The International Thermodynamic Equation Of Seawater 2010 (TEOS-10): Calculation and Use of Thermodynamic Properties

19 August 2009

T. J. McDougall[+], R. Feistel[#], F. J. Millero*, D. R. Jackett[+], D. G. Wright[&],
B. A. King[@], G. M. Marion[%], C-T. A. Chen[^], P. Spitzer[$], S. Seitz[$]

[+]Centre for Australian Weather and Climate Research:
 A partnership between CSIRO and the Bureau of Meteorology,
 Castray Esplanade, Hobart, TAS, Australia

[#]Leibniz-Institut fuer Ostseeforschung, Seestrasse 15
 D-18119 Warnemuende, Germany

*Rosenstiel School of Marine and Atmospheric Science
 Division of Marine and Atmospheric Chemistry, University of Miami
 4600 Rickenbacker Causeway, Miami, FL 33149-1098, USA

[&]Ocean Circulation Section, Bedford Institute of Oceanography,
 Dartmouth, NS, Canada B2Y 4A2

[@]National Oceanography Centre, Empress Dock
 Southampton, SO14 3ZH, UK

[%]Division of Earth and Ecosystem Sciences, Desert Research Institute,
 2215 Raggio Parkway, Reno, NV 89512, USA

[^]Institute of Marine Geology and Chemistry, National Sun Yat-Sen University
 Kaohsiung 80424, Taiwan, R.O.C.

[$]Physikalisch-Technische Bundesanstalt (PTB), Postfach 33 45, Bundesallee 100,
 D-38116 Braunschweig, Germany

The logos of SCOR, IAPSO, UNESCO-IOC appearing here

Global Ship-based Repeat Hydrography Manual, IOCCP Report No, 14, ICPO Publication Series No. 134.

Foreword

This document describes how the thermodynamic properties of seawater may be evaluated using the International Thermodynamic Equation Of Seawater – 2010 (TEOS-10 for short). Fundamental to TEOS-10 are the concepts of Absolute Salinity and Reference Salinity. These variables are described in detail, emphasising their relationship to Practical Salinity. The science underpinning TEOS-10 is described in a series of papers published in the refereed literature. The present document acts as a guide to those published papers and concentrates on how the thermodynamic properties obtained from TEOS-10 are used in oceanography.

Index

3. DERIVED QUANTITIES

Index (Continued)

Index (Continued)

Index (Continued)

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 potential 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 an SI variable and it incorporates the small spatial variations of the composition of seawater 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.

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 have become apparent and suggest that it is timely to redefine the thermodynamic properties of seawater.

- 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 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.

- 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 (entropy, enthalpy and internal energy were not available from EOS-80).

- 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 (Weiser (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.

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 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 (i.e., Absolute Salinity) whereas Practical Salinity depends only on conductivity. The properties of most dilute natural waters, including seawater containing added salts, are similar to the values of seawater at the same Absolute Salinity (Millero et al., 1978). 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 are the density, enthalpy etc. Similarly, if a small mass of say NaCl is added and the same mass of silicate is taken out of a seawater sample, Absolute Salinity will not have changed (and so the density, enthalpy etc will be almost unchanged) but the Practical Salinity will have increased. This issue is expanded upon in Appendix A.4 below.

This 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 to replace EOS-80 as the official description of seawater properties in marine science. This new approach to the thermodynamic properties of seawater and of ice Ih is referred to collectively as the "International Thermodynamic Equation Of Seawater – 2010", or "TEOS-10" for short. Appendix C summarizes 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 to 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 (the mass fraction of sea salt in seawater) is generally a derived quantity. That is, we calculate Practical Salinity 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. Calculated Practical Salinity is preferred over the actually measured in-situ conductivity value because of its conservative nature with respect to changes of temperature or pressure, or dilution with pure water. Second, it is imperative that confusion is not created in national data bases where a change in the reporting of salinity may be mishandled at some stage and later be misinterpreted as a real increase in the ocean's salinity. This second point argues strongly for no change in present practice in the reporting of Practical Salinity S_P in national data bases of oceanographic data. Thirdly, the algorithm for determining the "best" estimate of Absolute Salinity of seawater with non-standard composition is 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, (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. Since Reference Salinity covers a wider range of concentration and temperature than PSS-78, values of Reference Salinity obtained from suitable observational techniques (for example by direct measurement of density) should be converted to corresponding numbers of Practical Salinity for storage, as described in sections 2.3 - 2.5.

In order to improve the determination of Absolute Salinity we need to begin collecting and storing values of the salinity anomaly $\delta S_A = S_A - S_R$ based on measured values of density (such as can be measured with a vibrating tube densimeter, Kremling (1971)). The 4-letter GF3 code (IOC (1987)) DENS is currently defined for in-situ measurements or computed values from EOS-80. It seems preferable to store data in national data bases that are close to measured values rather than being computed values from a particular equation. Hence we discourage storing computed densities in such data bases. It is recommended that the salinity anomaly $\delta S_A = S_A - S_R$ be reported with the new GF3 code DELS at the laboratory temperature (TLAB in $°C$) and sea pressure (PLAB, usually 0 dbar). The Practical Salinity S_P should also be reported for these samples. The method for calculating $\delta S_A = S_A - S_R$ from measurements of a seawater sample's laboratory-determined density and Practical Salinity is described in McDougall et al. (2009a).

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. It is recognized 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 such an updated algorithm will appear on the www.TEOS-10.org web site.

We see the more prominent advantages of the new seawater description to be

- 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, the melting heat of ice and the latent heat of vapour. These quantities were not available from the International Equation of State but are central to a proper accounting of heat in the ocean and of the heat that is transferred between the ocean, the ice cover and the atmosphere above. For example a new temperature variable, Conservative Temperature, can be defined as being proportional to potential enthalpy and is a valuable temperature variable in oceanography and climate studies as it is approximately two orders of magnitude more conservative compared with either potential temperature or entropy.

- The thermodynamic quantities available from the new approach are totally consistent with each other.

- The new salinity variable, Absolute Salinity, is measured in standard SI units. Moreover the treatment of freshwater fluxes, and fluxes of mass in ocean models will be consistent with the use of Absolute Salinity, but are only approximately so for Practical Salinity.

- 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 so-called "thermal wind" relation).

- 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_2.

1.4 A guide to this seawater 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 three separate libraries (Libraries A, B and C) as described in Appendices I, J and K. Libraries A and B are in strict basic-SI units, both for their input parameters and for the outputs of the algorithms. Library A 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) than does Library B. Library A uses the

world-wide standard for the thermodynamic definition of pure water substance. Since this is defined over extended ranges of temperature and pressure, the algorithms are long and their evaluation time-consuming. Library B uses the Gibbs function of Feistel (2003) 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 third library, Library C (the so-called "gsw" library) moves beyond Library B in its quest for numerical efficiency. All routines in this library are highly optimized even compared to those in Library B. This computational efficiency is made possible by restricting the routines in this Library to a subset of those in Libraries A and B that are directly related to oceanic processes In addition, the input and output parameters of Library C 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, particularly compared with Library A, and because of the more familiar units compared with Library B. The library name "gsw" (Gibbs Sea Water) has been chosen to be similar to, but different from the existing "sw" (Sea Water) library maintained by CSIRO in Hobart Australia. This "gsw" library, initially mainly in MATLAB and FORTRAN, together with this UNESCO seawater thermodynamics manual is available from the website www.TEOS-10.org.

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

1.5 A remark on units

The most convenient variables and units in which to conduct thermodynamic investigations are Absolute Salinity S_A in units of kg kg^{-1}, Absolute Temperature T (K), and Absolute Pressure P in Pa. These are the parameters and units used in the software Libraries A and B that embody the TEOS-10 seawater thermodynamics. 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 Library C, the so-called "gsw" computer algorithm library, we adopt $°C$ for the temperature unit, pressure is sea pressure in dbar and Absolute Salinity S_A is expressed in units of g kg^{-1} so that it takes numerical values close to those of Practical Salinity. Adopting these non-basic-SI units does not come without a penalty as there are many thermodynamic formulae that are more conveniently manipulated when expressed in SI units. As an example, the freshwater fraction of seawater is written correctly as $(1-S_A)$, but it is clear

that in this instance Absolute Salinity must be expressed in $\mathrm{kg\ kg^{-1}}$ not in $\mathrm{g\ kg^{-1}}$. There are also cases within the "gsw" library in which SI units are required and this may occasionally cause some confusion. 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.

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 0.03mK in the temperature range between -2 °C and 10 °C. Hence we recommend that the oceanographic community continues to use the Saunders formula

$$\left(t_{68}/°C \right) = 1.00024 \left(t_{90}/°C \right). \tag{2.1.1}$$

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 p

Sea pressure p is defined to be the Absolute Pressure P less the Absolute Pressure of one standard atmosphere, $P_0 \equiv 101\,325\,\text{Pa}$; 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^{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 expressed as a function of sea pressure p (functionally equivalent to the use of Absolute Pressure P in the IAPWS Releases). It is not a function of gauge pressure.

2.3 Practical Salinity S_P

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 101 325 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 32.4356×10^{-3}. 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". 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_{68} temperature in which the PSS-78 algorithms were defined. The reader is also directed to the CDIAC chapter on "Method for Salinity Measurement" which describes best practice in measuring the conductivity ratio of seawater samples.

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 Reference-Composition Salinity

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. To within the known accuracy of present day measurements, this is the composition of Standard Seawater, being seawater from the surface waters of a certain region of the North Atlantic. Reference-Composition Salinity S_R (or Reference Salinity for short) is our best estimate of the Absolute Salinity S_A of seawater of Reference Composition and hence also our best estimate of the Absolute Salinity of 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

$$S_R \approx u_{PS}\, S_P \qquad \text{where} \qquad u_{PS} \equiv (35.165\,04/35)\ \text{g kg}^{-1}. \qquad (2.4.1)$$

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 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 $\pm 0.007\ g\,kg^{-1}$. 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.

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 S_A is defined as the mass fraction of dissolved material in seawater. For seawater of Reference Composition, the Reference Salinity gives our current best estimate of Absolute Salinity.

A practical procedure for estimating Absolute Salinity for an arbitrary seawater sample is via measurement of both the density and the Practical Salinity of a seawater sample. The "Reference-Composition density" is calculated from the equation of state with the sample's Reference Salinity as the salinity argument; this calculation essentially assumes that the seawater sample has Reference Composition. The difference between the measured density and the Reference-Composition density can then be used to estimate the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ (Millero et al. (2008a)).

In a series of papers (Millero et al. (1976a, 1978, 2000, 2008b), McDougall et al. (2009)), this procedure has yielded estimates of $\delta S_A = S_A - S_R$ from most of the major basins of the world ocean. They have then used this information along with estimates of seawater composition to estimate the relation between δS_A and composition anomalies. Thus, the Absolute Salinity Anomaly and hence the Absolute Salinity estimate itself can now be estimated

without making direct density measurements provided some knowledge of composition anomalies is available. This method for estimating Absolute Salinity is sketched in Figure 1.

