speed evaluated from the 25-term rational function Eqn. (K.1), has an rms error over the “funnel” of almost 0.25 m s$^{-1}$ which is approximately five times the rms error of the underlying sound speed data that was incorporated into the Feistel (2008) Gibbs function (see rows 7 to 9 of Table O.1 of appendix O). Hence, the 25-term expression for density is not a particularly accurate expression for the sound speed in seawater, even in the “funnel”. But for dynamical oceanography where $\alpha^\Theta$ and $\beta^\Theta$ are the aspects of the equation of state that, together with spatial gradients of $S_\lambda$ and $\Theta$ drive ocean currents and affect the calculation of the buoyancy frequency, we may take
the 25-term rational-function expression for density, Eqn. (K.1), as essentially reflecting the full accuracy of TEOS-10.

<table>
<thead>
<tr>
<th>$p^{25}_{\text{num}}$</th>
<th>Coefficients</th>
<th>$p^{25}_{\text{denom}}$</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>9.998 438 029 070 821 4 $\times 10^2$</td>
<td>$c_{13}$</td>
<td>1.0</td>
</tr>
<tr>
<td>$c_2$ $\Theta$</td>
<td>7.118 809 067 894 091 0 $\times 10^0$</td>
<td>$c_{14}$ $\Theta$</td>
<td>7.054 768 189 607 157 6 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$c_3$ $\Theta^3$</td>
<td>-1.945 992 251 337 968 7 $\times 10^{-2}$</td>
<td>$c_{15}$ $\Theta^3$</td>
<td>-1.175 369 560 585 864 7 $\times 10^{-5}$</td>
</tr>
<tr>
<td>$c_4$ $\Theta^5$</td>
<td>6.174 840 445 587 464 1 $\times 10^{-4}$</td>
<td>$c_{16}$ $\Theta^5$</td>
<td>5.921 980 948 827 490 3 $\times 10^{-7}$</td>
</tr>
<tr>
<td>$c_5$ $S_A$</td>
<td>2.892 573 154 127 765 3 $\times 10^0$</td>
<td>$c_{17}$ $\Theta^4$</td>
<td>3.488 790 222 801 251 9 $\times 10^{-10}$</td>
</tr>
<tr>
<td>$c_6$ $S_A\Theta$</td>
<td>2.147 149 549 326 832 4 $\times 10^{-3}$</td>
<td>$c_{18}$ $S_A$</td>
<td>2.077 771 608 561 845 8 $\times 10^{-3}$</td>
</tr>
<tr>
<td>$c_7$ $(S_A)^2$</td>
<td>1.945 753 175 118 305 9 $\times 10^{-3}$</td>
<td>$c_{19}$ $S_A\Theta$</td>
<td>-2.221 085 729 372 299 8 $\times 10^{-4}$</td>
</tr>
<tr>
<td>$c_8$ $p$</td>
<td>1.193 068 181 853 174 8 $\times 10^{-2}$</td>
<td>$c_{20}$ $S_A\Theta^3$</td>
<td>-3.662 814 106 789 528 2 $\times 10^{-10}$</td>
</tr>
<tr>
<td>$c_9$ $p\Theta^2$</td>
<td>2.696 914 801 183 075 8 $\times 10^{-7}$</td>
<td>$c_{21}$ $(S_A)^1.5$</td>
<td>3.468 821 075 791 734 0 $\times 10^{-6}$</td>
</tr>
<tr>
<td>$c_{10}$ $pS_A$</td>
<td>5.935 568 592 503 565 3 $\times 10^{-6}$</td>
<td>$c_{22}$ $(S_A)^1.5\Theta^2$</td>
<td>8.019 054 152 807 065 5 $\times 10^{-10}$</td>
</tr>
<tr>
<td>$c_{11}$ $p^2$</td>
<td>-2.594 338 980 742 903 9 $\times 10^{-8}$</td>
<td>$c_{23}$ $p$</td>
<td>6.831 462 955 412 332 4 $\times 10^{-6}$</td>
</tr>
<tr>
<td>$c_{12}$ $p^2\Theta^2$</td>
<td>-7.273 411 171 282 270 7 $\times 10^{-12}$</td>
<td>$c_{24}$ $p^2\Theta^3$</td>
<td>-8.529 479 483 448 544 6 $\times 10^{-17}$</td>
</tr>
<tr>
<td>$c_{25}$ $p^3\Theta$</td>
<td>-9.227 532 514 503 807 0 $\times 10^{-18}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Table K.1 Coefficients of the polynomials** $p^{25}_{\text{num}}(S_A, \Theta, p)$ and $p^{25}_{\text{denom}}(S_A, \Theta, p)$ that define the 25-term rational-function Eqn. (K.1) for density.

The same procedure has been used by McDougall *et al.* (2010b) to fit a rational function of the form of Eqn. (K.1) but where the polynomials in the numerator and denominator are functions of $(S_A, \theta, p)$ rather than of $(S_A, \Theta, p)$. This form of the 25-term rational function expression for density is of approximately the same accuracy as that described above, and the 25 coefficients of this expression are given in Table K.2. The coefficients $c_1-c_{12}$ in this table have units of kg m$^{-3}$ and the coefficients $c_{13}-c_{25}$ are dimensionless, and the normalizing values of $S_A$, $\theta$ and $p$ are taken to be 1 g kg$^{-1}$, 1 K and 1 dbar respectively.
<table>
<thead>
<tr>
<th>$P_{\text{num}}^{\alpha25}$</th>
<th>Coefficients</th>
<th>$P_{\text{denom}}^{\alpha25}$</th>
<th>Coefficients</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_1$</td>
<td>$9.998 , 427 , 704 , 040 , 868 , 8 \times 10^2$</td>
<td>$c_{13}$</td>
<td>$1.0$</td>
</tr>
<tr>
<td>$c_2$</td>
<td>$\theta$</td>
<td>$7.353 , 990 , 725 , 780 , 200 , 0 \times 10^0$</td>
<td>$c_{14}$</td>
</tr>
<tr>
<td>$c_3$</td>
<td>$\theta^2$</td>
<td>$-5.272 , 502 , 484 , 658 , 053 , 7 \times 10^{-2}$</td>
<td>$c_{15}$</td>
</tr>
<tr>
<td>$c_4$</td>
<td>$\theta^3$</td>
<td>$5.105 , 140 , 542 , 790 , 050 , 1 \times 10^{-4}$</td>
<td>$c_{16}$</td>
</tr>
<tr>
<td>$c_5$</td>
<td>$S_A$</td>
<td>$2.837 , 207 , 495 , 416 , 299 , 4 \times 10^0$</td>
<td>$c_{17}$</td>
</tr>
<tr>
<td>$c_6$</td>
<td>$S_A \theta$</td>
<td>$-5.746 , 287 , 373 , 866 , 898 , 5 \times 10^{-3}$</td>
<td>$c_{18}$</td>
</tr>
<tr>
<td>$c_7$</td>
<td>$(S_A)^2$</td>
<td>$2.016 , 582 , 840 , 401 , 100 , 5 \times 10^{-3}$</td>
<td>$c_{19}$</td>
</tr>
<tr>
<td>$c_8$</td>
<td>$p$</td>
<td>$1.150 , 668 , 012 , 876 , 069 , 5 \times 10^{-2}$</td>
<td>$c_{20}$</td>
</tr>
<tr>
<td>$c_9$</td>
<td>$p \theta^2$</td>
<td>$1.202 , 602 , 702 , 900 , 458 , 1 \times 10^{-7}$</td>
<td>$c_{21}$</td>
</tr>
<tr>
<td>$c_{10}$</td>
<td>$p S_A$</td>
<td>$5.536 , 190 , 936 , 504 , 846 , 6 \times 10^{-6}$</td>
<td>$c_{22}$</td>
</tr>
<tr>
<td>$c_{11}$</td>
<td>$p^2$</td>
<td>$-2.756 , 315 , 640 , 465 , 192 , 8 \times 10^{-8}$</td>
<td>$c_{23}$</td>
</tr>
<tr>
<td>$c_{12}$</td>
<td>$p^2 \theta^2$</td>
<td>$-5.883 , 476 , 945 , 993 , 336 , 4 \times 10^{-12}$</td>
<td>$c_{24}$</td>
</tr>
<tr>
<td>$c_{25}$</td>
<td>$p^3 \theta$</td>
<td>$-9.623 , 745 , 548 , 627 , 732 , 0 \times 10^{-18}$</td>
<td></td>
</tr>
</tbody>
</table>

**TABLE K.2** Coefficients of the polynomials $P_{\text{num}}^{\alpha25} (S_A, \theta, p)$ and $P_{\text{denom}}^{\alpha25} (S_A, \theta, p)$ that define the 25-term rational-function Eqn. (K.1) for density.
Appendix L: Recommended nomenclature, symbols and units in oceanography

L.1 Recommended nomenclature

The strict SI units of Absolute Salinity, temperature and pressure are kg kg$^{-1}$, Absolute Temperature in K and Absolute Pressure $P$ in Pa. These are the units predominantly adopted in the SIA computer software for the input and output variables. If oceanographers were to adopt this practice of using strictly SI quantities it would simplify many thermodynamic expressions at the cost of using unfamiliar units.

The GSW software library (appendix N) adopts as far as possible the currently used oceanographic units, so that the input variables for all the computer algorithms are Absolute Salinity in $S_A$ in g kg$^{-1}$, temperature in °C and pressure as sea pressure in dbar. The outputs of the functions are also generally consistent with this choice of units, but some variables are more naturally expressed in SI units.

It seems impractical to recommend that the field of oceanography fully adopt strict basic SI units. It is however very valuable to have the field adopt uniform symbols and units, and in the interests of achieving this uniformity we recommend the following symbols and units. These are the symbols and units we have adopted in the GSW software library.