COMPOSITION ANOMALIES

REFERENCE COMPOSITION

Local seawater sample

Estimate composition anomalies

Measure C, then calculate Practical Salinity S_P from PSS-78, $S_P(C, t, p)$

Calculate salinity anomaly, δS_A

Calculate Reference Salinity $S_R = (35.165\,04\text{ g kg}^{-1}/35)\, S_P$

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

Calculate density from $1/g_p(S_A, t, p)$
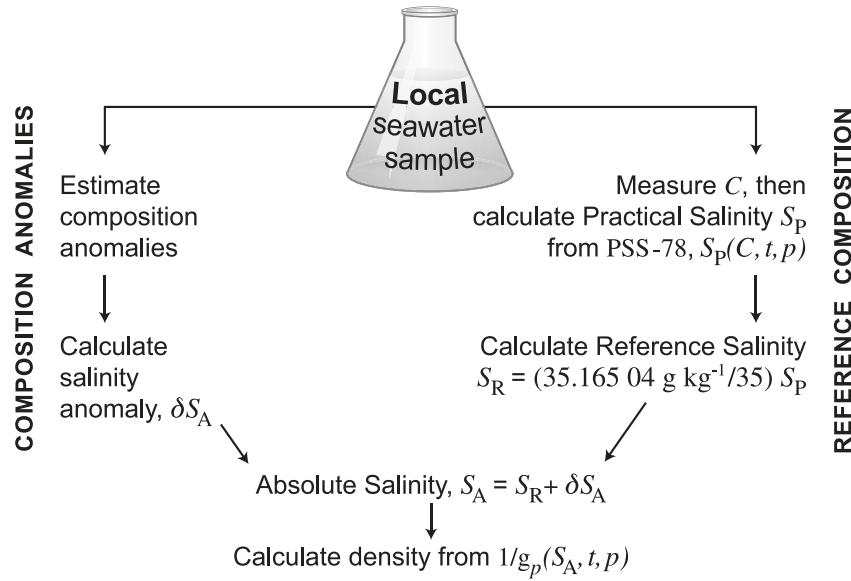
Figure 1. A sketch indicating how thermodynamic quantities such as density are calculated as functions of Absolute Salinity, and how this is found by adding an estimate of the Absolute Salinity Anomaly δS_A to the Reference Salinity.

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 density estimates. When composition anomalies are not known, the algorithm of McDougall et al. (2009a) may be used to estimate Absolute Salinity in terms of Practical Salinity and the spatial location of the measurement in the world oceans. This algorithm is based on the correlation between $S_A - S_R$ and the silicate of seawater samples (Millero et al., 2008), with the silicate estimated by interpolation of results from a global atlas (Gouretski and Koltermann (2004)). The algorithm takes the form

$$S_A \;=\; S_R + \delta S_A \;=\; S_A\left(S_P, \varphi, \lambda, p\right) \qquad\qquad (2.5.1)$$

where λ is latitude (degrees North), φ is longitude (degrees east, ranging from 0°E to 360°E) while p is pressure (sea pressure in dbar). 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. (2009a) algorithm the Baltic Sea is treated separately, following the work of Millero and Kremling (1976) and Feistel et al (2010), because some rivers flowing into the Baltic are unusually high in calcium carbonate.

The difference between Absolute Salinity and Reference Salinity, as estimated by the McDougall et al. (2009a) 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).
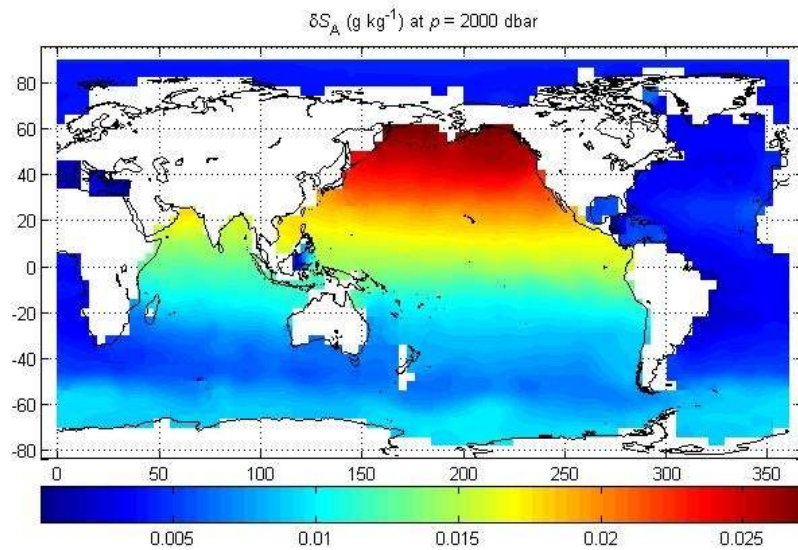
Figure 2 (a). Absolute Salinity Anomaly δS_A at p = 2000 dbar.
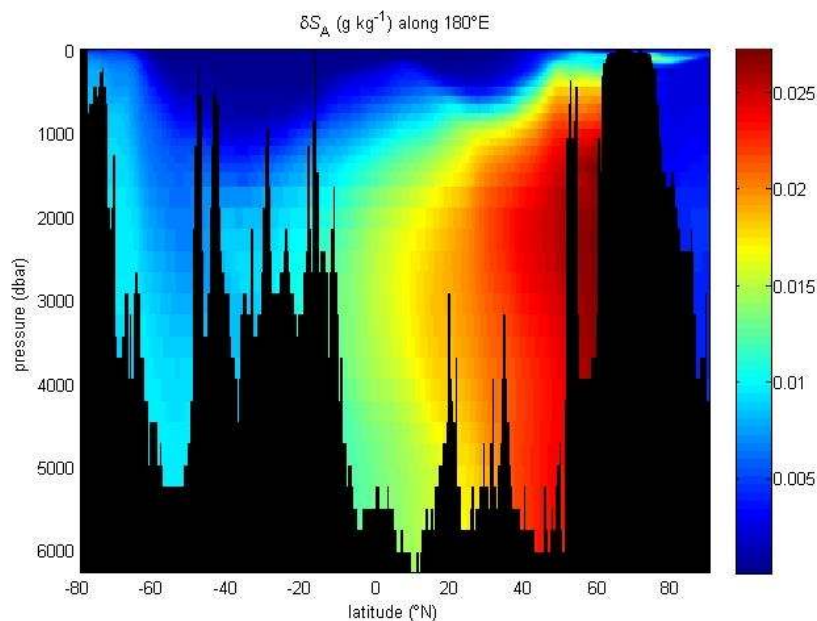
Figure 2 (b). A vertical section of Absolute Salinity Anomaly δS_A
along 180^oE in the Pacific Ocean.

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. (2009a) 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.

The present computer software, in both FORTRAN and MATLAB, which evaluates Absolute Salinity S_A given the input variables Practical Salinity S_P, longitude φ, latitude λ and sea pressure p (in dbar) is available at www.TEOS-10.org. As more density measurements are made from around the world ocean it is hoped that the algorithm for estimating the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ and hence for estimating Absolute Salinity S_A will be improved over the coming years.

2.6 The Gibbs Function of Seawater

The Gibbs function of seawater $g(S_A, t, p)$ is related to the specific enthalpy h and entropy s, by $g = h - (273.15 \text{ K} + t)\, s$ and is defined as the sum of a pure water part and the saline part (IAPWS-08)

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p). \tag{2.6.1}$$

The saline part of the Gibbs function of seawater is valid over the ranges $0 < S_A < 42$ g kg^{-1}, $-6.0\,°C < t < 40\,°C$ and $0 < p < 10^4$ dbar, and in its thermal and colligative properties up to $t = 80\,°C$ and $S_A = 120$ g kg^{-1} at $p = 0$.

The pure-water part of the Gibbs function can be obtained from the IAPWS-95 Helmholtz function of pure-water substance which is valid from the freezing temperature to 1273 K, and from the sublimation line to 1000 MPa or it 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 $40\,°C$ (specifically from $-\left[2.65 + (p + P_0) \times 0.0743 \text{ MPa}^{-1}\right]\,°C$ to 40 °C), and in the pressure range $0 < p < 10^4$ 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 $40\,°C$ and $80\,°C$ 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 Library A, 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 Libraries B and C. Libraries B and C are 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). We emphasize that models of seawater properties that use a single salinity variable, S_A, 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_A as the input variable (see section 2.5) but precipitation may cause large deviations from the nearly fixed ratios associated with standard

seawater. Under such extreme conditions models of seawater based on the Millero et al. (2008a) Reference Composition will no longer be applicable. As an example, Figure 3 illustrates $S_A - T$ boundaries of validity (determined by the onset of precipitation) for 2008 ($pCO_2 = 385$ µatm) and 2100 ($pCO_2 = 550$ µatm) (from Marion et al. (2009)).
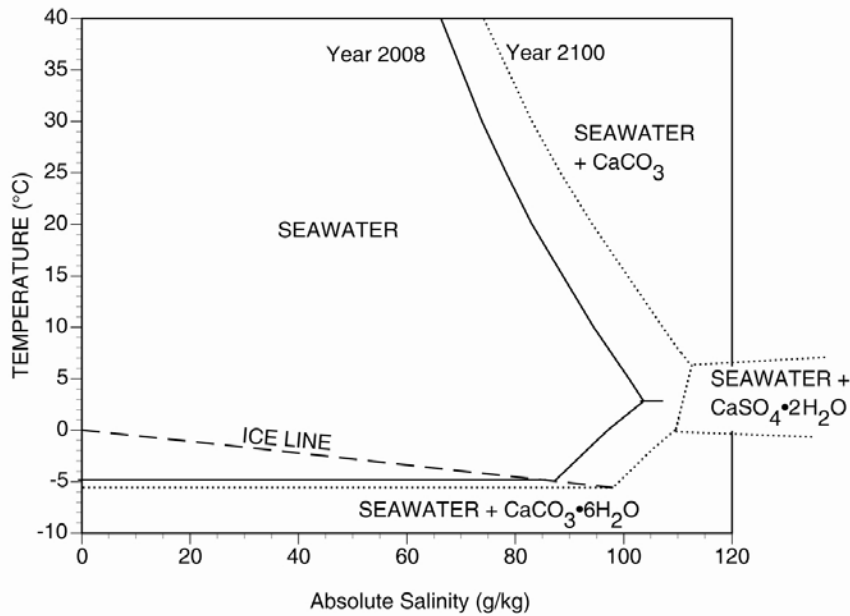
Figure 3. The boundaries of validity of the Millero et al. (2008a) composition at $p = 0$ in Year 2008 (solid lines) and potentially in Year 2100 (dashed lines). At high salinity, calcium sulphate saturates first and comes out of solution; thereafter the Reference Composition of Standard Seawater Millero et al. (2008a) does not apply.

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

$$\left[a_1 + a_2\left(T_0 + t\right)\right] + \left[a_3 + a_4\left(T_0 + t\right)\right]S_A \tag{2.6.2}$$

(see for example 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 pure water zero at the triple point

$$\eta^W\left(t_t, p_t\right) = 0 \tag{2.6.3}$$

and

$$u^W\left(t_t, p_t\right) = 0 \tag{2.6.4}$$

as described in IAPWS-95 and in more detail in Feistel et al. (2009) 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 F below. These values of g_{00} and g_{10} are not identical to the values in Feistel (2003) because the present values have been chosen to most accurately achieve the triple-point conditions (2.6.3) and (2.6.4) as discussed in Feistel et al. (2009).

The remaining two arbitrary constants a_3 and a_4 of (2.6.1) are determined by ensuring that the specific enthalpy h and specific entropy s of a sample of standard seawater with standard-ocean properties $(S_{SO}, t_{SO}, p_{SO}) = (35.165\ 04\ \mathrm{g\,kg^{-1}}, 0°C, 0\ \mathrm{dbar})$ are both zero, that is that

$$h(S_{SO}, t_{SO}, p_{SO}) = 0 \tag{2.6.5}$$

and

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

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

$$h^S(S_{SO}, t_{SO}, p_{SO}) = u^W(t_t, p_t) - h^W(t_{SO}, p_{SO}) \tag{2.6.7}$$

and

$$\eta^S(S_{SO}, t_{SO}, p_{SO}) = \eta^W(t_t, p_t) - \eta^W(t_{SO}, p_{SO}). \tag{2.6.8}$$

Written in this way, (2.6.7) and (2.6.8) use properties of the pure water definition (the right-hand sides) to constrain the arbitrary constants in the definition of 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 definition of pure water. While the two slightly different thermodynamic definitions 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 $3.3x10^{-3}$ J/kg from IAPWS-09 (as described in the table of Appendix F) compared with the round-off error of $2x10^{-8}$ J/kg when using IAPWS-95 with double-precision arithmetic.

The polynomial form and the coefficients for the pure water Gibbs function $g^W(t, p)$ from Feistel (2003) and IAPWS-09 are shown in Appendix F, 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 shown in Appendix G.

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 M. 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.