Table L.1. Recommended Symbols and Units in Oceanography

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinity</td>
<td>$Cl$</td>
<td>g kg$^{-1}$</td>
<td>WG127 is recommending that Chlorinity be defined in terms of a mass fraction as 0.328 523 4 times the ratio of the mass of pure silver required to precipitate all dissolved chloride, bromide and iodide in seawater to the mass of seawater. Hence WG127 recommends that mass fraction units are used for Chlorinity.</td>
</tr>
<tr>
<td>Standard Ocean Reference Salinity</td>
<td>$S_{SO}$</td>
<td>g kg$^{-1}$</td>
<td>35.165 04 g kg$^{-1}$ being exactly 35 $u_{PS}$, corresponding to the standard ocean Practical Salinity of 35.</td>
</tr>
<tr>
<td>Freezing temperatures</td>
<td>$t', \theta'$</td>
<td>°C</td>
<td><em>In situ</em>, potential and conservative values, each as a function of $S_A$ and $p$.</td>
</tr>
<tr>
<td>Absolute pressure</td>
<td>$P$</td>
<td>Pa</td>
<td>When absolute pressure is used it should always be in Pa, not in Mpa nor in dbar.</td>
</tr>
<tr>
<td>Sea pressure. Sea pressure is the pressure argument to all software in the GSW library.</td>
<td>$p$</td>
<td>dbar</td>
<td>Equal to $P - P^0$ and usually expressed in dbar not Pa.</td>
</tr>
<tr>
<td><strong>Gauge pressure.</strong> Gauge pressure (also called applied pressure) is sometimes reported from ship-born instruments.</td>
<td>$p^{\text{gauge}}$</td>
<td>dbar</td>
<td>Equal to the absolute pressure $P$ minus the local atmospheric pressure at the time of the instrument calibration, and expressed in dbar not Pa. Sea pressure $p$ is preferred over gauge pressure $p^{\text{gauge}}$, as $p$ is the argument to the seawater Gibbs function.</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td><strong>Reference pressure</strong></td>
<td>$P_r$</td>
<td>dbar</td>
<td>The value of the sea pressure $p$ to which potential temperature and/or potential density are referenced.</td>
</tr>
<tr>
<td><strong>One standard atmosphere</strong></td>
<td>$P_0$</td>
<td>Pa</td>
<td>exactly 101 325 Pa ($= 10.1325$ dbar)</td>
</tr>
<tr>
<td><strong>Isopycnal slope ratio</strong></td>
<td>$r$</td>
<td>1</td>
<td>( r = \frac{\alpha^\Theta (p)}{\beta^\Theta (p)} )</td>
</tr>
<tr>
<td><strong>Stability ratio</strong></td>
<td>$R_p$</td>
<td>1</td>
<td>( R_p = \frac{\alpha^\Theta(S)}{\beta^\Theta(S)} \approx \frac{\alpha^\Theta(S)}{\beta^\Theta(S)} )</td>
</tr>
<tr>
<td><strong>Isopycnal temperature gradient ratio</strong></td>
<td>$G^\alpha$</td>
<td>1</td>
<td>( G^\alpha = \left[ R_p - 1 \right] \left[ R_p - r \right] )</td>
</tr>
<tr>
<td><strong>Practical Salinity</strong></td>
<td>$S_p$</td>
<td>1</td>
<td>Defined in the range $2&lt;S_p&lt;42$ by PSS-78 based on measured conductivity ratios.</td>
</tr>
<tr>
<td><strong>Reference Salinity</strong></td>
<td>$S_R$</td>
<td>g kg$^{-1}$</td>
<td>Reference-Composition Salinity (or Reference Salinity for short) is the Absolute Salinity of seawater samples that have Reference Composition. At $S_p = 35$, $S_R$ is exactly $u_{ps}S_p$ while in the range $2&lt;S_p&lt;42$ $S_R = u_{ps}S_p$.</td>
</tr>
<tr>
<td><strong>Absolute Salinity</strong> (This is the salinity argument to all the GSW library functions.)</td>
<td>$S_A = S_A^{\text{dens}}$</td>
<td>g kg$^{-1}$</td>
<td>( S_A = S_R + \delta S_A = u_{ps}S_p + \delta S_A )</td>
</tr>
<tr>
<td><strong>Absolute Salinity Anomaly</strong></td>
<td>$\delta S_A$</td>
<td>g kg$^{-1}$</td>
<td>$\delta S_A = S_A - S_R$, the difference between Absolute Salinity, $S_A = S_A^{\text{dens}}$, and Reference-Composition Salinity. An algorithm to evaluate $\delta S_A$ is available (McDougall et al. (2008a) Reference-Salinity Scale and the Absolute Salinity Anomaly. The full symbol for $S_A$ is $S_A^{\text{dens}}$ as it is the type of absolute salinity which delivers the best estimate of density when used as the salinity argument of the TEOS-10 Gibbs function. Another name for $S_A = S_A^{\text{dens}}$ is “Density Salinity”</td>
</tr>
<tr>
<td><strong>“Preformed Absolute Salinity”, often shortened to “Preformed Salinity”</strong></td>
<td>$S_a$</td>
<td>g kg$^{-1}$</td>
<td>Preformed Absolute Salinity $S_a$ is a salinity variable that is designed to be as conservative as possible, by removing the estimated biogeochemical influences on the seawater composition from other forms of salinity (see Pawlowicz et al. (2010), Wright et al. (2010b) and appendix A.4 herein).</td>
</tr>
<tr>
<td><strong>“Solution Absolute Salinity”, often shortened to “Solution Salinity”</strong></td>
<td>$S_A^{\text{soln}}$</td>
<td>g kg$^{-1}$</td>
<td>The mass fraction of non-H$_2$O constituents in seawater after it has been brought to chemical equilibrium at $t = 25^\circ$C and $p = 0$ dbar (see Pawlowicz et al. (2010), Wright et al. (2010b) and appendix A.4 herein).</td>
</tr>
<tr>
<td><strong>“Added-Mass Salinity”</strong></td>
<td>$S_A^{\text{add}}$</td>
<td>g kg$^{-1}$</td>
<td>$S_A^{\text{add}} - S_R$ is the estimated mass fraction of non-H$_2$O constituents needed as ingredients to be added to Standard Seawater which when mixed and brought to chemical equilibrium at $t = 25^\circ$C and $p = 0$ dbar results in the observed seawater composition.</td>
</tr>
<tr>
<td>Property</td>
<td>Symbol</td>
<td>Unit</td>
<td></td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>--------</td>
<td>------</td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td>$T$</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>temperature derivatives</td>
<td>$T$</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Celsius zero point</td>
<td>$T_0$</td>
<td>K</td>
<td></td>
</tr>
<tr>
<td>Potential temperature</td>
<td>$\theta$</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Conservative Temperature</td>
<td>$\Theta$</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>A constant “specific heat”, for use with</td>
<td>$c_p^0$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Conservative Temperature</td>
<td>$c_p$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Enthalpy</td>
<td>$H$</td>
<td>J</td>
<td></td>
</tr>
<tr>
<td>Specific enthalpy</td>
<td>$h$</td>
<td>J kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Specific potential enthalpy</td>
<td>$h^0$</td>
<td>J kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Specific isobaric heat capacity</td>
<td>$c_p$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Internal energy</td>
<td>$U$</td>
<td>J</td>
<td></td>
</tr>
<tr>
<td>Specific internal energy</td>
<td>$u$</td>
<td>J kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Specific isochoric heat capacity</td>
<td>$c_v$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Gibbs function (Gibbs energy)</td>
<td>$G$</td>
<td>J</td>
<td></td>
</tr>
<tr>
<td>Specific Gibbs function (Gibbs energy)</td>
<td>$g$</td>
<td>J kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Specific Helmholtz Energy</td>
<td>$f$</td>
<td>J kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Unit conversion factor for salinities</td>
<td>$u_{PS}$</td>
<td>g kg$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Entropy</td>
<td>$\Sigma$</td>
<td>J K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Specific entropy</td>
<td>$\eta$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>$\rho$</td>
<td>kg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Density anomaly</td>
<td>$\sigma'$</td>
<td>kg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Potential density anomaly referenced to a sea pressure of 1000 dbar</td>
<td>$\sigma_1$</td>
<td>kg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Potential density anomaly referenced to a sea pressure of 4000 dbar</td>
<td>$\sigma_3$</td>
<td>kg m$^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient with respect to in situ temperature</td>
<td>$\alpha'$</td>
<td>K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Thermal expansion coefficient with respect to potential temperature $\theta$</td>
<td>$\alpha^\theta$</td>
<td>K$^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Property</td>
<td>Symbol</td>
<td>Unit</td>
<td>Equation</td>
</tr>
<tr>
<td>---------------------------------------------------------------</td>
<td>--------</td>
<td>-------</td>
<td>--------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Thermal expansion coefficient with respect to Conservative Temperature $\Theta$</td>
<td>$\alpha^\Theta$</td>
<td>$\text{K}^{-1}$</td>
<td>$v^{-1}\partial v / \partial \Theta \bigg</td>
</tr>
<tr>
<td>Haline contraction coefficient at constant in situ temperature</td>
<td>$\beta^i$</td>
<td>$\text{kg g}^{-1}$</td>
<td>$-v^{-1}\partial v / \partial S_A \bigg</td>
</tr>
<tr>
<td>Note that the units for $\beta^i$ are consistent with $S_A$ being in g kg$^{-1}$.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haline contraction coefficient at constant potential temperature</td>
<td>$\beta^\Theta$</td>
<td>$\text{kg g}^{-1}$</td>
<td>$-v^{-1}\partial v / \partial S_A \bigg</td>
</tr>
<tr>
<td>Note that the units for $\beta^\Theta$ are consistent with $S_A$ being in g kg$^{-1}$.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haline contraction coefficient at constant Conservative Temperature</td>
<td>$\beta^\Theta$</td>
<td>$\text{kg g}^{-1}$</td>
<td>$-v^{-1}\partial v / \partial S_A \bigg</td>
</tr>
<tr>
<td>Note that the units for $\beta^\Theta$ are consistent with $S_A$ being in g kg$^{-1}$.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Isothermal compressibility</td>
<td>$\kappa^i$</td>
<td>$\text{Pa}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Isentropic and isohaline compressibility</td>
<td>$\kappa^\Theta$</td>
<td>$\text{Pa}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Chemical potential of water in seawater</td>
<td>$\mu^w$</td>
<td>$\text{J g}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Chemical potential of sea salt in seawater</td>
<td>$\mu^S$</td>
<td>$\text{J g}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Relative chemical potential of (sea salt and water in seawater)</td>
<td>$\mu$</td>
<td>$\text{J g}^{-1}$</td>
<td>$(\partial g / \partial S_A)_{\rho,\rho} = \mu^S - \mu^w$</td>
</tr>
<tr>
<td>Dissipation rate of kinetic energy per unit mass</td>
<td>$\varepsilon$</td>
<td>$\text{J kg}^{-1} \text{s}^{-3} = \text{m}^2 \text{s}^{-3}$</td>
<td></td>
</tr>
<tr>
<td>Adiabatic lapse rate</td>
<td>$\Gamma$</td>
<td>$\text{K Pa}^{-1}$</td>
<td>$\Gamma = \left(\frac{\partial \ell}{\partial P}\bigg</td>
</tr>
<tr>
<td>Sound speed</td>
<td>$c$</td>
<td>$\text{m s}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Specific volume</td>
<td>$v$</td>
<td>$\text{m}^3 \text{kg}^{-1}$</td>
<td>$v = \rho^{-1}$</td>
</tr>
<tr>
<td>Specific volume anomaly</td>
<td>$\delta$</td>
<td>$\text{m}^3 \text{kg}^{-1}$</td>
<td></td>
</tr>
<tr>
<td>Thermobaric coefficient based on $\theta$</td>
<td>$T^\theta_b$</td>
<td>$\text{K Pa}^{-1}$</td>
<td>$T^\theta_b = \beta^\theta \partial \left(\alpha^\theta / \beta^\theta\right) / \partial P \bigg</td>
</tr>
<tr>
<td>Thermobaric coefficient based on $\Theta$</td>
<td>$T^\Theta_b$</td>
<td>$\text{K Pa}^{-1}$</td>
<td>$T^\Theta_b = \beta^\Theta \partial \left(\alpha^\Theta / \beta^\Theta\right) / \partial P \bigg</td>
</tr>
<tr>
<td>Cabbeling coefficient based on $\theta$</td>
<td>$C^\theta_b$</td>
<td>$\text{K}^{-2}$</td>
<td>$C^\theta_b = \partial \alpha^\theta / \partial \Theta \bigg</td>
</tr>
<tr>
<td>Cabbeling coefficient based on $\Theta$</td>
<td>$C^\Theta_b$</td>
<td>$\text{K}^{-2}$</td>
<td>$C^\Theta_b = \partial \alpha^\Theta / \partial \Theta \bigg</td>
</tr>
<tr>
<td>Buoyancy frequency</td>
<td>$N$</td>
<td>$\text{s}^{-1}$</td>
<td>$N^2 = g \left(\alpha^\Theta \Theta - \beta^\Theta S_A\right) = g \left(\alpha^\Theta \Theta - \beta^\Theta S_A\right)$</td>
</tr>
<tr>
<td>Neutral helicity</td>
<td>$H^\alpha$</td>
<td>$\text{m}^3$</td>
<td>Defined by Eqns. (3.13.1) and (3.13.2)</td>
</tr>
<tr>
<td>Neutral Density</td>
<td>$\gamma^\alpha$</td>
<td>$\text{kg m}^{-3}$</td>
<td>A density variable whose iso-surfaces are designed to be approximately neutral, i. e. $\alpha^\Theta \Theta \approx \beta^\Theta \Theta S_A$.</td>
</tr>
<tr>
<td>Neutral-Surface-Potential-Vorticity</td>
<td>$\text{NSPV}$</td>
<td>$\text{S}^{-3}$</td>
<td>$\text{NSPV} = -g \rho^{-1} \gamma^\alpha_z$ where $f$ is the Coriolis parameter.</td>
</tr>
<tr>
<td>Dynamic height anomaly</td>
<td>$\Phi'$</td>
<td>$\text{m}^2 \text{s}^{-2}$</td>
<td>$\text{Pa m}^{-1} = \text{m}^2 \text{s}^{-2}$</td>
</tr>
<tr>
<td>Montgomery geostrophic streamfunction</td>
<td>$\pi$</td>
<td>$\text{m}^2 \text{s}^{-2}$</td>
<td>$\text{Pa m}^{-1} = \text{m}^2 \text{s}^{-2}$</td>
</tr>
<tr>
<td>PISH (Pressure-Integrated Steric Height)</td>
<td>$\Psi'$</td>
<td>kg s⁻²</td>
<td>Streamfunction for $f$ times the depth-integrated relative mass flux, see Eqns. (3.31.1) – (3.31.5).</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Coriolis parameter</td>
<td>$f$</td>
<td>s⁻¹</td>
<td>1.458 42 x 10⁻⁴ sin $\phi$ s⁻¹, where $\phi$ is latitude</td>
</tr>
<tr>
<td>Molality</td>
<td>$m_{SW}$</td>
<td>mol kg⁻¹</td>
<td>$m_{SW} = \sum m_i = \frac{1}{M_s} \frac{S_M}{(1-S_M)}$ where $M_s$ is the mole-weighted average atomic weight of the elements of sea salt, $M_s = 31.403 , 821 , 8 , g , mol^{-1}$</td>
</tr>
<tr>
<td>Ionic strength</td>
<td>$I$</td>
<td>mol kg⁻¹</td>
<td>$I = \frac{1}{2} m_{SW} \langle Z^2 \rangle = \frac{1}{2} \sum m_i z_i^2$</td>
</tr>
<tr>
<td>Osmotic coefficient</td>
<td>$\phi$</td>
<td>1</td>
<td>$\phi(S_M, T, p) = \frac{g(0, t, p)<em>0 - \mu^W(S_M, t, p)}{m</em>{SW} R(T_0 + t)}$ where the molar gas constant, $R = 8.314 , 472 , J , mol^{-1} , K^{-1}$. See also Eqn. (3.40.9) for an equivalent definition of $\phi$.</td>
</tr>
</tbody>
</table>
L.2 Suggested Symbols when variables are functions of \( \eta, \theta \) and \( \Theta \)