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_A and in situ temperature t, that is

$$v = v(S_A, t, p) = g_p = \partial g / \partial p \big|_{S_A, T}. \tag{2.7.1}$$

Notice that specific volume is a function of Absolute Salinity S_A rather than of Reference Salinity S_R or Practical Salinity S_P. The importance of this point is discussed in section 2.8.

For many theoretical and modeling purposes in oceanography it is convenient to regard the independent temperature variable to be potential temperature θ or Conservative Temperature Θ 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 η, θ or Θ is also held constant as follows (from Appendix A.11)

$$\partial h / \partial p \big|_{S_A, \eta} = \partial h / \partial p \big|_{S_A, \Theta} = \partial h / \partial p \big|_{S_A, \theta} = v. \tag{2.7.2}$$

2.8 Density

The density of seawater ρ is the reciprocal of the specific volume. It is given by the inverse of the pressure derivative of the Gibbs function at constant Absolute Salinity S_A and in situ temperature t, that is

$$\rho = \rho(S_A, t, p) = \left(g_p\right)^{-1} = \left(\partial g / \partial p \big|_{S_A, T}\right)^{-1}. \tag{2.8.1}$$

Notice that density is a function of Absolute Salinity S_A rather than of Reference Salinity S_R or Practical Salinity S_P. This is an extremely important point. Note that Absolute Salinity S_A in units of g kg^{-1} is numerically greater than Practical Salinity by approximately 0.165 g kg^{-1} so that if Practical Salinity were inadvertently used as the salinity argument for the density algorithm, a significant density error of approximately 0.12 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 θ or Conservative Temperature Θ rather than of in situ temperature t. That is, it is convenient to form the following two functional forms of density,

$$\rho = \tilde{\rho}(S_A, \theta, p) = \hat{\rho}(S_A, \Theta, p), \tag{2.8.2}$$

where θ and Θ are respectively potential and Conservative Temperatures referenced to $p_r = 0$ dbar. We will adopt the convention (see Table I.2 in Appendix I) that when enthalpy h, specific volume v or density ρ are taken to be functions of potential temperature they attract an over-twiddle as in $\tilde{h}, \tilde{v}$ and $\tilde{\rho}$, and when they are taken to be functions of Conservative Temperature they attract a hat as in $\hat{h}, \hat{v}$ and $\hat{\rho}$. With this convention, expressions involving

partial derivatives such as (2.7.2) can be written more compactly as $\widehat{h}_p = \tilde{h}_p = \hat{h}_p = v$ since the other variables are taken to be constant during the partial differentiation. Appendix N lists expressions for many thermodynamic variables in terms of the thermodynamic potentials $h = \widehat{h}\left(S_A, \eta, p\right)$, $h = \tilde{h}\left(S_A, \theta, p\right)$ and $h = \hat{h}\left(S_A, \Theta, p\right)$.

2.9 Chemical Potentials μ, μ^W and μ^S

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))

$$G\left(m_W, m_S, t, p\right) = m_W \mu^W + m_S \mu^S \tag{2.9.1}$$

where the chemical potentials of water in seawater μ^W and of salt in seawater μ^S are defined by the partial derivatives

$$\mu^W = \left.\frac{\partial G}{\partial m_W}\right|_{m_S, T, p}, \quad \text{and} \quad \mu^S = \left.\frac{\partial G}{\partial m_S}\right|_{m_W, T, p}. \tag{2.9.2}$$

Introducing absolute salinity $S_A = m_S / \left(m_W + m_S\right)$, the mass fraction of salt dissolved in seawater (Millero et al. (2008a)), the specific Gibbs energy g is given by

$$g\left(S_A, t, p\right) = \frac{G}{m_W + m_S} = \left(1 - S_A\right)\mu^W + S_A \mu^S = \mu^W + S_A\left(\mu^S - \mu^W\right) \tag{2.9.3}$$

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) (μ^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 μ^W and μ^S in terms of the Gibbs function g as

$$\mu^W = \left.\frac{\partial\left[\left(m_W + m_S\right)g\right]}{\partial m_W}\right|_{m_S, T, p} = g + \left(m_W + m_S\right)\left.\frac{\partial g}{\partial S_A}\right|_{T,p}\left.\frac{\partial S_A}{\partial m_W}\right|_{m_S} = g - S_A\left.\frac{\partial g}{\partial S_A}\right|_{T,p} \tag{2.9.4}$$

and for the chemical potential of salt in seawater,

$$\mu^S = \left.\frac{\partial\left[\left(m_W + m_S\right)g\right]}{\partial m_S}\right|_{m_W, T, p} = g + \left(m_W + m_S\right)\left.\frac{\partial g}{\partial S_A}\right|_{T,p}\left.\frac{\partial S_A}{\partial m_S}\right|_{m_W} = g + \left(1 - S_A\right)\left.\frac{\partial g}{\partial S_A}\right|_{T,p}. \tag{2.9.5}$$

The relative chemical potential μ (commonly called the "chemical potential of seawater") follows from (2.9.4) and (2.9.5) as

$$\mu = \mu^S - \mu^W = \left.\frac{\partial g}{\partial S_A}\right|_{T,p}, \tag{2.9.6}$$

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 (eq. (A.7.1) in Appendix A.7) it follows that the chemical

potential of seawater μ describes the change of enthalpy dh if at constant pressure and entropy, a small mass fraction of water is replaced by salt, dS_A. Equations (2.9.4) – (2.9.6) serve to define the three chemical potentials in terms of the Gibbs function g of seawater.

In the computer code Libraries A and B that use basic SI units exclusively, S_A has units of $kg\ kg^{-1}$ and g, μ, μ^S and μ^W all have units of $J\ kg^{-1}$. In the "gsw" library of computer code (Library C, Appendix L) S_A has units of $g\ kg^{-1}$ while μ, μ^S and μ^W all have units of $J\ g^{-1}$. 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 it is clear that S_A must have units of $kg\ kg^{-1}$. The adoption of non-basic-SI units is common in oceanography, but always causes some difficulties such as this.

2.10 Entropy

The specific entropy of seawater η is given by

$$\eta = \eta(S_A, t, p) = -g_T = -\partial g/\partial T\big|_{S_A, p}. \tag{2.10.1}$$

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

2.11 Internal Energy

The specific internal energy of seawater u is given by

$$u = u(S_A, t, p) = g + (t + T_0)\eta - (p + P_0)v = g - (t + T_0)\frac{\partial g}{\partial T}\bigg|_{S_A, p} - (p + P_0)\frac{\partial g}{\partial p}\bigg|_{S_A, T}. \tag{2.11.1}$$

This expression is an example where the use of non-SI units presents a problem, because in the product $-(p + P_0)v$ in (2.11.1), p and P_0 must be in Pa if specific volume has its regular units of $m^3\ kg^{-1}$.

2.12 Enthalpy

The specific enthalpy of seawater h is given by

$$h = h(S_A, t, p) = g + (T_0 + t)\eta = g - (T_0 + t)\frac{\partial g}{\partial T}\bigg|_{S_A, p}. \tag{2.12.1}$$

2.13 Helmholtz Energy

The specific Helmholtz energy of seawater f is given by

$$f = f(S_A, t, p) = g - (p + P_0)v = g - (p + P_0)\frac{\partial g}{\partial p}\bigg|_{S_A, T}. \tag{2.13.1}$$

This expression is another example where the use of non-SI units presents a problem, because in the product $-(p + P_0)v$ in (2.13.1), p and P_0 must be in Pa if specific volume has its regular units of $m^3\ kg^{-1}$.

2.14 Osmotic Coefficient

The osmotic coefficient of seawater ϕ is given by

$$\phi = \phi\left(S_A, t, p\right) = -\left(g^S - S_A \left.\frac{\partial g}{\partial S_A}\right|_{T,p}\right)\left(mR\left(T_0 + t\right)\right)^{-1}. \tag{2.14.1}$$

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, $R\left(T_0 + t\right)$ (Millero and Leung (1976), Feistel and Marion (2007), Feistel (2008)),

$$\mu^W\left(0, t, p\right) = \mu^W\left(S_A, t, p\right) + mR\left(T_0 + t\right)\phi. \tag{2.14.2}$$

Here, $R = 8.314\ 472$ J mol^{-1} K^{-1} is the universal molar gas constant. The molality m 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 κ^t is defined by

$$\kappa^t = \kappa^t\left(S_A, t, p\right) = \rho^{-1}\left.\frac{\partial\rho}{\partial p}\right|_{S_A, T} = -v^{-1}\left.\frac{\partial v}{\partial p}\right|_{S_A, T} = -\frac{g_{pp}}{g_p} \tag{2.15.1}$$

where g_{pp} is simply the second derivative of g with respect to pressure at constant S_A and t.

The isothermal compressibility of seawater κ^t produced by the software Libraries A and B has units of Pa^{-1} whereas in the "gsw" library (Library C, Appendix L) κ^t has units of dbar^{-1}.

2.16 Isentropic and Isohaline Compressibility

When the entropy and salinity are held constant while the pressure is changed, the isentropic and isohaline compressibility κ is obtained:

$$\begin{aligned}
\kappa = \kappa\left(S_A, t, p\right) &= \rho^{-1}\left.\frac{\partial\rho}{\partial p}\right|_{S_A, \eta} = -v^{-1}\left.\frac{\partial v}{\partial p}\right|_{S_A, \eta} = \rho^{-1}\left.\frac{\partial\rho}{\partial p}\right|_{S_A, \theta} = \rho^{-1}\left.\frac{\partial\rho}{\partial p}\right|_{S_A, \Theta} \\
&= \frac{\left(g_{Tp}^2 - g_{TT}g_{pp}\right)}{g_p g_{TT}}.
\end{aligned} \tag{2.16.1}$$

The isentropic and isohaline compressibility κ 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 adiabatic change in pressure. The isentropic and isohaline compressibility of seawater κ produced by the software Libraries A and B has units of Pa^{-1} whereas in the "gsw" library (Library C, Appendix L) κ has units of dbar^{-1}.

2.17 Sound Speed

The speed of sound in seawater c is given by

$$c = c(S_A, t, p) = \sqrt{\partial p / \partial \rho \big|_{S_A, \eta}} = \sqrt{(\rho \kappa)^{-1}} = g_p \sqrt{g_{TT} / \left(g_{Tp}^2 - g_{TT} g_{pp} \right)}. \qquad (2.17.1)$$

The sound speed c output of all the computer software libraries is in units of m s^{-1}. Note that in the two middle expressions in (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 derivative must be in Pa and the isentropic compressibility κ must have units of Pa^{-1}.

2.18 Thermal Expansion Coefficients

The thermal expansion coefficient α^t with respect to *in situ* temperature t, is

$$\alpha^t = \alpha^t (S_A, t, p) = -\frac{1}{\rho} \frac{\partial \rho}{\partial T} \bigg|_{S_A, p} = \frac{1}{v} \frac{\partial v}{\partial T} \bigg|_{S_A, p} = \frac{g_{Tp}}{g_p}. \qquad (2.18.1)$$

The thermal expansion coefficient α^θ with respect to potential temperature θ, is (see Appendix A.15)

$$\alpha^\theta = \alpha^\theta (S_A, t, p, p_r) = -\frac{1}{\rho} \frac{\partial \rho}{\partial \theta} \bigg|_{S_A, p} = \frac{1}{v} \frac{\partial v}{\partial \theta} \bigg|_{S_A, p} = \frac{g_{Tp}}{g_p} \frac{g_{TT}(S_A, \theta, p_r)}{g_{TT}}, \qquad (2.18.2)$$

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

The thermal expansion coefficient α^Θ with respect to Conservative Temperature Θ, is (see Appendix A.15)

$$\alpha^\Theta = \alpha^\Theta (S_A, t, p) = -\frac{1}{\rho} \frac{\partial \rho}{\partial \Theta} \bigg|_{S_A, p} = \frac{1}{v} \frac{\partial v}{\partial \Theta} \bigg|_{S_A, p} = -\frac{g_{Tp}}{g_p} \frac{c_p^0}{(T_0 + \theta) g_{TT}}. \qquad (2.18.3)$$

Note that Conservative Temperature Θ is defined only with respect to a reference pressure of 0 dbar so that the θ in (2.18.3) is the potential temperature with $p_r = 0$ dbar. All the derivatives on the right-hand side of (2.18.3) are evaluated at (S_A, t, p).

2.19 Saline Contraction Coefficients

The saline contraction coefficient β^t at constant in situ temperature t, is

$$\beta^t = \beta^t(S_A, t, p) = \left.\frac{1}{\rho}\frac{\partial \rho}{\partial S_A}\right|_{T,p} = -\left.\frac{1}{v}\frac{\partial v}{\partial S_A}\right|_{T,p} = -\frac{g_{S_A p}}{g_p}. \tag{2.19.1}$$

The saline contraction coefficient β_θ at constant potential temperature θ, is (see Appendix A.15)

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

$$= \frac{g_{Tp}\left[g_{S_A T} - g_{S_A T}(S_A, \theta, p_r)\right] - g_{TT}g_{S_A p}}{g_p g_{TT}}, \tag{2.19.2}$$

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

The saline contraction coefficient β^Θ at constant Conservative Temperature Θ, is (see Appendix A.15)

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

$$= \frac{g_{Tp}\left[g_{S_A T} - (T_0 + \theta)^{-1}g_{S_A}(S_A, \theta, 0)\right] - g_{TT}g_{S_A p}}{g_p g_{TT}}. \tag{2.19.3}$$

Note that Conservative Temperature Θ 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 software Libraries A and B all three saline contraction coefficients are produced in units of kg kg^{-1} while in the "gsw" library (Library C, Appendix L) 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

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

The isobaric heat capacity c_p varies over the $S_A - \Theta$ plane at $p = 0$ by approximately 5%, as illustrated in Figure 4.
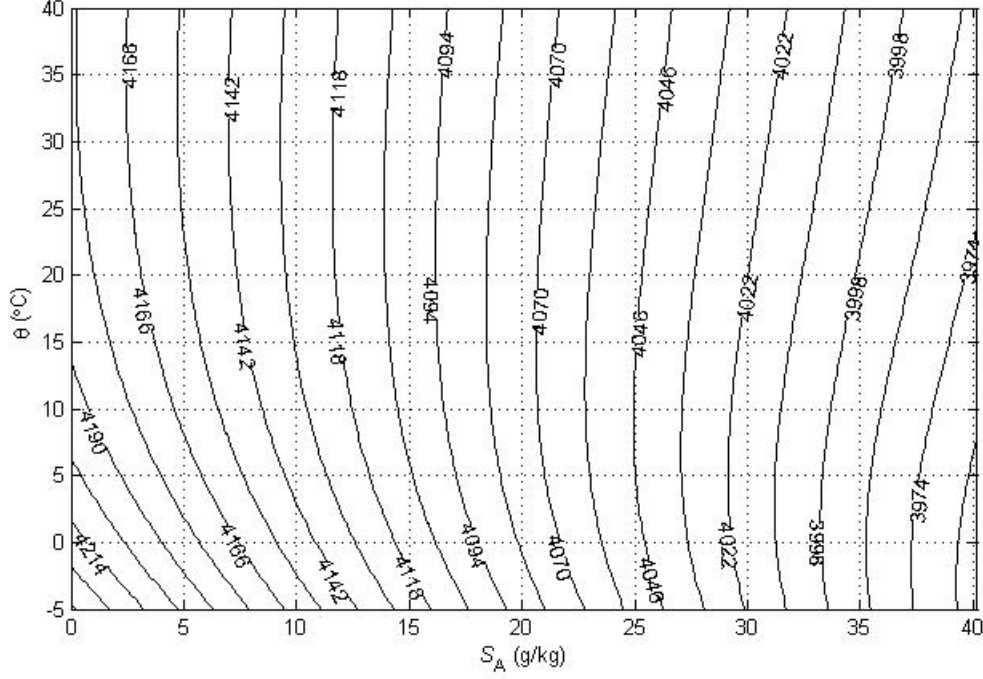
Figure 4. Contour lines of constant isobaric specific heat capacity c_p

of seawater (in J kg^{-1} K^{-1}), eq. (34), at $p = 0$.

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

$$c_v = c_v(S_A, t, p) = \left.\frac{\partial u}{\partial T}\right|_{S_A, v} = -(T_0 + t)\left(g_{TT} g_{pp} - g_{Tp}^2\right)\big/ g_{pp}. \qquad (2.21.1)$$

Note that the isochoric and isobaric heat capacities are related by

$$c_v = c_p - \frac{(T_0 + t)\left(\alpha^t\right)^2}{\left(\rho \kappa^t\right)}, \quad \text{and by} \quad c_v = c_p \frac{\kappa}{\kappa^t}. \qquad (2.21.2)$$

2.22 The Adiabatic Lapse Rate

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

$$\Gamma = \Gamma(S_A, t, p) = \left.\frac{\partial t}{\partial p}\right|_{S_A, \eta} = \left.\frac{\partial t}{\partial p}\right|_{S_A, \Theta} = -\frac{g_{Tp}}{g_{TT}} = \left.\frac{\partial^2 v}{\partial \eta \partial p}\right|_{S_A}$$

$$\qquad (2.22.1)$$

$$= \left.\frac{\partial v}{\partial \eta}\right|_{S_A, p} = \frac{(T_0 + t)\alpha^t}{\rho c_p} = \frac{(T_0 + \theta)}{c_p^0}\left.\frac{\partial v}{\partial \Theta}\right|_{S_A, p}.$$

The adiabatic (and isohaline) lapse rate is commonly 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 is that change in temperature that is required to keep the entropy (and also θ and Θ) of a seawater parcel constant when its pressure is increased in an adiabatic and isohaline manner. The reference pressure of the potential temperature θ that appears in (2.22.1) is $p_r = 0$ dbar.

The adiabatic lapse rate Γ output of software Libraries A and B is in units of $K\ Pa^{-1}$ while it is $K\ dbar^{-1}$ in the "gsw" library (Library C, Appendix L). Note that the expressions in the second line of the definition of Γ in (2.22.1) naturally lead to Γ being in $K\ Pa^{-1}$.

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 (1888b)). 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 reads that the requirement of a reversible process is that the process occurs at constant entropy. However this requirement is insufficient in the ocean 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.

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

$$\theta = \theta(S_A, t, p, p_r) = t + \int_p^{p_r} \Gamma(S_A, \theta[S_A, t, p, p'], p')\, dp'. \tag{3.1.1}$$

The algorithm that is used with the present Gibbs function approach is based on equating the specific entropies of two seawater parcels, one before and the other after the isentropic and isohaline pressure change. In this way, potential temperature θ is evaluated using a Newton-Raphson iterative solution technique to solve the following equation for θ

$\eta(S_A, \theta, p_r) = \eta(S_A, t, p)$, or, in terms of the Gibbs function, g,

$$-g_T(S_A, \theta, p_r) = -g_T(S_A, t, p). \tag{3.1.2}$$

The difference between the potential and in situ temperatures is not due to the work done in compressing a fluid parcel on going from one pressure to another:- even 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 θ output of software Libraries A and B is in units of K while the output from the "gsw" library (Library C, Appendix L) is in °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 eq. (2.8.2))

$$
\begin{aligned}
h^0\left(S_{\mathrm{A}},t,p\right) = h\left(S_{\mathrm{A}},\theta,0\right) = \tilde{h}^0\left(S_{\mathrm{A}},\theta\right) &= h\left(S_{\mathrm{A}},t,p\right) - \int_0^p v\left(S_{\mathrm{A}},\theta[S_{\mathrm{A}},t,p,p'],p'\right) dp' \\
&= h\left(S_{\mathrm{A}},t,p\right) - \int_0^p \hat{v}\left(S_{\mathrm{A}},\eta,p'\right) dp' \\
&= h\left(S_{\mathrm{A}},t,p\right) - \int_0^p \tilde{v}\left(S_{\mathrm{A}},\theta,p'\right) dp' \\
&= h\left(S_{\mathrm{A}},t,p\right) - \int_0^p \hat{v}\left(S_{\mathrm{A}},\Theta,p'\right) dp'
\end{aligned}
\tag{3.2.1}
$$

and in terms of the Gibbs function, potential enthalpy h^0 is evaluated as

$$
h^0\left(S_{\mathrm{A}},t,p\right) = h\left(S_{\mathrm{A}},\theta,0\right) = g\left(S_{\mathrm{A}},\theta,0\right) - \left(T_0 + \theta\right) g_T\left(S_{\mathrm{A}},\theta,0\right).
\tag{3.2.2}
$$

3.3 Conservative Temperature

Conservative Temperature Θ is defined to be proportional to potential enthalpy according to

$$
\Theta\left(S_{\mathrm{A}},t,p\right) = \tilde{\Theta}\left(S_{\mathrm{A}},\theta\right) = h^0\left(S_{\mathrm{A}},t,p\right) / c_p^0 = \tilde{h}^0\left(S_{\mathrm{A}},\theta\right) / c_p^0
\tag{3.3.1}
$$

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

$$
c_p^0 \approx \frac{\left[h\left(S_{\mathrm{SO}}, 25\,°\mathrm{C}, 0\right) - h\left(S_{\mathrm{SO}}, 0\,°\mathrm{C}, 0\right)\right]}{(25\ \mathrm{K})} \approx 3991.867\,957\,119\,63\ \ \mathrm{J\,kg^{-1}\,K^{-1}},
\tag{3.3.2}
$$

noting that $h\left(S_{\mathrm{SO}}, 0\,°\mathrm{C}, 0\,\mathrm{dbar}\right)$ is zero according to the way the Gibbs function is defined in (2.6.7). In fact we adopt the exact definition for c_p^0 to be the 15-digit value in (3.3.2), so that

$$
c_p^0 \equiv 3991.867\,957\,119\,63\ \ \mathrm{J\,kg^{-1}\,K^{-1}}.
\tag{3.3.3}
$$

When IAPWS-95 is used for the pure water part of the Gibbs function, $\Theta\left(S_{\mathrm{SO}}, 0\,°\mathrm{C}, 0\right)$ and $\Theta\left(S_{\mathrm{SO}}, 25\,°\mathrm{C}, 0\right)$ differ from 0 °C and 25 °C respectively by the round-off amount of 5×10^{-12} °C. When IAPWS-09 (which is based on the paper of Feistel (2003), see Appendix F) is used for the pure water part of the Gibbs function, $\Theta\left(S_{\mathrm{SO}}, 0\,°\mathrm{C}, 0\right)$ differs from 0 °C by -8.25×10^{-8} °C and $\Theta\left(S_{\mathrm{SO}}, 25\,°\mathrm{C}, 0\right)$ differs from 25 °C by 9.3×10^{-6} °C. Over the temperature range from $0\,°\mathrm{C}$ to $40\,°\mathrm{C}$ the difference between Conservative Temperature using IAPWS-95 and IAPWS-09 as the pure water part is no more than $\pm 1.5 \times 10^{-5}$ °C.

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 software libraries A, B and C each include an algorithm for determining Conservative Temperature from values of Absolute Salinity S_A and potential temperature θ referenced to zero sea pressure. In addition these libraries also have an algorithm for evaluating potential temperature (referenced to 0 dbar) from Absolute Salinity S_A and Conservative Temperature Θ. This inverse algorithm, $\hat{\theta}(S_A, \Theta)$, has an initial seed based on a polynomial approximation and achieves the result to machine precision in one iteration of a modified Newton-Raphson technique (see McDougall et al. (2003) and Jackett et al. (2006)).