Note that whether using standard notation or variants from it, all variables should be explicitly defined in publications when first used. Standard notation should be considered as an additional aid to improve readability, not as a replacement for explicit definitions.

Note that oxygen should be reported in \( \mu \text{mol/kg} \) and not \( \text{cm}^3\text{dm}^{-3}, \text{ml/l} \) or \( \mu \text{mol/l} \) (this reflects a desire for consistency with reporting of other quantities and will avoid problems associated with conversion between moles and ml using the gas equations).

When thermodynamic variables are taken to be functions of variables other than the standard combination \((S_A,t,p)\) it is convenient to indicate this by a marking on the variable. This greatly simplifies the nomenclature for partial derivatives. Table L.2 lists the suggested markings on the variables that arise commonly in this context. The thermodynamic variables are related to the thermodynamic potentials \( h = h(S_A,\eta,p), \)

\( h = \hat{h}(S_A,\theta,p) \) and \( h = \hat{h}(S_A,\Theta,p) \) by the expressions in appendix P.

### Table L.2. Suggested Symbols when variables are functions of \( \eta, \theta \) and \( \Theta \)

<table>
<thead>
<tr>
<th>quantity</th>
<th>function of</th>
<th>symbol for this functional form</th>
</tr>
</thead>
<tbody>
<tr>
<td>enthalpy, ( h )</td>
<td>((S_A,t,p))</td>
<td>( h = h(S_A,t,p) )</td>
</tr>
<tr>
<td>specific volume, ( v )</td>
<td>((S_A,t,p))</td>
<td>( v = v(S_A,t,p) )</td>
</tr>
<tr>
<td>density, ( \rho )</td>
<td>((S_A,t,p))</td>
<td>( \rho = \rho(S_A,t,p) )</td>
</tr>
<tr>
<td>entropy, ( \eta )</td>
<td>((S_A,t,p))</td>
<td>( \eta = \eta(S_A,t,p) )</td>
</tr>
<tr>
<td>enthalpy, ( h )</td>
<td>((S_A,\eta,p))</td>
<td>( h = \hat{h}(S_A,\eta,p) )</td>
</tr>
<tr>
<td>specific volume, ( v )</td>
<td>((S_A,\eta,p))</td>
<td>( v = \hat{v}(S_A,\eta,p) )</td>
</tr>
<tr>
<td>density, ( \rho )</td>
<td>((S_A,\eta,p))</td>
<td>( \rho = \hat{\rho}(S_A,\eta,p) )</td>
</tr>
<tr>
<td>potential temperature, ( \theta )</td>
<td>((S_A,\eta,p))</td>
<td>( \theta = \hat{\theta}(S_A,\eta) )</td>
</tr>
<tr>
<td>enthalpy, ( h )</td>
<td>((S_A,\theta,p))</td>
<td>( h = \hat{h}(S_A,\theta,p) )</td>
</tr>
<tr>
<td>specific volume, ( v )</td>
<td>((S_A,\theta,p))</td>
<td>( v = \hat{v}(S_A,\theta,p) )</td>
</tr>
<tr>
<td>density, ( \rho )</td>
<td>((S_A,\theta,p))</td>
<td>( \rho = \hat{\rho}(S_A,\theta,p) )</td>
</tr>
<tr>
<td>entropy, ( \eta )</td>
<td>((S_A,\theta,p))</td>
<td>( \eta = \hat{\eta}(S_A,\theta) )</td>
</tr>
<tr>
<td>enthalpy, ( h )</td>
<td>((S_A,\Theta,p))</td>
<td>( h = \hat{h}(S_A,\Theta,p) )</td>
</tr>
<tr>
<td>specific volume, ( v )</td>
<td>((S_A,\Theta,p))</td>
<td>( v = \hat{v}(S_A,\Theta,p) )</td>
</tr>
<tr>
<td>density, ( \rho )</td>
<td>((S_A,\Theta,p))</td>
<td>( \rho = \hat{\rho}(S_A,\Theta,p) )</td>
</tr>
<tr>
<td>entropy, ( \eta )</td>
<td>((S_A,\Theta,p))</td>
<td>( \eta = \hat{\eta}(S_A,\Theta) )</td>
</tr>
</tbody>
</table>
Appendix M:
Seawater-Ice-Air (SIA) library of computer software

This software library, the Seawater-Ice-Air library (the SIA library for short), contains the TEOS-10 subroutines for evaluating a wide range of thermodynamic properties of pure water (using IAPWS-95), seawater (using IAPWS-08 for the saline part), ice Ih (using IAPWS-06) and for moist air (using Feistel et al. (2010a), IAPWS (2010)). It is divided into six levels (levels 0 through 5) with each successive level building on the functional capabilities introduced at lower levels. Briefly,

- level 0 defines fundamental constants, sets options used throughout the library and provides routines to convert between Practical Salinity and Absolute Salinity
- level 1 defines a complete set of independent and consistent elements that are based on previous work and form the essential building blocks for the rest of the library routines
- level 2 provides access to a set of properties for individual mediums (liquid or vapour water, ice, seawater and dry or humid air) that can be calculated from the level 0 and 1 routines without additional approximations
- level 3 introduces additional functions that require numerical solution of equations. Most importantly, it is at this level that the density of pure fluid water is determined from temperature and pressure information. This permits the definition of Gibbs functions for pure water and seawater that make use of the IAPWS-95 Helmholtz function as a fundamental building block
- level 4 deals with a fairly broad (but not exhaustive) selection of equilibrium properties involving fluid water, seawater, ice and air; and
- level 5 includes a set of routines that build on the SIA routines but violate principals adhered to throughout levels 0 through 4. In particular, non-basic SI units are permitted at this level as discussed below.

As a general rule, the inputs and the outputs of the algorithms in the SIA library are in basic SI units. Hence the salinity is Absolute Salinity $S_A$ in units of kg kg$^{-1}$ (so that for example standard ocean Reference Salinity is input to SIA functions as 0.035 165 04 (kg kg$^{-1}$) rather than 35.165 04 (g kg$^{-1}$), in situ temperature is input as Absolute Temperature $T$ in K, and pressure is input as Absolute Pressure $P$ in Pa. Use of these basic SI units simplifies the calculation of theoretical expressions in thermodynamics. The only exceptions to this rule for the units of the inputs and outputs in the SIA library are as follows.

- The function $S_A = S_A(S_p, \phi, \lambda, P)$ that calculates Absolute Salinity (in kg kg$^{-1}$) when given Practical Salinity $S_p$ (which is unitless and takes numbers like 35 not 0.035) as its salinity input variable, along with location in the form of longitude $\lambda$ (°E) latitude $\phi$ (°N) and Absolute Pressure $P$ (Pa). Location is required in this routine to account for the influence of composition anomalies through a lookup table adopted from the GSW library.
- The inverse function $S_p = S_p(S_A, \phi, \lambda, P)$. This and the previous routine are found at level 0 since Absolute Salinity is required as an input to many of the higher level library routines.
• General purpose routines that allow for conversions between a broad range of pressure, temperature and salinity units that are in common usage are provided at level 5. The numerical input value and its unit are provided by the user and results are returned in a specified output unit.

• Algorithms are included at level 5 that use non-basic SI units as input and as output. Most noteworthy is the GSW library module that uses the SIA routines to mimic many of the routines in the GSW software library. These routines use IAPWS-09 for pure water in place of IAPWS-95 to provide improved computational efficiency. They have been used to provide independent checks on the corresponding routines in the GSW software library.

Because the IAPWS-95 description of pure water substance (both liquid and vapour) is the world-wide standard for pure water substance, the SIA library is the official description of seawater, although it should be noted that the computer software does not come with any warranty. Rather it is the underlying papers as listed in appendix C that are the officially warranted descriptions.

The SIA library benefits from the full range of applicability of the IAPWS-95 Helmholtz function for pure water, \(0 \text{ kg m}^{-3} < \rho < 1200 \text{ kg m}^{-3}, 130 \text{ K} < T < 1273 \text{ K}\), plus an extension down to 50 K introduced by Feistel et al. (2010a). It does however have two disadvantages as far as the field of oceanography is concerned. First, because IAPWS-95 is valid over very wide ranges of temperature and pressure, it is necessarily an extensive series of polynomials and exponentials which is not as fast computationally as the equation of state EOS-80 with which oceanographers are familiar. Second, the IAPWS-95 thermodynamic potential is a Helmholtz function which expresses thermodynamic properties in terms of density and temperature rather than pressure and temperature as normally used in oceanography. Since IAPWS-95 describes not only liquid water but also water vapour, this Helmholtz form of the thermodynamic potential is natural. Although the library also includes a Gibbs function formulation with temperature and pressure as independent variables, the core routines implement this formulation by first solving \(P = \rho^2 f_p(T, \rho)\) for \(\rho\) and then using IAPWS-95, which is a computationally expensive procedure.

In the GSW library (appendix N) we present an alternative thermodynamic description of seawater properties based on the IAPWS-09 description of the pure liquid water part as a Gibbs function. The GSW formulation is limited to the Neptunian range (i.e. the oceanographic range) of temperature and pressure and deals only with liquid water, but it is far more computationally efficient since the limited range of validity allows equivalent accuracy with fewer terms and the Gibbs function formulation avoids the need to invert the relation \(P = \rho^2 f_p(T, \rho)\). This formulation is also implemented at level 5 of the SIA library as a cross-check on the GSW routines and for the convenience of SIA library users working on applications requiring increased computational efficiency. Note however that some of routines in the SIA implementation of the GSW routines are not as fully optimized as the corresponding routines in the GSW library.