3.4 Potential Density

Potential density ρ^θ 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

$$\rho^\theta\left(S_A, t, p, p_r\right) = \rho\left(S_A, t, p\right) + \int_p^{p_r} \rho\left(S_A, \theta[S_A, t, p, p'], p'\right) \ \kappa\left(S_A, \theta[S_A, t, p, p'], p'\right) dp'. \quad (3.4.1)$$

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

$$\rho^\theta\left(S_A, t, p, p_r\right) = \rho\left(S_A, \theta[S_A, t, p, p_r], p_r\right) = g_p^{-1}\left(S_A, \theta[S_A, t, p, p_r], p_r\right). \quad (3.4.2)$$

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

$$\rho^\theta\left(S_A, t, p, p_r\right) = \tilde{\rho}\left(S_A, \theta, p = p_r\right) = \hat{\rho}\left(S_A, \Theta, p = p_r\right), \quad (3.4.3)$$

where we note that the potential temperature θ in the middle 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).

Following the discussion after equation (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 $h = \hat{h}(S_A, \Theta, p)$ for enthalpy as (see also Appendix N)

$$\rho^{\theta}\left(S_{\mathrm{A}}, t, p, p_{\mathrm{r}}\right) = \left[\tilde{h}_p\left(S_{\mathrm{A}}, \theta, \, p = p_{\mathrm{r}}\right)\right]^{-1} = \left[\hat{h}_p\left(S_{\mathrm{A}}, \Theta, \, p = p_{\mathrm{r}}\right)\right]^{-1}. \tag{3.4.4}$$

3.5 Density Anomaly

Density anomaly σ^t is an old-fashioned density measure (a poor-man's potential density) that is now hardly ever used. It is simply the density evaluated at the in situ temperature but at zero pressure, minus 1000 kg m^{-3},

$$\sigma^t\left(S_{\mathrm{A}}, t, p\right) = \rho\left(S_{\mathrm{A}}, t, 0\right) - 1000 \text{ kg m}^{-3} = g_p^{-1}\left(S_{\mathrm{A}}, t, 0\right) - 1000 \text{ kg m}^{-3}. \tag{3.5.1}$$

3.6 Potential Density Anomaly

Potential density anomaly σ^{θ} is simply potential density minus 1000 kg m^{-3},

$$\begin{aligned}
\sigma^{\theta}\left(S_{\mathrm{A}}, t, p\right) &= \rho^{\theta}\left(S_{\mathrm{A}}, t, p\right) - 1000 \text{ kg m}^{-3} \\
&= g_p^{-1}\left(S_{\mathrm{A}}, \theta[S_{\mathrm{A}}, t, p, p_{\mathrm{r}}], p_{\mathrm{r}}\right) - 1000 \text{ kg m}^{-3}.
\end{aligned} \tag{3.6.1}$$

3.7 Specific Volume Anomaly

The specific volume anomaly δ is defined as the difference between the specific volume and a given function of pressure. Traditionally δ has been defined as

$$\delta\left(S_{\mathrm{A}}, t, p\right) = v\left(S_{\mathrm{A}}, t, p\right) - v\left(S_{\mathrm{SO}}, 0°C, p\right) \tag{3.7.1}$$

(where the traditional value of $S_{\mathrm{P}} = 35$ has been updated to $S_{\mathrm{SO}} = 35u_{PS} = 35.16504$ g kg^{-1} in the present formulation). Note that the second term, $v\left(S_{\mathrm{SO}}, 0°C, p\right)$, is a function only of pressure. In order to have a surface of constant specific volume anomaly more accurately approximate neutral tangent planes, it is advisable to replace the arguments S_{SO} and 0°C with more general values $\widehat{S}_{\mathrm{A}}$ and $\widehat{t}$ 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

$$\widehat{\delta}\left(S_{\mathrm{A}}, t, p\right) = v\left(S_{\mathrm{A}}, t, p\right) - v\left(\widehat{S}_{\mathrm{A}}, \widehat{t}, p\right) = g_p\left(S_{\mathrm{A}}, t, p\right) - g_p\left(\widehat{S}_{\mathrm{A}}, \widehat{t}, p\right). \tag{3.7.2}$$

The last terms in (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 in situ temperature) as $\hat{v}\left(S_{\mathrm{A}}, \Theta, p\right)$ and $\hat{h}\left(S_{\mathrm{A}}, \Theta, p\right)$ and write a slightly different definition of specific volume anomaly as

$$\widehat{\tilde{\delta}}\left(S_{\mathrm{A}}, \Theta, p\right) = \hat{v}\left(S_{\mathrm{A}}, \Theta, p\right) - \hat{v}\left(\widehat{\tilde{S}}_{\mathrm{A}}, \widehat{\tilde{\Theta}}, p\right) = \hat{h}_p\left(S_{\mathrm{A}}, \Theta, p\right) - \hat{h}_p\left(\widehat{\tilde{S}}_{\mathrm{A}}, \widehat{\tilde{\Theta}}, p\right). \tag{3.7.3}$$

The same can also be done with potential temperature so that in terms of the specific volume $\tilde{v}\left(S_A,\theta,p\right)$ and enthalpy $\tilde{h}\left(S_A,\theta,p\right)$ we can write another form of the specific volume anomaly as

$$\tilde{\tilde{\delta}}\left(S_A,\theta,p\right) = \tilde{v}\left(S_A,\theta,p\right) - \tilde{v}\left(\tilde{\tilde{S}}_A,\tilde{\tilde{\theta}},p\right) = \tilde{h}_p\left(S_A,\theta,p\right) - \tilde{h}_p\left(\tilde{\tilde{S}}_A,\tilde{\tilde{\theta}},p\right). \tag{3.7.4}$$

These expressions exploit the fact that (see Appendix A.11)

$$\partial h/\partial p\big|_{S_A,\eta} = \partial h/\partial p\big|_{S_A,\Theta} = \partial h/\partial p\big|_{S_A,\theta} = v \, . \tag{3.7.5}$$

3.8 The 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 θ the thermobaric coefficient is (McDougall, (1987b))

$$T_b^\theta = T_b^\theta\left(S_A,t\,p\right) = \beta^\theta \frac{\partial\left(\alpha^\theta/\beta^\theta\right)}{\partial p}\Bigg|_{S_A,\theta} = \frac{\partial\alpha^\theta}{\partial p}\Bigg|_{S_A,\theta} - \frac{\alpha^\theta}{\beta^\theta}\frac{\partial\beta^\theta}{\partial p}\Bigg|_{S_A,\theta} . \tag{3.8.1}$$

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 in situ temperature, that is, with density expressed in the functional form $\rho = \tilde{\rho}\left(S_A,\theta,p\right)$.

With respect to Conservative Temperature Θ the thermobaric coefficient is

$$T_b^\Theta = T_b^\Theta\left(S_A,t\,p\right) = \beta^\Theta \frac{\partial\left(\alpha^\Theta/\beta^\Theta\right)}{\partial p}\Bigg|_{S_A,\Theta} = \frac{\partial\alpha^\Theta}{\partial p}\Bigg|_{S_A,\Theta} - \frac{\alpha^\Theta}{\beta^\Theta}\frac{\partial\beta^\Theta}{\partial p}\Bigg|_{S_A,\Theta} . \tag{3.8.2}$$

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 in situ temperature, that is, with density expressed in the functional form $\rho = \hat{\rho}\left(S_A,\Theta,p\right)$.

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 $e^{Tb} = -gN^{-2}K\,T_b^\theta\nabla_n\theta\cdot\nabla_n p$ or $e^{Tb} = -gN^{-2}K\,T_b^\Theta\nabla_n\Theta\cdot\nabla_n p$ 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 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, $-K\nabla_n\Theta$, 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 (2010b)). 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, $T_b^\theta\nabla_n\theta = T_b^\Theta\nabla_n\Theta$. Hence the thermobaric dianeutral advection e^{Tb} is the same whether it is calculated as $-gN^{-2}K\,T_b^\theta\nabla_n\theta\cdot\nabla_n p$ or as $-gN^{-2}K\,T_b^\Theta\nabla_n\Theta\cdot\nabla_n p$.

This thermobaric vertical advection process is absent from standard layered ocean models in which the vertical coordinate is a function only of S_A and Θ (such as σ_2, potential density referenced to 2000 dbar). As described in Appendix A.26 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 cabbeling advection through the coordinate surfaces but does not allow the thermobaric advection through these surfaces (Klocker and McDougall (2010b)). Expressions for T_b^θ and T_b^Θ in terms of enthalpy in the functional forms $\tilde{h}(S_A, \theta, p)$ and $\hat{h}(S_A, \Theta, p)$ can be found in Appendix N.

In the software Libraries A and B both versions of the thermobaric parameter T_b^θ and T_b^Θ are output in units of $\text{K}^{-1}\,\text{Pa}^{-1}$ while in the "gsw" software library (Library C, Appendix L) they are output in units of $\text{K}^{-1}\,\text{dbar}^{-1}$.

3.9 The 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 θ the cabbeling coefficient is (McDougall, (1987b))

$$C_b^\theta = C_b^\theta(S_A, t\, p) = \left.\frac{\partial \alpha^\theta}{\partial \theta}\right|_{S_A, p} + 2\frac{\alpha^\theta}{\beta^\theta}\left.\frac{\partial \alpha^\theta}{\partial S_A}\right|_{\theta, p} - \left(\frac{\alpha^\theta}{\beta^\theta}\right)^2 \left.\frac{\partial \beta^\theta}{\partial S_A}\right|_{\theta, p}. \tag{3.9.1}$$

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 $\rho = \tilde{\rho}(S_A, \theta, p)$.

With respect to Conservative Temperature Θ the cabbeling coefficient is

$$C_b^\Theta = C_b^\Theta(S_A, t\, p) = \left.\frac{\partial \alpha^\Theta}{\partial \Theta}\right|_{S_A, p} + 2\frac{\alpha^\Theta}{\beta^\Theta}\left.\frac{\partial \alpha^\Theta}{\partial S_A}\right|_{\Theta, p} - \left(\frac{\alpha^\Theta}{\beta^\Theta}\right)^2 \left.\frac{\partial \beta^\Theta}{\partial S_A}\right|_{\Theta, p}. \tag{3.9.2}$$

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 $e^{Cab} = -gN^{-2}K C_b^\Theta \nabla_n\Theta \cdot \nabla_n\Theta$ (or less accurately by $e^{Cab} \approx -gN^{-2}K C_b^\theta \nabla_n\theta \cdot \nabla_n\theta$) 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 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, $-K\nabla_n\Theta$, 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 (2010b)). It is shown in Appendix A.14 that $C_b^\theta \nabla_n\theta \cdot \nabla_n\theta \neq C_b^\Theta \nabla_n\Theta \cdot \nabla_n\Theta$ 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 less accurate because of the non-conservative nature of potential temperature.

Expressions for C_b^{θ} and C_b^{Θ} in terms of enthalpy in the functional forms $\tilde{h}\left(S_A, \theta, p\right)$ and $\hat{h}\left(S_A, \Theta, p\right)$ can be found in Appendix N.

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)

$$
\begin{aligned}
g^{-1} N^2 &= -\rho^{-1}\rho_z + \kappa p_z = -\rho^{-1}\left(\rho_z - p_z / c^2\right) \\
&= \alpha^{\theta}\theta_z - \beta^{\theta}\left. \partial S_A / \partial z\right|_{x,y} \\
&= \alpha^{\Theta}\Theta_z - \beta^{\Theta}\left. \partial S_A / \partial z\right|_{x,y}.
\end{aligned}
\tag{3.10.1}
$$

For two seawater parcels separated by a small distance Δz 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 procedure calculates the buoyancy frequency N according to

$$
g^{-1} N^2 = -\frac{1}{\rho}\frac{\Delta\rho^{\theta}}{\Delta z},
\tag{3.10.2}
$$

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.