The presence of dissolved salts in seawater reduces the range of applicability of the SIA and GSW seawater routines in comparison with the IAPWS-95 range of applicability for pure fluid water, whether or not the IAPWS-09 Gibbs formulation is used to represent pure water properties. This is because the range of applicability of the saline component of the Gibbs function is limited to \(0 \text{ kg kg}^{-1} \leq S_A \leq 0.12 \text{ kg kg}^{-1}, 262 \text{ K} \leq T \leq 353 \text{ K},\) and \(100 \text{ Pa} \leq P \leq 10^8 \text{ Pa}\).

Since this manual focuses on seawater, we refer the reader to Feistel et al. (2010b) and Wright et al. (2010a) for details on the ice and air components of the SIA library. However, below, we discuss a few features of the library that relate to these additional
components. First, we note that the thermodynamic potentials of pure water, ice, the saline part of the seawater Gibbs function and the Gibbs function of moist air have been carefully adjusted to make them fully compatible with each other (Feistel et al. (2008a)). Only by so doing can the equilibrium properties of coincident phases be accurately evaluated (for example, the freezing temperature of pure water and of seawater). Many functions involving equilibrium properties of water, vapour, ice, seawater and dry or humid air are implemented in level 4 of the SIA library. To provide an indication of the range of functions available, we have listed the routine names in Table M.1 below. This table comes from Table 3.1 of Wright et al. (2010a); we refer the interested reader to Feistel et al. (2010b) and Wright et al. (2010a) for detailed information. Wright et al. (2010a) provide a supplementary table that is cross-referenced to their Table 3.1 to give details on the usage of each routine and each table in their supplement references in turn the relevant sections of Feistel et al. (2010b) for additional background information.

Due to the fact that each level of the SIA library builds on lower levels and the fact that multiple phases may be involved in the equilibrium calculations, the determination of the ranges of validity of the routines in the SIA library can become rather involved. To deal with this issue, a procedure has been implemented in the library to return an error code for function evaluations that depend on results from any of the basic building block routines from outside of their individual ranges of validity. Numerical check values are provided with each of the routines in the library and auxiliary routines are provided to assist users in the validation of local implementations.

Further details of the SIA software library are provided in the papers Feistel et al. (2010b) and Wright et al. (2010a) and the software is served from the www.TEOS-10.org web site.
Table M.1. The SIA library contents. Module names are in bold and user-accessible routines are in plain type. Each of the Public Routines can be accessed by users. The underlined routines are thermodynamic potential functions including first and second derivatives. The bracketed numbers preceding most module names give the related table numbers in the supplement to Wright et al. (2010a) where detailed information on the use of each function is provided.

<table>
<thead>
<tr>
<th>Level 0 routines</th>
<th>Constants_0</th>
<th>Constants_0 (Cont’d)</th>
<th>Maths_0</th>
<th>(S2) Convert_0</th>
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<tbody>
<tr>
<td>Public Parameter Values</td>
<td>Parameter Values (cont’d)</td>
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<table>
<thead>
<tr>
<th>Level 1 routines</th>
<th>(S3) Flu_1 (IAPWS95)</th>
<th>(S4) Ice_1 (IAPWS06)</th>
<th>(S5) Sal_1 (IAPWS08)</th>
<th>(S6) Air_1</th>
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<tr>
<td>Public Routines</td>
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</table>
## Level 2 routines

### (S7) Flu_2

- Use: constants_0, flu_1
- Public Routines:
  - flu_cp_si
  - flu_cv_si
  - flu_enthalpy_si
  - flu_entropy_si
  - flu_expansion_si
  - flu_gibbs_energy_si
  - flu_kappa_s_si
  - flu_kappa_t_si
  - flu_lapserate_si
  - flu_pressure_si
  - flu_soundspeed_si

### (S8) Ice_2

- Use: constants_0, ice_1
- Public Routines:
  - ice_chempot_si
  - ice_cp_si
  - ice_density_si
  - ice_enthalpy_si
  - ice_entropy_si
  - ice_expansion_si
  - ice_helmholtz_energy_si
  - ice_kappa_s_si
  - ice_kappa_t_si
  - ice_lapserate_si
  - ice_p_coefficient_si
  - ice_specific_volume_si

### (S9) Sal_2

- Use: constants_0, sal_1
- Public Routines:
  - sal_act_coeff_si
  - sal_act_potential_si
  - sal_activity_w_si
  - sal_chem_coeff_si
  - sal_chempot_h2o_si
  - sal_chempot_rel_si
  - sal_dilution_si
  - sal_q_si
  - sal_mixenthalpy_si
  - sal_mixentropy_si
  - sal_mixvolume_si
  - sal_molality_si
  - sal_osm_coeff_si
  - sal_saltenthalpy_si
  - sal_saltentropy_si
  - sal_saltvolume_si

### (S10) Air_2

- Use: constants_0, flu_1, air_1
- Public Routines:
  - air_f_si
  - air_f_cp_si
  - air_f_cv_si
  - air_f_enthalpy_si
  - air_f_entropy_si
  - air_f_gibbs_energy_si
  - air_f_internal_energy_si
  - air_f_kappa_s_si
  - air_f_kappa_t_si
  - air_f_mix_si
  - air_f_pressure_si
  - air_f_soundspeed_si
  - chk_iapws10_table

## Level 3 routines

### (S11) Flu_3a

- Use: constants_0, convert_0, maths_0, flu_1
- Public Routines:
  - get_it_ctrl_density
  - liq_density_si
  - liq_g_si
  - set_it_ctrl_density
  - vap_density_si
  - vap_g_si

### (S12) Sea_3a

- Use: constants_0, sal_1, sal_2, flu_3a (convert_0, maths_0, flu_1)
- Public Routines:
  - chk_iapws08_table8a
  - chk_iapws08_table8b
  - chk_iapws08_table8c
  - sea_chempot_h2o_si
  - sea_chempot_rel_si
  - sea_cp_si
  - sea_density_si
  - sea_enthalpy_si
  - sea_entropy_si
  - sea_g_si
  - sea_g_contraction_t_si
  - sea_g_expansion_si
  - sea_gibbs_energy_si
  - sea_internal_energy_si
  - sea_kappa_s_si
  - sea_kappa_t_si
  - sea_lapserate_si
  - sea_osm_coeff_si
  - sea_soundspeed_si
  - sea_temp_maxdensity_si

### (S13) Air_3a

- Use: constants_0, convert_0, maths_0, air_1, air_2 (flu_1)
- Public Routines:
  - air_density_si
  - air_g_si
  - get_it_ctrl_airdensity
  - set_it_ctrl_airdensity
<table>
<thead>
<tr>
<th>(S14) Flu_3b</th>
<th>(S15) Sea_3b</th>
<th>(S16) Air_3b</th>
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<td><strong>Uses</strong></td>
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(S17) Sea_3c

**Uses**
constants_0, sea_3a, sea_3b
(convert_0, maths_0, flu_1, sal_1, sal_2, flu_3a)

**Public Routines**
sea_h_si
sea_h_contraction_h_si
sea_h_contraction_t_si
sea_h_contraction_theta_si
sea_h_density_si
sea_h_entropy_si
sea_h_expansion_h_si
sea_h_expansion_t_si
sea_h_expansion_theta_si
sea_h_potdensity_si
sea_h_potenthalpy_si
seawater_si
set_it_ctrl_pottemp

(S18) Air_3c

**Uses**
constants_0, convert_0, air_2, air_3a, air_3b
(maths_0, air_1, flu_1)

**Public Routines**
air_h_si
air_perturbation
air_potential
air_potential_temp
air_temperature_seq
set_it_ctrl_air_pottemp

(S19) Sea_3d

**Uses**
constants_0, sal_2, flu_3a
(convert_0, maths_0, flu_1, sal_1)

**Public Routines**
sea_sa_si
set_it_ctrl_salinity
### Level 4 routines

**(S20) Liq_Vap_4**

**Uses**
- constants_0, maths_0, flu_1, flu_2, flu_3a (Convert_0)

**Public Routines**
- chk_icepws95_table8
- liq_vap_boilingtemperature_si
- liq_vap_density_liq_si
- liq_vap_density_vap_si
- liq_vap_enthalpy_evap_si
- liq_vap_entropy_evap_si
- liq_vap_entropy_liq_si
- liq_vap_entropy_vap_si
- liq_vap_temperature_si
- liq_vap_volume_evap_si
- set_liq_vap_eq_at_p
- set_liq_vap_eq_at_t
- set_it_ctrl_liq_vap

**(S21) Ice_Vap_4**

**Uses**
- constants_0, maths_0, flu_1, flu_2, ice_1, ice_2

**Public Routines**
- ice_vap_chempot_si
- ice_vap_density_ice_si
- ice_vap_density_vap_si
- ice_vap_enthalpy_ice_si
- ice_vap_enthalpy_vap_si
- ice_vap_entropy_ice_si
- ice_vap_entropy_vap_si
- ice_vap_pressure_vap_si
- ice_vap_sublimationpressure_si
- ice_vap_sublimationtemp_si
- ice_vap_temperature_si
- ice_vap_volume_subl_si
- set_ice_vap_eq_at_p
- set_ice_vap_eq_at_t
- set_it_ctrl_ice_vap

**(S22) Sea_Vap_4**

**Uses**
- constants_0, maths_0, flu_1, sal_1, sal_2, flu_3a, sea_3a, flu_3b (Convert_0, flu_2)

**Public Routines**
- sea_vap_boilingtemperature_si
- sea_vap_brinefraction_seavap_si
- sea_vap_brinesalinity_si
- sea_vap_cp_seavap_si
- sea_vap_density_sea_si
- sea_vap_density_seavap_si
- sea_vap_entropy_sea_si
- sea_vap_entropy_seavap_si
- sea_vap_entropy_vap_si
- sea_vap_enthalpy_sea_si
- sea_vap_enthalpy_seavap_si
- sea_vap_enthalpy_vap_si
- sea_vap_expansion_seavap_si
- sea_vap_g_si
- sea_vap_kappa_t_seavap_si
- sea_vap_pressure_si
- sea_vap_salinity_si
- sea_vap_temperature_si
- sea_vap_vapourpressure_si
- sea_vap_volume_evap_si
- set_sea_vap_eq_at_s_p
- set_sea_vap_eq_at_s_t
- set_sea_vap_eq_at_t_p

**(S23) Ice_Liq_4**

**Uses**
- constants_0, maths_0, flu_1, ice_1, ice_2

**Public Routines**
- ice_liq_chempot_si
- ice_liq_density_ice_si
- ice_liq_density_liq_si
- ice_liq_enthalpy_ice_si
- ice_liq_enthalpy_liq_si
- ice_liq_entropy_ice_si
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- ice_liq_meltingpressure_si
- ice_liq_meltingtemperature_si
- ice_liq_pressure_liq_si
- ice_liq_temperature_si
- ice_liq_volume_melt_si
- set_ice_liq_eq_at_p
- set_ice_liq_eq_at_t
- set_it_ctrl_ice_liq

**(S24) Sea_Liq_4**

**Uses**
- constants_0, flu_1, sal_1, flu_2, sal_2, flu_3a (Convert_0, maths_0)

**Public Routines**
- sea_liq_osmoticpressure_si
- set_sea_liq_eq_at_s_t_p
- set_it_ctrl_sea_liq
### (S25) Sea_Ice_4

**Uses**
- constants_0, convert_0,
- maths_0, flu_1, ice_1, sal_1,
- ice_2, sal_2, flu_3a, sea_3a,
- flu_3b (flu_2)

**Public Routines**
- sea_ice_brinefraction_seaice_si
- sea_ice_brinesalinity_si
- sea_ice_cp_seaice_si
- sea_ice_density_ice_si
- sea_ice_density_sea_si
- sea_ice_density_seaice_si
- sea_ice_dffdp_si
- sea_ice_dffds_si
- sea_ice_enthalpy_ice_si
- sea_ice_enthalpy_melt_si
- sea_ice_enthalpy_sea_si
- sea_ice_enthalpy_seaice_si
- sea_ice_entropy_ice_si
- sea_ice_entropy_sea_si
- sea_ice_entropy_seaice_si
- sea_ice_expansion_seaice_si
- sea_ice_freezingtemperature_si
- sea_ice_g_si
- sea_ice_kappa_t_seaice_si
- sea_ice_meltingpressure_si
- sea_ice_pressure_si
- sea_ice_salinity_si
- sea_ice_temperature_si
- sea_ice_volume_melt_si
- set_it_ctrl_sea_ice
- set_sea_ice_eq_at_s_p
- set_sea_ice_eq_at_s_t
- set_sea_ice_eq_at_t_p

### (S26) Sea_Air_4

**Uses**
- constants_0, convert_0,
- maths_0, flu_1, sal_1, air_1,
- flu_2, sal_2, air_2, flu_3a,
- sea_3a, air_3a, air_3b,
- liq_vap_4, liq_air_4a

**Public Routines**
- sea_air_chempot_evap_si
- sea_air_condense_temp_si
- sea_air_density_air_si
- sea_air_density_vap_si
- sea_air_enthalpy_evap_si
- sea_air_entropy_air_si
- sea_air_massfraction_air_si
- sea_air_vapourpressure_si
- set_it_ctrl_sea_air
- set_sea_air_eq_at_s_a_p
- set_sea_air_eq_at_s_t_p
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### (S31) Liq_Air_4b

**Uses**
- constants_0, flu_3a, air_3a, liq_air_4a (convert_0, maths_0, flu_1, air_1, flu_2, air_2, air_3b, liq_vap_4)

**Public Routines**
- liq_air_g_si
- liq_air_g_cp_si
- liq_air_g_density_si
- liq_air_g_enthalpy_si
- liq_air_g_entropy_si
- liq_air_g_expansion_si
- liq_air_g_kappa_t_si
- liq_air_g_lapserate_si
- liq_air_vapourfraction_si

### (S32) Ice_Air_4b

**Uses**
- constants_0, convert_0, ice_1, air_3a, ice_air_4a (maths_0, flu_1, air_1, flu_2, air_2, air_3b, ice_vap_4)

**Public Routines**
- ice_air_g_si
- ice_air_g_cp_si
- ice_air_g_density_si
- ice_air_g_enthalpy_si
- ice_air_g_entropy_si
- ice_air_g_expansion_si
- ice_air_g_kappa_t_si
- ice_air_g_lapserate_si
- ice_air_vapourfraction_si

### (S33) Liq_Air_4c

**Uses**
- constants_0, air_3a, ice_liq_4, liq_air_4a, liq_air_4b (convert_0, maths_0, flu_1, ice_1, air_1, flu_2, ice_2, air_2, air_3b, liq_vap_4)

**Public Routines**
- liq_air_h_si
- liq_air_h_cp_si
- liq_air_h_density_si
- liq_air_h_kappa_s_si
- liq_air_h_lapserate_si
- liq_air_h_temperature_si
- liq_air_potenthalpy_si
- liq_air_potdensity_si
- set_it_ctrl_liq_air_pottemp

### (S34) Ice_Air_4c

**Uses**
- constants_0, convert_0, ice_liq_4, ice_air_4b (maths_0, flu_1, ice_1, air_1, flu_2, ice_2, air_2, air_3a, air_3b, ice_vap_4)

**Public Routines**
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- ice_air_h_cp_si
- ice_air_h_density_si
- ice_air_h_kappa_s_si
- ice_air_h_lapserate_si
- ice_air_h_temperature_si
- ice_air_potenthalpy_si
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- set_it_ctrl_ice_air_pottemp

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Appendix N: Gibbs-SeaWater (GSW) library of computer software

This software library, the Gibbs-SeaWater library (the GSW library for short), contains the TEOS-10 subroutines for evaluating the thermodynamic properties of pure water (using IAPWS-09), seawater (using IAPWS-08 for the saline part) and ice Ih (using IAPWS-06). The GSW library does not provide properties of moist air (these properties can be found in the SIA library). This GSW library does not adhere to strict basic-SI units but rather oceanographic units are adopted. While it is comfortable for oceanographers to adopt these familiar non-basic SI units, doing so comes at a price, since many of the thermodynamic expressions demand that variables be expressed in basic-SI units. The simplest example is the pure water fraction (the so-called “freshwater fraction”) which is \(1-S_A\) only when Absolute Salinity \(S_A\) is in basic-SI units. The price that one pays with adopting comfortable units is that one must be vigilant when evaluating thermodynamic expressions; there are traps for the unwary particularly concerning the units of Absolute Salinity and of pressure.

This GSW library has inputs in “oceanographic” units, namely Absolute Salinity \(S_A\) in g kg\(^{-1}\) (so that for example standard ocean reference salinity \(S_{SO}^\text{d}\) is 35.165 04 g kg\(^{-1}\) [not 0.035 165 04 kg kg\(^{-1}\)]), \(in\ situ\) temperature \(t\) in \(^\circ\)C and pressure as sea pressure \(p\) in dbar.

The only exceptions to this rule for the units for the inputs are
- the function that calculates Practical Salinity \(S_p\) from conductivity ratio (PSS-78),
- the function that calculates Absolute Salinity, which has Practical Salinity \(S_p\) (which is unitless) as its salinity input variable, along with longitude \(\lambda\) (\(^\circ\)E) latitude \(\phi\) (\(^\circ\)N) and pressure \(p\) (dbar),
- the inverse function \(S_p = S_p(S_A, \phi, \lambda, p)\).

The GSW library is designed as a successor to the Seawater library of oceanographic Matlab routines which has been widely used by oceanographers in the past fifteen years; see \url{http://www.cmar.csiro.au/datacentre/ext_docs/seawater.htm} Many of the non-thermodynamic subroutines of the Seawater library have been retained or updated in the GSW library (for example, a subroutine to calculate distance between points at any depth on a spherical earth, and a subroutine to evaluate the gravitational acceleration as a function of latitude and pressure in the ocean). The paper by McDougall et al. (2010b) describes many of these subroutines. The GSW library is available from the web site at \url{www.TEOS-10.org}. Some of the function names are given in the following table.
Table N.1. A Selection of Functions in version 2.0 of the GSW Library at www.TEOS-10.org.

<table>
<thead>
<tr>
<th>Thermodynamic Property</th>
<th>Function name (in Matlab)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absolute Salinity $S_A$</td>
<td>gsw_SA_from_SP.m</td>
<td>the McDougall, Jackett and Millero (2010a) algorithm for $S_A$ using a look-up table for $\delta S_A$</td>
</tr>
<tr>
<td>Practical Salinity $S_p$</td>
<td>gsw_SP_from_SA.m</td>
<td>inverse function of gsw_SA_from_SP.m</td>
</tr>
<tr>
<td>Practical Salinity $S_p$</td>
<td>gsw_SP_from_cndr.m</td>
<td>$S_p$ from conductivity ratio, from PSS-78</td>
</tr>
<tr>
<td>Gibbs function $g$ and its 1st and 2nd derivatives</td>
<td>gsw_gibbs.m</td>
<td>the sum of the IAPWS-09 and IAPWS-08 Gibbs functions, and the derivatives of this sum</td>
</tr>
<tr>
<td>specific volume $v$</td>
<td>gsw_specvol.m</td>
<td>$v(S_A, t, p)$ specific volume using gsw_gibbs.m</td>
</tr>
<tr>
<td>density $\rho$</td>
<td>gsw_rho.m</td>
<td>$\rho(S_A, t, p)$ in situ density using gsw_gibbs.m</td>
</tr>
<tr>
<td>density $\rho$</td>
<td>gsw_rho_CT25.m</td>
<td>$\hat{\rho}(S_A, \Theta, p)$, in situ density using the 25-term expression for density in terms of Conservative Temperature (CT for short), $\Theta$</td>
</tr>
<tr>
<td>specific entropy $\eta$</td>
<td>gsw_entropy.m</td>
<td>$\eta(S_A, t, p)$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>specific enthalpy $h$</td>
<td>gsw_enthalpy.m</td>
<td>$h(S_A, t, p)$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>first derivatives of enthalpy with respect to Conservative Temperature</td>
<td>gsw_enthalpy_first_derivative.m</td>
<td>$\hat{h}<em>\Theta$ and $\hat{h}</em>{S_A}$ using gsw_gibbs.m (see Eqns. (A.11.15) and (A.11.18))</td>
</tr>
<tr>
<td>second derivatives of enthalpy with respect to Conservative Temperature</td>
<td>gsw_enthalpy_second_derivative.m</td>
<td>$\hat{h}<em>{\Theta\Theta}$, $\hat{h}</em>{\Theta S_A}$ and $\hat{h}_{S_A S_A}$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>sound speed $c$</td>
<td>gsw_sound_speed.m</td>
<td>$c(S_A, t, p)$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>Conservative Temperature $\Theta$</td>
<td>gsw_CT_from_pt.m</td>
<td>$\Theta(S_A, p)$, found directly from gsw_gibbs.m. Here $\Theta$ is potential temperature with $p_i = 0$.</td>
</tr>
<tr>
<td>potential temperature $\theta$</td>
<td>gsw_pt_from_t.m</td>
<td>$\theta(S_A, t, p, p_i)$ found by using gsw_gibbs.m and by equating two values of entropy</td>
</tr>
<tr>
<td>potential temperature $\theta$</td>
<td>gsw_pt0_from_t.m</td>
<td>$\theta(S_A, t, p)$, a computationally faster version of gsw_pt_from_t.m when $p_i = 0$ dbar.</td>
</tr>
<tr>
<td>potential temperature $\theta$</td>
<td>gsw_pt_from_CT.m</td>
<td>$\theta(S_A, \Theta)$, found by Newton-Raphson iteration, being the inverse function of gsw_CT_from_pt.m</td>
</tr>
<tr>
<td>thermal expansion coefficient with respect to Conservative Temperature $\alpha^\Theta$</td>
<td>gsw_alpha_CT.m</td>
<td>$\alpha^\Theta(S_A, t, p)$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>saline contraction coefficient at constant Conservative Temperature $\Theta$</td>
<td>gsw_beta_CT.m</td>
<td>$\beta^\Theta(S_A, t, p)$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>density, thermal expansion and saline contraction coefficient</td>
<td>gsw_rho_alpha_beta_CT25.m</td>
<td>$\hat{\rho}(S_A, \Theta, p)$, $\alpha^\Theta(S_A, \Theta, p)$ and $\beta^\Theta(S_A, \Theta, p)$ using the 25-term expression for density in terms of Conservative Temperature $\Theta$</td>
</tr>
<tr>
<td>potential density $\rho^\Theta$</td>
<td>gsw_pot_rho.m</td>
<td>$\rho^\Theta(S_A, t, p, p_i)$ using gsw_gibbs.m</td>
</tr>
<tr>
<td>potential density $\rho^\Theta$</td>
<td>gsw_pot_rho_CT25.m</td>
<td>$\rho^\Theta(S_A, \Theta, p_i)$, uses the 25-term expression for density in terms of Conservative Temperature. This is the same as calling gsw_rho_CT25.m with the input pressure being $p_i$.</td>
</tr>
<tr>
<td>dynamic height</td>
<td>gsw_geo_str_dyn_height.m</td>
<td>geostrophic streamfunction in an isobaric surface</td>
</tr>
<tr>
<td>McDougall-Klocker geostrophic streamfunction</td>
<td>gsw_geo_str_McD_Klocker.m</td>
<td>geostrophic streamfunction in an approximately neutral surface, see Eqn. (3.30.1)</td>
</tr>
<tr>
<td>Montgomery geostrophic streamfunction</td>
<td>gsw_geo_str_Montgomery.m</td>
<td>geostrophic streamfunction in a specific volume anomaly surface, see Eqn. (3.28.1)</td>
</tr>
</tbody>
</table>
Appendix O:
Checking the Gibbs function of seawater
against the original thermodynamic data

One of the tasks undertaken by SCOR/IAPSO Working Group 127 was to verify the
accuracy of the Feistel (2003) and Feistel (2008) Gibbs functions against the underlying
laboratory data to which these Gibbs functions were fitted. This checking was performed
by Giles M. Marion, and is reported here.