3.11 Neutral Tangent Plane

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

$$
\begin{aligned}
g^{-1} N^2 \mathbf{n} &= -\rho^{-1}\nabla\rho + \kappa\nabla p = -\rho^{-1}\left(\nabla\rho - \nabla p / c^2\right) \\
&= \alpha^{\theta}\nabla\theta - \beta^{\theta}\nabla S_A \\
&= \alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\nabla S_A.
\end{aligned}
\tag{3.11.1}
$$

As defined, $\mathbf{n}$ is not quite a unit normal vector, rather its vertical component is exactly $\mathbf{k}$, that is, its vertical component is unity. It can be shown that $\alpha^{\theta}\nabla\theta - \beta^{\theta}\nabla S_A$ is exactly equal to $\alpha^{\Theta}\nabla\Theta - \beta^{\Theta}\nabla S_A$ (McDougall et al. (2009b)). Interestingly, both $\alpha^{\theta}\nabla\theta$ and $\beta^{\theta}\nabla S_A$ are independent of the four arbitrary constants of the Gibbs function (see equation (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 (3.11.1).

Expressing the two-dimensional gradient of properties in the neutral tangent plane by ∇_n (see McDougall (1995) for the definition of this operator) the property gradients in a neutral tangent plane obey

$$
\begin{aligned}
-\rho^{-1}\nabla_n \rho + \kappa \nabla_n p \ &= \ -\rho^{-1}\left(\nabla_n \rho - \nabla_n p / c^2\right) \\
&= \ \alpha^\theta \nabla_n \theta - \beta^\theta \nabla_n S_A \\
&= \ \alpha^\Theta \nabla_n \Theta - \beta^\Theta \nabla_n S_A \\
&= \ \mathbf{0}.
\end{aligned}
\tag{3.11.2}
$$

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

$$
- T_b^\Theta \int_1^2 \left(p - \bar{p}\right) d\Theta,
\tag{3.11.3}
$$

is described in section 2 and Appendix A(c) of Jackett and McDougall (1997). An equally accurate finite amplitude version of (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 The 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 $\nabla_z p$ so that the geostrophic equation is

$$
f\,\mathbf{k} \times \rho \mathbf{u} \ = \ -\nabla_z p \quad \text{or} \quad f\mathbf{v} \ = \ \frac{1}{\rho}\,\mathbf{k} \times \nabla_z p \ .
\tag{3.12.1}
$$

where $\mathbf{u}$ is the three dimensional velocity and $\mathbf{v}$ is the horizontal velocity.

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

$$
p_z = -g\rho.
\tag{3.12.2}
$$

The so called "thermal wind" equation is an equation for the vertical gradient of the horizontal velocity under the geostrophic approximation. Vertically differentiating (3.12.1), using the hydrostatic equation (3.12.2) and ignoring the tiny term in ρ_z, the thermal wind can be written as

$$
f\mathbf{v}_z \ = \ \frac{1}{\rho}\,\mathbf{k} \times \nabla_z\left(p_z\right) \ = \ -\frac{g}{\rho}\,\mathbf{k} \times \nabla_z \rho \ = \ \frac{N^2}{g\rho}\,\mathbf{k} \times \nabla_n p,
\tag{3.12.3}
$$

where ∇_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, to the slope of the neutral tangent plane (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 $\alpha^\Theta \nabla\Theta - \beta^\Theta \nabla S_A$ with its curl,

$$H^n \equiv \left(\alpha^\Theta \nabla\Theta - \beta^\Theta \nabla S_A\right)\cdot \nabla\times\left(\alpha^\Theta \nabla\Theta - \beta^\Theta \nabla S_A\right) \tag{3.13.1}$$

and this is proportional to the thermobaric coefficient T_b^Θ of the equation of state according to

$$\begin{aligned}
H^n &= \beta^\Theta T_b^\Theta \nabla p \cdot \nabla S_A \times \nabla\Theta \\
&= p_z \beta^\Theta T_b^\Theta \left(\nabla_p S_A \times \nabla_p \Theta\right)\cdot \mathbf{k} \\
&= g^{-1} N^2 T_b^\Theta \left(\nabla_n p \times \nabla_n \Theta\right)\cdot \mathbf{k} \\
&\approx g^{-1} N^2 T_b^\Theta \left(\nabla_a p \times \nabla_a \Theta\right)\cdot \mathbf{k}
\end{aligned} \tag{3.13.2}$$

where p_z is simply the vertical gradient of pressure and $\nabla_n \Theta$ and $\nabla_p \Theta$ are the two-dimensional gradients of Θ in the neural tangent plane and in the horizontal plane (actually the isobaric surface) respectively. The gradients $\nabla_a \Theta$ and $\nabla_a \Theta$ are taken in an approximately neutral surface. Since $\alpha^\theta \nabla\theta - \beta^\theta \nabla S_A$ and $\alpha^\Theta \nabla\Theta - \beta^\Theta \nabla S_A$ are exactly equal, neutral helicity can be defined as the scalar product of this vector with its curl based on either formulation, so that (from the third line of (3.13.2), and bearing in mind that $\Theta = \Theta(S_A, \theta)$) 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}.

Neutral helicity is proportional to the component of the vertical shear of the geostrophic velocity ($\mathbf{v}_z$, the "thermal wind") in the direction of the temperature gradient along the neutral tangent plane $\nabla_n \Theta$, since, from (3.12.3) and the middle line of (3.13.2) we find that

$$H^n = \rho T_b^\Theta f \mathbf{v}_z \cdot \nabla_n \Theta. \tag{3.13.3}$$

In the evolution equation of potential vorticity defined with respect to potential density ρ^θ 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))

$$\rho^{-2} \nabla\rho^\theta \cdot \nabla\rho \times \nabla p \approx \left(p_r - p\right) H^n \tag{3.13.4}$$

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

$$\nabla_\sigma \times \left(\tfrac{1}{\rho}\nabla_z p\right)\cdot \mathbf{k} = H^n \left(p_r - p\right)\left(-\frac{\partial\rho^\Theta}{\partial z}\right)^{-1}. \tag{3.13.5}$$

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 Θ 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. (2009, 2010))

$$\mathbf{v} \cdot \mathbf{k} \times \frac{\nabla_n \Theta}{|\nabla_n \Theta|} = -\frac{H^n}{\phi_z \rho f T_b^\Theta |\nabla_n \Theta|} + \frac{v_z^\perp}{\phi_z}, \tag{3.13.6}$$

so that the full expression for the horizontal velocity is

$$\mathbf{v} = \left\{ -\frac{H^n}{\phi_z \rho f T_b^\Theta |\nabla_n \Theta|} + \frac{v_z^\perp}{\phi_z} \right\} \mathbf{k} \times \frac{\nabla_n \Theta}{|\nabla_n \Theta|} + v^\perp \frac{\nabla_n \Theta}{|\nabla_n \Theta|}. \tag{3.13.7}$$

Here ϕ_z is the rate of spiraling (radians per meter) in the vertical of the Θ contours on neutral tangent planes, and $v^\perp$ is the velocity component across the Θ 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 $\bar{\mathbf{v}}_z$ in the direction across the Θ contour on the neutral tangent plane (see (3.13.3)). This equation (3.13.7) for the mean Eulerian velocity $\mathbf{v}$ shows that in the absence of mixing processes (so that $v^\perp = v_z^\perp = 0$) and so long as (i) the epineutral Θ 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.

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 γ^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

$$\mathbf{s} = \nabla_n z - \nabla_a z = g N^{-2} \left(\beta^\Theta \nabla_a S_A - \alpha^\Theta \nabla_a \Theta \right) \tag{3.14.1}$$

where $\nabla_n z$ is the slope of the neutral tangent plane, $\nabla_a z$ is the slope of the approximately neutral surface and ∇_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 equation (A.24.4)). Since neutral density is not a thermodynamic variable, it will not be described more fully in this manual.

3.15 Stability Ratio R_ρ

The stability ratio R_ρ 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

$$R_\rho = \frac{\alpha^\Theta \Theta_z}{\beta^\Theta (S_A)_z} \approx \frac{\alpha^\theta \theta_z}{\beta^\theta (S_A)_z}.$$

(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)

$$\begin{aligned} Tu &= \tan^{-1}\left(\alpha^\Theta \Theta_z + \beta^\Theta (S_A)_z,\ \alpha^\Theta \Theta_z - \beta^\Theta (S_A)_z\right) \\ &\approx \tan^{-1}\left(\alpha^\theta \theta_z + \beta^\theta (S_A)_z,\ \alpha^\theta \theta_z - \beta^\theta (S_A)_z\right) \end{aligned}$$

(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 Θ and S_A. 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 φ along a potential density surface $\nabla_\sigma \varphi$ is related to the corresponding gradient in the neutral tangent plane $\nabla_n \varphi$ by (from McDougall (1987a))

$$\nabla_\sigma \varphi = \nabla_n \varphi + \frac{\varphi_z}{\Theta_z} \frac{R_\rho [r-1]}{[R_\rho - r]} \nabla_n \Theta$$

(3.17.1)

where r is defined by

$$r = \frac{\alpha^\Theta (S_A, \Theta, p) / \beta^\Theta (S_A, \Theta, p)}{\alpha^\Theta (S_A, \Theta, p_r) / \beta^\Theta (S_A, \Theta, p_r)},$$

(3.17.2)

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

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

$$\nabla_\sigma \Theta \;=\; \frac{r\left[R_\rho - 1\right]}{\left[R_\rho - r\right]} \nabla_n \Theta \;=\; G^\Theta \nabla_n \Theta \tag{3.17.3}$$

where the "isopycnal temperature gradient ratio"

$$G^\Theta \;=\; r\left[R_\rho - 1\right]\Big/\left[R_\rho - r\right] \tag{3.17.4}$$

has been defined as a shorthand expression for future use. Substituting $\varphi = S_A$ into (3.17.1) gives the following relation between the (parallel) isopycnal and epineutral gradients of S_A

$$\nabla_\sigma S_A \;=\; \frac{\left[R_\rho - 1\right]}{\left[R_\rho - r\right]} \nabla_n S_A. \tag{3.17.5}$$

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 in that surface. The slope difference between the neutral tangent plane and a potential density surface with reference pressure p_r is given by (McDougall (1988))

$$\nabla_n z - \nabla_\sigma z \;=\; \frac{R_\rho\left[1 - r\right]}{\left[R_\rho - r\right]} \frac{\nabla_n \Theta}{\Theta_z} \;=\; \frac{R_\rho\left[1 - r\right]}{r\left[R_\rho - 1\right]} \frac{\nabla_\sigma \Theta}{\Theta_z}. \tag{3.18.1}$$

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 θ or Θ (Eden and Willebrand (1999), McDougall and Jackett (2005b)). The most recent method for forming approximately neutral surfaces is that of Klocker et al. (2009). 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. (2009).

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

3.19 Slopes of In Situ Density Surfaces and Specific Volume Anomaly Surfaces

The slope of an in situ density surface, $\nabla_\rho z$, can be expressed as

$$\nabla_\rho z - \nabla_p z \;=\; \left(\nabla_n z - \nabla_p z\right)\left[1 + \frac{g^2/c^2}{N^2}\right]^{-1}, \tag{3.19.1}$$

where c is the speed of sound and N is the buoyancy frequency (McDougall (1989)). In the upper water column where the square of the buoyancy frequency is significantly larger than $g^2/c^2 \approx 4.3x10^{-5}\, s^{-2}$, the in situ density surface has a similar slope to the neutral tangent plane $\nabla_n z$. 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 $N^2 \approx 10^{-5} s^{-2}$, 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 quite incompressible. 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, $\nabla_\delta z$, can be expressed as

$$\nabla_\delta z - \nabla_p z \;=\; \left(\nabla_n z - \nabla_p z\right)\left[1 + \frac{g^2/c^2}{N^2} - \frac{g^2/\tilde{\tilde{c}}^2}{N^2}\right]^{-1}, \tag{3.19.2}$$

where $\tilde{\tilde{c}}$ is the sound speed of the reference parcel $\left(\tilde{\tilde{S}}_{\rm A}, \tilde{\tilde{\Theta}}\right)$ 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 (3.19.2) is equal to $\rho g N^{-2}\, \partial\delta/\partial z$ (from section 7 of McDougall (1989)).