Verification of the Feistel (2003) Gibbs function

Table 9 of Feistel (2003) included a root mean square (r.m.s.) estimate of the fit of the
Gibbs function to the original experimental data. In Table O.1 here, this estimate is the
column labeled “Resulting r.m.s.”. All the data in Table O.1 are from Feistel (2003) except
for the last column, where Giles M. Marion has estimated an independent “Verifying
r.m.s.”.

The seawater properties that were used to develop the Feistel (2003) Gibbs function
(see Column 1 of Table O.1) included density $\rho$, isobaric specific heat capacity $c_p$,
thermal expansion coefficient $\alpha'$, sound speed $c$, specific volume $\nu$, freezing
temperature $t_f$, mixing heat $\Delta h$. This dataset included 1834 observations. Column 2 of
Table O.1 are the data sources that are listed in the references. The r.m.s. values were
calculated with the equation:

$$r.m.s = \left[ \frac{1}{n} \sum_n (F03 - \text{expt.datum})^2 \right]^{0.5}$$  \hspace{1cm} (O.1)

where F03 refers to output of the FORTRAN code that implements Feistel’s (2003) Gibbs
function. In many cases, the experimental data had to be adjusted to bring this data into
conformity with recent definitions of temperature and the thermal properties of pure
water (see Feistel (2003) for the specifics of the datasets used and the internal
assumptions involved in developing the Gibbs function).

Comparisons of the “Resulting” (Feistel) and “Verifying” (Marion) columns in Table
O.1 show that they are in excellent agreement. The small differences between the two
r.m.s. columns are likely due to (1) the number of digits used in the calculations, (2) small
variations in the exact equations used for the calculations, or (3) small errors in model
inputs. In any case, these small differences are insignificant.

There were two typographical errors in the original Table 9 of Feistel (2003) in the
“Resulting r.m.s.” column. The original value for the PG93 dataset was listed as 11.3
ppm, which is slightly different from the verifying value of 11.9 ppm. A subsequent
check indicated that this value should have been listed as 12.0 ppm, which is in excellent
agreement with the value of 11.9 ppm. Similarly, the original “Resulting r.m.s.” value for
the BDSW70 dataset was listed as 0.54 J/(kg K), which is significantly at variance from the
verifying estimate of 1.43 J/(kg K). A subsequent check indicated that this value should
have been listed as 1.45 J/(kg K), which is in excellent agreement with the independent
estimate of 1.43 J/(Kg K).

There were three minor errors between the original literature data and the Feistel
(2003) compilation of this data. In the BS70 dataset, two $S_p$ columns were mislabeled as
30.504 and 30.502, where the correct order should have been 30.502 and 30.504. In the CM76 dataset, the correct value at $S_p = 20.062$, $\rho = 25$ °C, and $p = 588.0$ bars should have been 0.964393 kg m$^{-3}$, not 0.964383 kg m$^{-3}$. These minor errors are insignificant. The independent comparisons in Table O.1 verify the accuracy of the Feistel (2003) Gibbs function.

**Verification of the Feistel (2008) saline part of the Gibbs function of seawater**

The saline Gibbs function Feistel (2008) was designed to increase the temperature range up to 80 °C and the salinity range up to 120 g kg$^{-1}$ (Feistel, 2008). Table 7 of Feistel (2008) included a root mean square (r.m.s.) estimate of the model fit to the original experimental data (see the column “Resulting r.m.s.” in the attached Table O.2). All the data in this table are from the Feistel (2008) paper except for the last column, where Giles M. Marion has estimated an independent “Verifying r.m.s.”

The new seawater salinity databases that were used to develop the Feistel (2008) Gibbs function (see Column 1 of Table O.2) included isobaric specific heat capacity $c_p$, mixing heat $\Delta h$, freezing point depression $t_f$, water vapour pressure $p^\text{vap}$, and the Debye-Hückel limiting law $g^{ll}$. This salinity dataset included 602 observations. Column 2 of Table O.2 are the data sources that are listed in the references. In many cases, the experimental data had to be adjusted to bring this data into conformity with recent definitions of temperature and the thermal properties of pure water (see Feistel (2008) for the specifics on the datasets used and the internal assumptions involved in model development).

Comparisons of the “Resulting” (Feistel) and “Verifying” (Marion) “r.m.s.” columns show that they are in excellent agreement. The most likely explanation for the few small differences is the number of digits used in the calculations. In general, the greater the number of digits used in these calculations, the more accurate the calculations.

This independent check reveals that there are no significant differences between the Feistel and Marion estimations of r.m.s. values for these comparisons (Table O.2), which verifies the accuracy of the Feistel (2008).

**Verification of the Pure Water part of the Feistel (2003) Gibbs function**

The pure water part of the Feistel (2003) Gibbs function was itself a fit to the IAPWS-95 Helmholtz function of pure water substance. The accuracy of this fit to IAPWS-95 in the oceanographic ranges of temperature and pressure has been checked independently by two members of the SCOR/IAPSO Working Group 127 (Dan G. Wright and David R. Jackett). The accuracy of this pure water part of the Feistel (2003) Gibbs function has also been checked by an evaluation committee of IAPWS in the process of approving the Feistel (2003) Gibbs function as an IAPWS Release (IAPWS-09). In IAPWS-09 it is shown that the pure water part of the Feistel (2003) Gibbs function fits the IAPWS-95 properties more precisely than the uncertainty of the data that underlies IAPWS-95. Hence we can be totally comfortable with the use of the Feistel (2003) Gibbs function to represent the properties of pure liquid water in the oceanographic ranges of temperature and pressure.
### Table O.1. Summary of data used in the regression to determine the coefficients of the Feistel (2003) Gibbs potential.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Source</th>
<th>$S_{\text{a}}$ [g kg$^{-1}$]</th>
<th>$t$ /°C</th>
<th>$P$ /MPa</th>
<th># Points</th>
<th>Required r.m.s.</th>
<th>Resulting r.m.s.</th>
<th>Verifying r.m.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>MGW76c</td>
<td>0.5-40</td>
<td>0-40</td>
<td>0</td>
<td>122</td>
<td>4 ppm</td>
<td>4.1 ppm</td>
<td>4.2 ppm</td>
</tr>
<tr>
<td>$\rho$</td>
<td>PBB80</td>
<td>5-42</td>
<td>0-30</td>
<td>0</td>
<td>345</td>
<td>4 ppm</td>
<td>4.0 ppm</td>
<td>4.2 ppm</td>
</tr>
<tr>
<td>$\rho$</td>
<td>PG93</td>
<td>34-50</td>
<td>15-30</td>
<td>0</td>
<td>81</td>
<td>10 ppm</td>
<td>12.0 ppm</td>
<td>11.9 ppm</td>
</tr>
<tr>
<td>$c_p$</td>
<td>BDSW70</td>
<td>10-50</td>
<td>0-40</td>
<td>0</td>
<td>25</td>
<td>2 J/(kg K)</td>
<td>1.45 J/(kg K)</td>
<td>1.43 J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>MPD73</td>
<td>1-40</td>
<td>5-35</td>
<td>0</td>
<td>48</td>
<td>0.5 J/(kg K)</td>
<td>0.52 J/(kg K)</td>
<td>0.45 J/(kg K)</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>C78</td>
<td>10-30</td>
<td>-6-1</td>
<td>0.7-33</td>
<td>31</td>
<td>0.6x10$^{-6}$ K$^{-1}$</td>
<td>0.73x10$^{-6}$ K$^{-1}$</td>
<td>0.74x10$^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>$c$</td>
<td>D74(I-III)</td>
<td>29-43</td>
<td>0-35</td>
<td>0-2</td>
<td>92</td>
<td>5 cm/s</td>
<td>1.7 cm/s</td>
<td>1.6 cm/s</td>
</tr>
<tr>
<td>$c$</td>
<td>D74(IVa-d)</td>
<td>29-43</td>
<td>0-30</td>
<td>0.1-5</td>
<td>32</td>
<td>5 cm/s</td>
<td>1.2 cm/s</td>
<td>1.2 cm/s</td>
</tr>
<tr>
<td>$c$</td>
<td>D74(V-VI)</td>
<td>33-37</td>
<td>0-5</td>
<td>0-100</td>
<td>128</td>
<td>5 cm/s</td>
<td>3.5 cm/s</td>
<td>3.5 cm/s</td>
</tr>
<tr>
<td>$v_x$</td>
<td>CM76</td>
<td>5-40</td>
<td>0-40</td>
<td>0-100</td>
<td>558</td>
<td>10 ppm</td>
<td>11.0 ppm</td>
<td>11.2 ppm</td>
</tr>
<tr>
<td>$v_x$</td>
<td>BS70</td>
<td>30-40</td>
<td>-2-30</td>
<td>1-100</td>
<td>221</td>
<td>4 ppm</td>
<td>2.6 ppm</td>
<td>2.6 ppm</td>
</tr>
<tr>
<td>$t_f$</td>
<td>DK74</td>
<td>4-40</td>
<td>-2-0</td>
<td>0</td>
<td>32</td>
<td>2 J/kg</td>
<td>1.8 J/kg</td>
<td>1.9 J/kg</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>B68</td>
<td>0-33</td>
<td>25</td>
<td>0</td>
<td>24</td>
<td>4 J</td>
<td>2.4 J</td>
<td>2.4 J</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>MHH73</td>
<td>1-41</td>
<td>0-30</td>
<td>0</td>
<td>95</td>
<td>0.4 J/kg</td>
<td>0.5 J/kg</td>
<td>0.5 J/kg</td>
</tr>
</tbody>
</table>

i) The original value in Table 9 of Feistel (2003) of 11.3 ppm refers to the specific volume.

ii) The original value in Table 9 of Feistel (2003) was 0.54 J/(kg K), which apparently was a typographical error.

### Table O.2. Summary of extra datasets used in the regression to determine the coefficients of the Feistel (2008) Gibbs potential.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Source</th>
<th>$S_{\text{a}}$ [g kg$^{-1}$]</th>
<th>$t$ /°C</th>
<th>$P$ /MPa</th>
<th>Points</th>
<th>Resulting r.m.s.</th>
<th>Verifying r.m.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p$</td>
<td>BDCW67</td>
<td>11-117</td>
<td>2-80</td>
<td>0</td>
<td>221</td>
<td>3.46 J/(kg K)</td>
<td>3.46 J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>MPD73</td>
<td>1-40</td>
<td>5-35</td>
<td>0</td>
<td>48</td>
<td>0.57 J/(kg K)</td>
<td>0.57 J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>MP05</td>
<td>1-35</td>
<td>10-40</td>
<td>0</td>
<td>41</td>
<td>1.30 J/(kg K)</td>
<td>1.30 J/(kg K)</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>B68</td>
<td>0-97</td>
<td>25</td>
<td>0</td>
<td>33</td>
<td>0.75 J/kg</td>
<td>0.75 J/kg</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>C70</td>
<td>35-36</td>
<td>2-25</td>
<td>0</td>
<td>19</td>
<td>7.2 J/kg</td>
<td>7.1 J/kg</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>MHH73</td>
<td>1-35</td>
<td>0-30</td>
<td>0</td>
<td>120</td>
<td>3.3 J/kg</td>
<td>3.3 J/kg</td>
</tr>
<tr>
<td>$t_f$</td>
<td>DK74</td>
<td>4-40</td>
<td>-0.2(-2.2)</td>
<td>0</td>
<td>32</td>
<td>1.6 mK</td>
<td>1.6 mK</td>
</tr>
<tr>
<td>$t_f$</td>
<td>FM07</td>
<td>5-109</td>
<td>-0.3(-6.9)</td>
<td>0</td>
<td>22</td>
<td>1.2 mK</td>
<td>1.0 mK</td>
</tr>
<tr>
<td>$p_{\text{vap}}$</td>
<td>R54</td>
<td>18-40</td>
<td>25</td>
<td>0</td>
<td>13</td>
<td>2.8 J/kg</td>
<td>2.8 J/kg</td>
</tr>
<tr>
<td>$l_{\text{boi}}$</td>
<td>BSRSR74</td>
<td>6-70</td>
<td>60-80</td>
<td>0</td>
<td>32</td>
<td>9.1 J/kg</td>
<td>9.3 J/kg</td>
</tr>
<tr>
<td>$g_{\text{1L}}$</td>
<td>F08</td>
<td>35</td>
<td>-5-95</td>
<td>0</td>
<td>21</td>
<td>0.091 J/kg</td>
<td>0.092 J/kg</td>
</tr>
</tbody>
</table>
Appendix P: Thermodynamic properties
based on \( g(S_A,t,p), \hat{h}(S_A,\eta,p), \hat{h}(S_A,\theta,p) \) and \( \hat{h}(S_A,\Theta,p) \)

The thermodynamic potential on which TEOS-10 is based is the Gibbs function of seawater. Being a Gibbs function, \( g(S_A,t,p) \) is naturally a function of Absolute Salinity, in situ temperature and pressure. There are other choices for a thermodynamic potential. One such choice is enthalpy \( h \) as a function of Absolute Salinity, entropy and pressure, and we give this functional form for enthalpy a boomerang over the \( h \) so that \( h = \hat{h}(S_A,\eta,p) \). It proves theoretically convenient to consider the additional functional forms \( h = \hat{h}(S_A,\theta,p) \) and \( h = \hat{h}(S_A,\Theta,p) \) for enthalpy. These two functional forms do not constitute a complete thermodynamic description of seawater but when supplemented by the expressions \( \eta = \bar{\eta}(S_A,\theta) \) and \( \eta = \bar{\eta}(S_A,\Theta) \) for entropy, they do form complete thermodynamic potentials. In the expressions \( h = \hat{h}(S_A,\theta,p) \) and \( \eta = \bar{\eta}(S_A,\theta) \) it is possible to choose any fixed reference pressure \( p_t \) for the definition of potential temperature, \( \theta \). However there is no advantage to choosing the reference pressure to be different from \( p_t = 0 \) and it is this value that is taken in Table P.1 and throughout this appendix. Table P.1 lists expressions for some common thermodynamic quantities in terms of these potential functions (the results in this table for \( \hat{h}(S_A,\eta,p) \) mostly come from Feistel (2008) and Feistel et al. (2010b)). Note that the reference pressure \( p_t \) that appears in the last three columns of the \( \rho^o \) row of Table P.1 is the reference pressure of potential density, not of \( \theta \), whereas in the Gibbs function column, this general reference pressure must also be used to evaluate \( \theta \).

In addition to Table P.1 we have the following expressions for the thermobaric and cabling coefficients (of Eqns. (3.8.1) – (3.9.2))

\[
T^o_b = \frac{\hat{h}_{psa}}{h_p} - \frac{\hat{h}_{p}}{h_p} \frac{\hat{h}_{psa}}{h_p} = \frac{\ddot{v}_p}{\ddot{v}} - \frac{\ddot{v}_p}{\ddot{v}_{s_A}} = - \frac{\ddot{\rho}_p}{\ddot{\rho}} + \frac{\ddot{\rho}_p}{\ddot{\rho}_{s_A}} \frac{\ddot{\rho}_{psa}}{\ddot{\rho}}, \tag{P.1}
\]

\[
T^\theta_b = \frac{\hat{h}_{psa}}{h_p} - \frac{\hat{h}_{p}}{h_p} \frac{\hat{h}_{psa}}{h_p} = \frac{\ddot{v}_p}{\ddot{v}} - \frac{\ddot{v}_p}{\ddot{v}_{s_A}} = - \frac{\ddot{\rho}_p}{\ddot{\rho}} + \frac{\ddot{\rho}_p}{\ddot{\rho}_{s_A}} \frac{\ddot{\rho}_{psa}}{\ddot{\rho}}, \tag{P.2}
\]

\[
C^o_b = \frac{\hat{h}_{p0}}{h_p} - 2 \frac{\hat{h}_{p0}}{h_p} \frac{\hat{h}_{psa}}{h_p} + \left( \frac{\hat{h}_{pa}}{h_p} \right)^2 \frac{\hat{h}_{psa}}{h_p} = \frac{\ddot{v}_{p0}}{\ddot{v}} - 2 \frac{\ddot{v}_p}{\ddot{v}_{s_A}} + \left( \frac{\ddot{v}_p}{\ddot{v}_{s_A}} \right)^2 \frac{\ddot{v}_{s_A s_A}}{\ddot{v}} \tag{P.3}
\]

\[
C^\theta_b = \frac{\hat{h}_{p0}}{h_p} - 2 \frac{\hat{h}_{p0}}{h_p} \frac{\hat{h}_{psa}}{h_p} + \left( \frac{\hat{h}_{pa}}{h_p} \right)^2 \frac{\hat{h}_{psa}}{h_p} = \frac{\ddot{v}_{p0}}{\ddot{v}} - 2 \frac{\ddot{v}_p}{\ddot{v}_{s_A}} + \left( \frac{\ddot{v}_p}{\ddot{v}_{s_A}} \right)^2 \frac{\ddot{v}_{s_A s_A}}{\ddot{v}} \tag{P.4}
\]

Here follows some interesting expressions that can be gleaned from Table P.1.
\[ c_p(0) = \tilde{h}_0(0) = c_p^0 \theta = \frac{-\theta^2}{\eta\phi(0)}, \quad (T_0 + \theta) = \frac{c_p^0}{\bar{\eta} \phi}, \quad (T_0 + t) = \frac{\tilde{h}_0}{c_p^0} = \frac{\partial h}{\partial h_{\lambda, \rho}}. \]  

(P.5)

\[ \frac{\partial \theta}{\partial \Theta}_{\lambda, \rho} = \frac{\partial \Theta}{\partial \Theta}_{\lambda, \rho} = \frac{1}{\Theta_{\theta}} - \frac{\partial \theta}{\partial \Theta_{\lambda, \rho}} = - \frac{\left( T_0 + \theta \right)^2}{\eta^2} = \frac{c_p^0}{\bar{\eta} \phi} = \frac{c_p^0}{\partial \Theta_{\lambda, \rho}}. \]  

(P.6)

\[ \mu(0) = - \frac{c_p^0 \tilde{\eta}_{\lambda, \rho}}{\eta_{\phi}} = -(T_0 + \theta) \tilde{\eta}_{\lambda, \rho}, \]  

(P.7)

\[ \frac{\partial \theta}{\partial \Theta_{\lambda, \rho}} = \frac{\partial \Theta_{\lambda, \rho}}{\partial \Theta_{\lambda, \rho}} = \frac{-\tilde{\eta}_{\lambda, \rho}}{\Theta_{\theta}} = - \frac{c_p^0 \tilde{\eta}_{\lambda, \rho}}{\eta_{\phi}} = \frac{c_p^0 \partial \Theta_{\lambda, \rho}}{\partial \Theta_{\lambda, \rho}} = - \frac{\left( T_0 + \theta \right)^2 \tilde{\eta}_{\lambda, \rho}}{c_p^0}. \]  

(P.8)

See also Eqn. (A.12.6) for an alternative expression for \( \tilde{\theta}_{\lambda, \rho} \). Equation (P.8) can also be written as

\[ \frac{\partial (T_0 + \theta)^{-1}}{\partial \Theta_{\lambda, \rho}} = \frac{\tilde{\eta}_{\lambda, \rho}}{c_p^0}. \]  

(P.9)

Now we consider how all the terms in the last column of Table P.1 may be evaluated in terms of the expression \( \tilde{h}^{25}(S_{\lambda}, \Theta, \rho) \) of Eqn. (A.30.6); this being the expression for specific enthalpy that follows from the 25-term expression for density as a function of \((S_{\lambda}, \Theta, \rho)\) as described in Eqn. (K.1) and Table K.1. The superscript “25” is added to \( \tilde{h}^{25}(S_{\lambda}, \Theta, \rho) \) to emphasize that this is an approximate expression for specific enthalpy. The first step is to evaluate \( \theta \) exactly from the following implicit expression for \( \Theta \) in terms of the Gibbs function at \( p = 0 \) (see Eqn. (2.12.1)), as discussed in section 3.3,

\[ c_p^0 \Theta = h(S_{\lambda}, t = \theta, 0) = g(S_{\lambda}, t = \theta, 0) - (T_0 + \theta) g_T(S_{\lambda}, t = \theta, 0). \]  

(P.10)

Next, we recall that we know the functional forms of \( \tilde{\eta}(S_{\lambda}, \theta), \tilde{\Theta}(S_{\lambda}, \theta) \) and \( \tilde{\mu}(S_{\lambda}, \theta, 0) \) in terms of the coefficients of the Gibbs function of seawater as the exact polynomial and logarithm terms given by (from Eqns. (2.10.1) and (2.9.6))

\[ \tilde{\eta}(S_{\lambda}, \theta) = -g_T(S_{\lambda}, t = \theta, 0), \quad \tilde{\mu}(S_{\lambda}, \theta, 0) = g_S(S_{\lambda}, t = \theta, 0), \]  

(P.11a, b)

and Eqn. (P.10) is repeated here emphasizing the functional form of the left-hand side,

\[ c_p^0 \tilde{\Theta}(S_{\lambda}, \theta) = g(S_{\lambda}, t = \theta, 0) - (T_0 + \theta) g_T(S_{\lambda}, t = \theta, 0). \]  

(P.12)

The partial derivatives with respect to \( \Theta \) and with respect to \( \theta \), both at constant \( S_{\lambda} \) and \( p \), and the partial derivatives with respect to \( S_{\lambda} \), are related by

\[ \frac{\partial}{\partial \Theta_{\lambda, \rho}} = \frac{1}{\Theta_{\theta}} - \frac{\partial \Theta_{\lambda, \rho}}{\partial \Theta_{\lambda, \rho}} = \frac{\partial}{\partial S_{\lambda}} - \frac{\partial \Theta_{\lambda, \rho}}{\partial \Theta_{\lambda, \rho}}. \]  

(P.13a, b)

Use of these expressions, acting on entropy yields (with \( p = 0 \) everywhere, and using Eqn. (P.7) [or Eqn. (A.12.8b)] and Eqn. (P.8))

\[ \tilde{\eta}_\theta = \frac{\tilde{\eta}}{\Theta_{\theta}} = \frac{c_p^0}{(T_0 + \theta)}, \quad \tilde{\eta}_{\phi} = \frac{1}{\Theta_{\theta}} - \frac{c_p^0}{(T_0 + \theta)^2}, \quad \tilde{\eta}_S = \frac{-\tilde{\mu}(S_{\lambda}, \theta, 0)}{(T_0 + \theta)}, \]  

(P.14a, b, c)

\[ \tilde{\eta}_{S, \theta} = \frac{\tilde{\Theta}_{S_{\lambda}, \theta}}{(T_0 + \theta)^2}, \quad \tilde{\eta}_{S, \phi} = \frac{-\tilde{\mu}(S_{\lambda}, \theta, 0)}{(T_0 + \theta)^2} - \frac{(\tilde{\Theta}_{S_{\lambda}})^2}{\Theta_{\theta}} \frac{c_p^0}{(T_0 + \theta)}, \]  

(P.15a, b)

in terms of the partial derivatives of the exact polynomial expressions (P.11b) and (P.12).