3.20 Potential Vorticity

Planetary potential vorticity is the Coriolis parameter f times the vertical gradient of a suitable density variable. Potential density is sometimes used for that density 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 equation (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

$$\text{NSPV} = -g\rho^{-1} f \gamma_z^{\text{n}} \approx f N^2 \exp\left\{ -\int_{\text{ans}} \rho g^2 N^{-2} T_b^\Theta \left(\nabla_a \Theta - \Theta_p \nabla_a p \right) \cdot d\mathbf{l} \right\}. \tag{3.20.1}$$

The exponential expression was derived by McDougall (1988) (his equation (47)) and is approximate because the variation of the saline contraction coefficient β^Θ with pressure was neglected in comparison with the larger proportional change in the thermal expansion coefficient α^Θ with pressure. The integral in (3.20.1) is taken along an approximately neutral surface from a location where NSPV is equal to $f N^2$. Interestingly the combination $\nabla_a \Theta - \Theta_p \nabla_a p$ is simply the isobaric gradient of Conservative Temperature, $\nabla_p \Theta$, which is almost the same as the horizontal gradient, $\nabla_z \Theta$. A more accurate version of this equation which does not ignore the variation of the saline contraction coefficient can be shown to be

$$\begin{aligned}
\text{NSPV} = -g\rho^{-1} f \gamma_z^{\text{n}} &= f N^2 \exp\left\{ -\int_{\text{ans}} g^2 N^{-2} \left((\rho \alpha^\Theta)_p \nabla_p \Theta - (\rho \beta^\Theta)_p \nabla_p S_{\text{A}} \right) \cdot d\mathbf{l} \right\} \\
&= f N^2 \exp\left\{ \int_{\text{ans}} g^2 N^{-2} \nabla_p (\rho \kappa) \cdot d\mathbf{l} \right\}.
\end{aligned} \tag{3.20.2}$$

The exponential factor in (3.20.2) is the integrating factor b that allows spatial integrals of $\rho b \left(\beta^\Theta \nabla S_{\text{A}} - \alpha^\Theta \nabla \Theta \right) \approx \nabla \gamma^{\text{n}}$ to be approximately independent of path for "vertical paths", that is, for paths in surfaces whose normal has zero vertical component. NSPV has the units s^{-3}.

The gradient of $f N^2$ is related to that of NSPV by (from (3.20.2) and (3.20.1))

$$\begin{aligned}
\nabla_a \left(\ln f N^2 \right) - \nabla_a \left(\ln \text{NSPV} \right) &= -g^2 N^{-2} \nabla_p (\rho \kappa) \\
&\approx \rho g^2 N^{-2} T_b^\Theta \left(\nabla_a \Theta - \Theta_p \nabla_a p \right).
\end{aligned} \tag{3.20.3}$$

The deficiencies of $f N^2$ as a form of planetary potential vorticity do not seem to be widely appreciated. Even in a lake or in the simple situation where temperature does not vary along a density surface ($\nabla_a \Theta = \mathbf{0}$), the use of $f N^2$ as planetary potential vorticity is inaccurate since the right-hand side of (3.20.3) is then approximately $-\rho g^2 N^{-2} T_b^\Theta \Theta_p \nabla_a p = \left[(R_\rho - 1)^{-1} T_b^\Theta / \alpha^\Theta \right] \nabla_a p$ and the mere fact that the density surface has a slope ($\nabla_a p \neq \mathbf{0}$) means that the contours of $f N^2$ will not be parallel to contours of NSPV on the density surface. In this situation the contours of NSPV coincide with those of isopycnal-potential-vorticity (IPV), the potential vorticity defined with respect to potential density variations along approximately neutral surfaces.

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

$$\frac{\text{IPV}}{f N^2} = \frac{-g\rho^{-1} \rho_z^\Theta}{N^2} = \frac{\beta^\Theta (p_{\text{r}}) \left[R_\rho / r - 1 \right]}{\beta^\Theta (p) \left[R_\rho - 1 \right]} \approx \frac{\left[R_\rho / r - 1 \right]}{\left[R_\rho - 1 \right]}, \tag{3.20.4}$$

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

$$\frac{\text{NSPV}}{\text{IPV}} = \frac{\beta^\Theta (p)}{\beta^\Theta (p_{\text{r}})} \frac{\left[R_\rho - 1 \right]}{\left[R_\rho / r - 1 \right]} \exp\left\{ \int_{\text{ans}} g^2 N^{-2} \nabla_p (\rho \kappa) \cdot d\mathbf{l} \right\}. \tag{3.20.5}$$

You and McDougall (1991) show that because of the highly differentiated nature of potential vorticity, even at the reference pressure of the potential density variable, isolines of IPV do not coincide with those of NSPV (see equations (14) – (16) and Figure 14 of that paper).

3.21 The 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 $\rho^{FW}(E - P)$ 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 ρ^{FW}; this density being that of pure water at the sea surface temperature and at atmospheric pressure). The same mass flux $\rho^{FW}(E - P)$ 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 $\eta(x, y, z, t)$ can be expressed as $w - \mathbf{V}_H \cdot \nabla \eta - \partial \eta / \partial t$ (where w is the vertical velocity through the geopotential surface) and the mass flux associated with this dia-surface vertical velocity component is this vertical velocity times the density of the seawater, ρ. 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))

$$w - \mathbf{V}_H \cdot \nabla \eta - \partial \eta / \partial t = \rho^{-1} \rho^{FW}(E - P). \tag{3.21.1}$$

3.22 Freshwater Content and Freshwater Flux

Oceanographers traditionally call the pure water fraction of seawater the "freshwater fraction" or the "freshwater content". This is less than ideal because in some science circles "freshwater" is used to describe water of low but non-zero salinity. Here we retain the oceanographic use of "freshwater" as being synonymous with "pure water". The freshwater content of seawater is $(1 - S_A) = (1 - 0.001 S_A / (\mathrm{g\ kg^{-1}}))$. 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 $(1 - 0.001 S_P)$.

The advective flux of mass per unit area is ρu 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 $\rho (1 - S_A) u$.

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_p^0 times the flux of Conservative Temperature Θ, where c_p^0 is given by (3.3.3). By contrast, the same heat flux across the sea surface changes potential temperature θ 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 equation (A.13.1) of Appendix A.13, can be approximated as

$$\rho c_p^0 \frac{d\Theta}{dt} \approx -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \qquad (3.23.1)$$

with an error in Θ that is less than one percent of the error incurred by treating either $c_p^0 \theta$ or $c_p(S_A, \theta, 0) \theta$ as the "heat content" of seawater (McDougall (2003)). 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 $\rho \varepsilon$ in this equation.

Because the left-hand side of the First Law of Thermodynamics, (3.23.1), can be written as density times the material derivative of $c_p^0 \Theta$ it follows that Θ can be treated as a conservative variable in the ocean and that $c_p^0 \Theta$ 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 $\rho v h^0 = \rho v c_p^0 \Theta$ (here v is the northward velocity). The error in comparing this advective meridional "heat flux" with the air-sea heat flux is less than 1% of the error in so interpreting the area integral of either $\rho v c_p^0 \theta$ or $\rho v c_p(S_A, \theta, 0) \theta$. Similarly, turbulent diffusive fluxes of heat are accurately given by a turbulent diffusivity times the spatial gradient of $c_p^0 \Theta$ but are less accurately approximated by the same turbulent diffusivity times the spatial gradient of $c_p^0 \theta$ (see Appendix A.14 for a discussion of this point).

Because potential enthalpy is unknown and unknowable up to a linear function of Absolute Salinity (i. e. up to the arbitrary function $(a_1 - a_2 T_0) + (a_3 - a_4 T_0)S_A$ in terms of the constants defined in equation (2.6.2)), the advective transport of potential enthalpy $\rho h^0 \mathbf{u} = \rho c_p^0 \Theta \mathbf{u}$ is unknown up to arbitrary additional advective transports of mass $\rho \mathbf{u}$ and of salt $\rho S_A \mathbf{u}$. But since both mass and Absolute Salinity are conservative variables, this does not alter the conservation of potential enthalpy. Hence the fact that potential enthalpy is unknowable up to a linear function of Absolute Salinity does not affect the usefulness of potential enthalpy as a measure of "heat content" (this issue is discussed at length in McDougall (2003)).

3.24 Geopotential

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

$$\Phi = \int_0^z g(z') \, dz'. \qquad (3.24.1)$$

If the gravitational acceleration is taken to be constant Φ is simply gz. Note that height and Φ 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 Φ is measured in $J\,kg^{-1} = m^2\,s^{-2}$. If the ocean is assumed to be in hydrostatic balance so that $p_z = -g\rho$ (or $-g\,dz' = v\,dp'$) then the geopotential (3.24.1) may be expressed as the vertical pressure integral of the specific volume in the water column,

$$\Phi = \Phi^0 - \int_0^p v(p')\,dp', \tag{3.24.2}$$

where Φ^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.

3.25 Total Energy

The total energy $\mathcal{E}$ is the sum of specific internal energy u, kinetic energy per unit mass $0.5\mathbf{u}\cdot\mathbf{u}$, and the geopotential Φ,

$$\mathcal{E} = u + \Phi + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}. \tag{3.25.1}$$

Total energy $\mathcal{E}$ is not a function of only (S_A, 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 Φ,

$$\mathcal{B} = h + \Phi + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}. \tag{3.26.1}$$

Using the expression (3.2.1) that relates enthalpy and potential enthalpy, together with equation (3.24.2) for Φ, the Bernoulli function (3.26.1) may be written as

$$\mathcal{B} = h^0 + \Phi^0 + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} - \int_0^p v(p') - \hat{v}(S_A, \Theta, p')\,dp'. \tag{3.26.2}$$

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, Eq. (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 equation (3.7.3) has been used by Saunders (1995) to write (3.26.2) as (with the dynamic height anomaly Ψ defined in (3.27.1))

$$\mathcal{B} = h^0 + \Phi^0 + \Psi + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} - \int_0^p \hat{v}(S_{\mathrm{SO}}, 0°C, p') - \hat{v}(S_{\mathrm{A}}, \Theta, p')\, dp' \tag{3.26.3}$$

$$= h^0 + \Phi^0 + \Psi + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} - \hat{h}(S_{\mathrm{SO}}, 0°C, p) + \hat{h}(S_{\mathrm{SO}}, 0°C, 0) + \hat{h}(S_{\mathrm{A}}, \Theta, p) - \hat{h}(S_{\mathrm{A}}, \Theta, 0).$$

3.27 Dynamic Height Anomaly

The dynamic height anomaly Ψ given by the vertical integral

$$\Psi = -\int_0^p \delta(S_{\mathrm{A}}[p'], t[p'], p')\, dp' \tag{3.27.1}$$

is the geostrophic streamfunction for the flow at pressure p with respect to the flow at the sea surface. Thus the two-dimensional gradient of Ψ 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

$$\mathbf{k} \times \nabla_p \Psi = f\mathbf{v} - f\mathbf{v}_0. \tag{3.27.2}$$

This definition of dynamic height anomaly applies to all choices of the reference values $\tilde{S}_{\mathrm{A}}$ and $\hat{t}, \tilde{\theta}$ or $\hat{\Theta}$ in the definition $(3.7.1 - 3.7.4)$ of the specific volume anomaly δ. The specific volume anomaly δ in (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 (3.27.2) as 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 that worked with single-precision variables. Since computers now regularly employ double-precision, this issue has been overcome and consequently either δ or v can be used in the integrand of (3.27.1), so making it either the "dynamic height anomaly" or the "dynamic height".

The dynamic height anomaly Ψ should be quoted in units of $m^2\, s^{-2}$. These are the units in which the "gsw" library (Library C, Appendix L) outputs dynamic height anomaly. Note that the integration (3.27.1) of specific volume anomaly with pressure in dbar would yield dynamic height anomaly in units of $m^3\, kg^{-1} dbar$, however the use of these units in (3.27.2) would not give the resultant horizontal gradient in the same units as the product of the Coriolis parameter (units of s^{-1}) and the velocity (units of $m\, s^{-1}$) would normally be expressed in. This is the reason why dynamic height anomaly is output in $m^2\, s^{-2}$.