All of the thermodynamic variables of the last column of Table P.1 can now be evaluated using the partial derivatives of \( \tilde{h}^{25}(S_{\lambda}, \Theta, \rho) \) and the exact expressions (P.14) and (P.15) which are written in terms of potential temperature \( \theta \) which is found from the exact implicit equation (P.10). This completes the discussion of how \( \tilde{h}^{25}(S_{\lambda}, \Theta, \rho) \) can be used as an alternative thermodynamic potential of seawater. The partial derivatives of entropy in Eqns. (P.14) and (P.15) are available in the GSW computer software library from functions gsw_e1a_first_derivatives and gsw_e1a_2nd_derivatives.
Table P.1. Expressions for various thermodynamic variables based on four different thermodynamic potentials

<table>
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<tr>
<th></th>
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<th>Expressions based on ( h(S_A,\eta,p) )</th>
<th>Expressions based on ( \tilde{h}(S_A,\theta,p) ) and ( \tilde{\eta}(S_A,\theta) )</th>
<th>Expressions based on ( \tilde{h}(S_A,\Theta,p) ) and ( \tilde{\eta}(S_A,\Theta) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( t )</td>
<td>( t )</td>
<td>( (T_0 + t) = \tilde{h}_\eta )</td>
<td>( (T_0 + t) = \tilde{h}<em>\theta / \eta</em>\theta )</td>
<td>( (T_0 + t) = \tilde{h}<em>\Theta / \eta</em>\Theta )</td>
</tr>
<tr>
<td>( \theta )</td>
<td>( g_T(S_A,\theta,p_t) = g_T(S_A,t,p) )</td>
<td>( (T_0 + \theta) = \tilde{h}_\eta (0) )</td>
<td>( \theta; \ (T_0 + \theta) = \tilde{h}<em>\theta (0) / \eta</em>\theta )</td>
<td>( (T_0 + \theta) = \epsilon_p^0 / \eta_\Theta )</td>
</tr>
<tr>
<td>( \Theta )</td>
<td>( \Theta = \frac{g(S_A,\theta,0) - (T_0 + \theta)g_T(S_A,\theta,0)}{c_p^0} )</td>
<td>( \Theta = \tilde{h}(0) / c_p^0 )</td>
<td>( \Theta; \ \Theta = \tilde{h}(0) / c_p^0 )</td>
<td>( \Theta; \ \Theta = \tilde{h}(0) / c_p^0 )</td>
</tr>
<tr>
<td>( g )</td>
<td>( g = g(S_A,t,p) )</td>
<td>( g = \tilde{h} - \eta \tilde{h}_\eta )</td>
<td>( g = \tilde{h} - \eta \tilde{h}<em>\theta / \eta</em>\theta )</td>
<td>( g = \tilde{h} - \eta \tilde{h}<em>\Theta / \eta</em>\Theta )</td>
</tr>
<tr>
<td>( \eta )</td>
<td>( \eta = -g_T )</td>
<td>( \eta )</td>
<td>( \eta = \tilde{\eta}(S_A,\Theta) )</td>
<td>( \eta = \tilde{\eta}(S_A,\Theta) )</td>
</tr>
<tr>
<td>( h )</td>
<td>( h = g - (T_0 + t)g_T )</td>
<td>( h = \tilde{h}(S_A,\eta,p) )</td>
<td>( h = \tilde{h}(S_A,\theta,p) )</td>
<td>( h = \tilde{h}(S_A,\Theta,p) )</td>
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<tr>
<td>( v )</td>
<td>( v = g_p )</td>
<td>( v = \tilde{h}_p )</td>
<td>( v = \tilde{h}_p )</td>
<td>( v = \tilde{h}_p )</td>
</tr>
<tr>
<td>( \rho )</td>
<td>( \rho = (g_p)^{-1} )</td>
<td>( \rho = (\tilde{h}_p)^{-1} )</td>
<td>( \rho = (\tilde{h}_p)^{-1} )</td>
<td>( \rho = (\tilde{h}_p)^{-1} )</td>
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<tr>
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<td>( \mu = \tilde{h}<em>{S_A} - \eta</em>\Theta \tilde{h}<em>\Theta / \eta</em>\Theta )</td>
<td>( \mu = \tilde{h}<em>{S_A} - \eta</em>\Theta \tilde{h}<em>\Theta / \eta</em>\Theta )</td>
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<td>( u )</td>
<td>( u = g - (T_0 + t)g_T - (p + P_0)g_p )</td>
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<td>( u = \tilde{h} - (p + P_0)\tilde{h}_p )</td>
<td>( u = \tilde{h} - (p + P_0)\tilde{h}_p )</td>
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<td>( f = \tilde{h} - \eta \tilde{h}_\Theta -(p + P_0)\tilde{h}_p )</td>
<td>( f = \tilde{h} - \eta \tilde{h}_\Theta -(p + P_0)\tilde{h}_p )</td>
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<td>( c_p = -(T_0 + t)g_{T_T} )</td>
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<td>( c_p = \tilde{h}_p / \eta_p )</td>
<td>( c_p = \tilde{h}_p / \eta_p )</td>
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<td>( \tilde{h}_0 = \tilde{h}(0) )</td>
<td>( \tilde{h}_0 = \tilde{h}(0) )</td>
<td>( \tilde{h}_0 = \tilde{h}(0) )</td>
</tr>
<tr>
<td>( \rho^\theta )</td>
<td>( \rho^\theta = [g_p(S_A,\theta,p_t)]^{-1} )</td>
<td>( \rho^\theta = [\tilde{h}_p (p_t)]^{-1} )</td>
<td>( \rho^\theta = [\tilde{h}_p (p_t)]^{-1} )</td>
<td>( \rho^\theta = [\tilde{h}_p (p_t)]^{-1} )</td>
</tr>
<tr>
<td>( \kappa^\rho )</td>
<td>( \kappa^\rho = -g_p^{-1}g_{pp} )</td>
<td>( \kappa^\rho = -\tilde{h}<em>p^{-1}\tilde{h}</em>{pp} )</td>
<td>( \kappa^\rho = -\tilde{h}<em>p^{-1}\tilde{h}</em>{pp} )</td>
<td>( \kappa^\rho = -\tilde{h}<em>p^{-1}\tilde{h}</em>{pp} )</td>
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<tr>
<td>( \kappa )</td>
<td>( \kappa = -g_p^{-1}g_{pp} + g_p^{-1}g_{TT}^2 )</td>
<td>( \kappa = -\tilde{h}<em>p^{-1}\tilde{h}</em>{pp} )</td>
<td>( \kappa = -\tilde{h}<em>p^{-1}\tilde{h}</em>{pp} )</td>
<td>( \kappa = -\tilde{h}<em>p^{-1}\tilde{h}</em>{pp} )</td>
</tr>
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<td></td>
<td>Expressions based on $g(S_A,T,p)$</td>
<td>Expressions based on $h(S_A,T,p)$</td>
<td>Expressions based on $\hat{h}(S_A,\theta,p)$ and $\hat{\eta}(S_A,\theta)$</td>
<td>Expressions based on $\hat{h}(S_A,\Theta,p)$ and $\hat{\eta}(S_A,\Theta)$</td>
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<td>$c$</td>
<td>$c = \frac{g_p}{g_{TT}/\left(g_{TP}^2 - g_{TT}g_{PP}\right)}$</td>
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<td>$c = \mu_p/\sqrt{-\theta_p}$</td>
<td>$c = \mu_p/\sqrt{-\theta_p}$</td>
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<tr>
<td>$\Gamma$</td>
<td>$\Gamma = -\frac{g_{TP}}{g_{TT}}$</td>
<td>$\Gamma = \mu_{pq}$</td>
<td>$\Gamma = \mu_{pq}/\mu_{p\theta}$</td>
<td>$\Gamma = \mu_{pq}/\mu_{p\theta}$</td>
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<tr>
<td>$\alpha'$</td>
<td>$\alpha' = \frac{g_{TP}}{g_p}$</td>
<td>$\alpha' = \frac{\mu_p}{h_{pq}}$</td>
<td>$\alpha' = -\frac{\mu_p}{h_{pq}}\frac{\hat{\eta}_{pq}^2}{\hat{\theta}<em>p\hat{\eta}</em>{pq} - \hat{\theta}_p\hat{\eta}_0}$</td>
<td>$\alpha' = -\frac{\mu_p}{h_{pq}}\frac{\hat{\eta}_{pq}^2}{\hat{\theta}<em>p\hat{\eta}</em>{pq} - \hat{\theta}_p\hat{\eta}_0}$</td>
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<td>$\alpha^0$</td>
<td>$\alpha^0 = \frac{g_{TP}}{g_p} \frac{g_{TT}(S_A,\theta,p)}{g_{TT}}$</td>
<td>$\alpha^0 = \frac{\mu_p}{h_{pq}} \frac{\hat{\eta}_{pq}^2}{\hat{\theta}<em>p\hat{\eta}</em>{pq} - \hat{\theta}_p\hat{\eta}_0}$</td>
<td>$\alpha^0 = \frac{\mu_p}{h_{pq}} \frac{\hat{\eta}_{pq}^2}{\hat{\theta}<em>p\hat{\eta}</em>{pq} - \hat{\theta}_p\hat{\eta}_0}$</td>
<td>$\alpha^0 = \frac{\mu_p}{h_{pq}} \frac{\hat{\eta}_{pq}^2}{\hat{\theta}<em>p\hat{\eta}</em>{pq} - \hat{\theta}_p\hat{\eta}_0}$</td>
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<tr>
<td>$\alpha^\alpha$</td>
<td>$\alpha^\alpha = \frac{\mu_p}{(T_0 + \theta)g_{TT}}$</td>
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<td>$\alpha^\alpha = \frac{\mu_p}{h_{pq}} \frac{\hat{\eta}_{pq}^2}{\hat{\theta}<em>p\hat{\eta}</em>{pq} - \hat{\theta}_p\hat{\eta}_0}$</td>
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<tr>
<td>$\beta'$</td>
<td>$\beta' = -\frac{g_p}{g_{PSA}}$</td>
<td>$\beta' = -\frac{\mu_p}{h_{PSA}}$</td>
<td>$\beta' = -\frac{\mu_p}{h_{PSA}}$</td>
<td>$\beta' = -\frac{\mu_p}{h_{PSA}}$</td>
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<td>$\beta^\alpha$</td>
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<td>$\beta^\alpha = -\frac{\mu_p}{h_{PSA}} \frac{\mu_{\tau p}}{h_{pq} \hat{\eta}_{pq}^2}$</td>
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Changes made to this TEOS-10 manual, since the 13th April 2010 version which was printed by IOC.

17th April 2010  Page 102, line 6, an error in the inequality fixed, and changed to be in terms of $\hat{h}$.

4th July 2010  Page 39, Eqn. (3.20.4). An error fixed in this equation; an extra factor of $R_\rho$.

20th Aug 2010  Throughout the document, changed $h_p$ to $h_P$ and so help to clarify when pressure must be expressed in Pa rather than dbar.

3rd Sept 2010  Extensive changes to page 122 (the description of enthalpy obtained from the 25-term expression for density), page 174 (the list of GSW Toolbox function names) and page 179 (the description of how the 25-term expression for density, along with knowledge of the exact Gibbs function at $p = 0$ dbar, can be used as the full thermodynamic potential of seawater).

14th Sept 2010  Corrected a typo on the left-hand side of Eqn. (A.11.16); $\bar{h}_{s_A}$ was replaced by $\hat{h}_{s_A}$.

In this TEOS-10 Manual the text is 10.5 pt Palatino linotype at exactly 14 pt vertical spacing. The references are 10 pt Palatino linotype at exactly 13 pt vertical spacing. The text is both right and left justified. Left margin is 3.17cm and the right margin is 3.10cm respectively. The top and bottom margins are both 2.05cm. The header and footer are both 70% grey. The MATHTEXT size settings are 10.5, 7, 6, 16, 9, 75%, 100% and 150% respectively.
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