3.28 Montgomery Geostrophic Streamfunction

The Montgomery "acceleration potential" π defined by

$$\pi = p\delta - \int_0^p \delta(S_{\mathrm{A}}[p'], t[p'], p')\, dp' \tag{3.28.1}$$

is the geostrophic streamfunction for the flow in the specific volume anomaly surface $\delta(S_{\mathrm{A}}, t, p) = \delta_1$ relative to the flow at 0 dbar. Thus the two-dimensional gradient of π in the

δ_1 specific volume anomaly surface is simply related to the difference between the horizontal geostrophic velocity $\mathbf{v}$ in the $\delta = \delta_1$ surface and at the sea surface $\mathbf{v}_0$ according to

$$\mathbf{k} \times \nabla_{\delta_1} \pi = f\mathbf{v} - f\mathbf{v}_0 \quad \text{or} \quad \nabla_{\delta_1} \pi = -\mathbf{k} \times \left(f\mathbf{v} - f\mathbf{v}_0 \right). \tag{3.28.2}$$

The definition (3.28.1) of the Montgomery potential applies to all choices of the reference values $\widehat{S}_A$ and $\widehat{t}$ in the definition (3.7.2) of the specific volume anomaly δ. By carefully choosing these reference values the differences between the neutral tangent plane and the specific volume anomaly surface can be reduced (McDougall and Jackett (2007)).

It is not uncommon to read of authors using the Montgomery potential (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 potential (3.28.1) in a neutral tangent plane becomes (instead of (3.28.2) in the $\delta = \delta_1$ surface)

$$\nabla_n \pi = -\mathbf{k} \times \left(f\mathbf{v} - f\mathbf{v}_0 \right) + p \nabla_n \delta \tag{3.28.3}$$

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) showed that an arbitrary pressure offset, $\bar{p}$, can be subtracted from p in the first term in (3.28.1) without changing the properties of the Montgomery streamfunction in the δ_1 surface. That is, an alternative (and preferable) version of (3.28.1) is

$$\pi^{\text{Z-H}} = (p - \bar{p})\delta - \int_0^p \delta\left(S_A[p'], t[p'], p' \right) dp' \tag{3.28.4}$$

The gradient of the Montgomery potential (3.28.4) in a neutral tangent plane becomes

$$\nabla_n \pi^{\text{Z-H}} = -\mathbf{k} \times \left(f\mathbf{v} - f\mathbf{v}_0 \right) + (p - \bar{p})\nabla_n \delta , \tag{3.28.5}$$

where the last term can be made significantly smaller than the corresponding term in (3.28.3) by choosing the constant pressure $\bar{p}$ to be close to the average pressure on the surface (this was Zhang and Hogg's insight).

This term can be further minimized by suitably choosing the constant reference values $\tilde{S}_A$ and $\tilde{\Theta}$ in the definition (3.7.3) of specific volume anomaly $\tilde{\delta}$ so that this surface more closely approximates the neutral tangent plane (McDougall (1989)). This improvement is available because it can be shown that

$$\rho \nabla_n \tilde{\delta} = -\left[\kappa\left(S_A, \Theta, p \right) - \kappa\left(\tilde{S}_A, \tilde{\Theta}, p \right) \right] \nabla_n p \approx T_b^\Theta \left(\Theta - \tilde{\Theta} \right) \nabla_n p. \tag{3.28.6}$$

The last term in (3.28.5) is then approximately

$$(p - \bar{p})\nabla_n \tilde{\delta} \approx \tfrac{1}{2} \rho^{-1} T_b^\Theta \left(\Theta - \tilde{\Theta} \right) \nabla_n (p - \bar{p})^2 \tag{3.28.7}$$

and hence suitable choices of $\bar{p}$, $\tilde{S}_A$ and $\tilde{\Theta}$ can reduce the last term in (3.28.5) that represents the error in interpreting the Montgomery potential (3.28.4) as the geostrophic streamfunction in a surface that is more neutral than a specific volume anomaly surface.

The Montgomery potential should be quoted in units of $\text{m}^2 \text{ s}^{-2}$. These are the units in which the "gsw" library (Library C, Appendix L) outputs dynamic height anomaly. Note that the integration (3.28.1) or (3.28.4) of specific volume anomaly with pressure in dbar would

yield dynamic height anomaly in units of $\mathrm{m}^3\,\mathrm{kg}^{-1}\mathrm{dbar}$, however the use of these units in (3.28.2), (3.28.3) or (3.28.5) would not give the resultant horizontal gradient in the same units as normally used for the product of the Coriolis parameter (units of s^{-1}) and the velocity (units of $\mathrm{m\,s}^{-1}$). This is the reason why pressure in (3.28.4) is expressed in Pa and the Montgomery potential is output in $\mathrm{m}^2\,\mathrm{s}^{-2}$.

3.29 Cunningham Geostrophic Streamfunction

Cunningham (2000) and Alderson and Killworth (2005), following Killworth (1986) and Saunders (1995), suggested that a suitable streamfunction on a density surface in a compressible ocean would be the difference between the Bernoulli function $\mathscr{B}$ 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

$$
\begin{aligned}
\Pi \;&\equiv\; \mathscr{B} - h^0 - \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} - \Phi^0 \\
&= h - h^0 + \Phi - \Phi^0 \\
&= h(S_A,\Theta,p) - h(S_A,\Theta,0) - \int_0^p \hat{v}\big(S_A(p'),\Theta(p'),p'\big)\,dp'.
\end{aligned}
\tag{3.29.1}
$$

The last line of this equation has used the hydrostatic equation $p_z = -g\rho$ to express $\Phi \approx gz$ in terms of the vertical pressure integral of specific volume and the height of the sea surface where the geopotential is Φ^0.

The definition of potential enthalpy, (3.2.1), is used to rewrite the last line of (3.29.1), showing that Cunningham's Π is also equal to

$$
\Pi \;=\; -\int_0^p \hat{v}\big(S_A(p'),\Theta(p'),p'\big) - \hat{v}\big(S_A,\Theta,p'\big)\,dp'.
\tag{3.29.2}
$$

In this form it appears very similar to the expression (3.27.1) for dynamic height anomaly, the only difference being that in (3.27.1) the pressure-independent values of Absolute Salinity and Conservative Temperature were $(S_{SO},0°C)$ whereas here they are the local values on the surface, (S_A,Θ). While these local values of Absolute Salinity and Conservative Temperature are constant during the pressure integral in (3.29.2), they do vary with latitude and longitude along any "density" surface.

The gradient of Π along the neutral tangent plane is (from McDougall and Klocker (2010))

$$
\nabla_n \Pi \;\approx\; \left\{\tfrac{1}{\rho}\nabla_z p - \nabla\Phi_0\right\} - \tfrac{1}{2}\frac{T_b^\Theta}{\rho}p^2\nabla_n\Theta,
\tag{3.29.3}
$$

so that the error in $\nabla_n\Pi$ in using Π as the geostrophic streamfunction is approximately $-\tfrac{1}{2}\rho^{-1}T_b^\Theta\,p^2\nabla_n\Theta$. When using the Cunningham streamfunction Π in a potential density surface, the error in $\nabla_\sigma\Pi$ is approximately $-\tfrac{1}{2}\rho^{-1}T_b^\Theta\,p\big(2p_r-p\big)\nabla_\sigma\Theta$.

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 ω-surface of Klocker et al (2009) or a neutral density surface of Jackett and McDougall (1997)) a suitable reference seawater parcel $\left(\tilde{S}_A, \tilde{\Theta}, \tilde{p}\right)$ is selected from the approximately neutral surface that one is considering, and the specific volume anomaly $\tilde{\tilde{\delta}}$ is defined as in (3.7.3) above. The approximate geostrophic streamfunction is given by (from McDougall and Klocker (2010))

$$\varphi^n\left(S_A, \Theta, p\right) \;=\; \tfrac{1}{2}\left(p - \tilde{p}\right)\tilde{\tilde{\delta}}\left(S_A, \Theta, p\right) \;-\; \tfrac{1}{12}\frac{T_b^\Theta}{\rho}\left(\Theta - \tilde{\Theta}\right)\left(p - \tilde{p}\right)^2 \;-\; \int_0^p \tilde{\tilde{\delta}}\, dp'. \qquad (3.30.1)$$

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 $\nabla_n\varphi^n \approx \frac{1}{\rho}\nabla_z p - \nabla\Phi_0 = -\mathbf{k}\times\left(f\mathbf{v} - f\mathbf{v}_0\right)$ to a very good approximation.

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 $p_z = -g\rho$, the depth-integrated mass flux $\int \rho\mathbf{v}\,dz$ is given by $-g^{-1}\int \mathbf{v}\,dp$ and this motivates taking the pressure integral of the Dynamic Height Anomaly Ψ (from equation (3.27.1)) to form the Pressure-Integrated-Steric-Height PISH (also called Depth-Integrated Steric Height DISH by Godfrey (1989)),

$$\text{PISH} \;=\; \Psi' \;=\; g^{-1}\int_0^p \Psi\left(p''\right) dp'' \;=\; -g^{-1}\int_0^p \int_0^{p''} \delta\left(S_A[p'], t[p'], p'\right) dp'\, dp''$$

$$= -g^{-1}\int_0^p \left(p - p'\right)\delta\left(S_A[p'], t[p'], p'\right) dp'. \qquad (3.31.1)$$

The two-dimensional gradient of Ψ' is related to the depth-integrated mass flux of the velocity difference with respect to the velocity at zero pressure, $\mathbf{v}_0$, according to

$$\mathbf{k}\times\nabla_p\Psi' \;=\; f\int_{z(p)}^{z(p=0)} \rho\left[\mathbf{v}(z') - \mathbf{v}_0\right] dz' \;=\; g^{-1}f\int_0^p \left[\mathbf{v}(p') - \mathbf{v}_0\right] dp'. \qquad (3.31.2)$$

The definition (3.31.1) of PISH applies to all choices of the reference values $\hat{\hat{S}}_A$, $\tilde{S}_A$ and $\hat{\hat{t}}$, $\tilde{\theta}$ or $\tilde{\Theta}$ in the definition (3.7.2 – 3.7.4) of the specific volume anomaly.

Since the velocity at depth in the ocean is generally much smaller that at the sea surface, it is customary to take the reference pressure to be some constant (deep) pressure p_1 so that (3.27.1) becomes

$$\Psi \;=\; \int_p^{p_1} \delta\left(S_A[p'], t[p'], p'\right) dp' \qquad (3.31.3)$$

and PISH is

$$\mathrm{PISH} = \Psi' = g^{-1} \int\limits_0^{p_1} \Psi(p'') \, dp'' = g^{-1} \int\limits_0^{p_1} \int\limits_{p''}^{p_1} \delta\big(S_\mathrm{A}[p'], t[p'], p'\big) \, dp' \, dp''$$

$$= g^{-1} \int\limits_0^{p_1} p' \, \delta\big(S_\mathrm{A}[p'], t[p'], p'\big) \, dp' \tag{3.31.4}$$

$$= \tfrac{1}{2} g^{-1} \int\limits_0^{p_1^2} \delta\big(S_\mathrm{A}[p'], t[p'], p'\big) \, d\big(p'^2\big).$$

The two-dimensional gradient of Ψ' is now related to the depth-integrated mass flux of the velocity difference with respect to the velocity at p_1, $\mathbf{v}_1$, according to

$$\mathbf{k} \times \nabla_p \Psi' = f \int\limits_{z(p_1)}^{z(p=0)} \rho\big[\mathbf{v}(z') - \mathbf{v}_1\big] dz' = g^{-1} f \int\limits_0^{p_1} \big[\mathbf{v}(p') - \mathbf{v}_1\big] dp'. \tag{3.31.5}$$

The specific volume anomaly δ in (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 Ψ' does not affect (3.31.2) or (3.31.5) as the additional term is a function only of pressure. With specific volume in place of specific volume anomaly, (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)).

PISH 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 $\rho\big[\mathbf{v}(z') - \mathbf{v}_1\big]$ times the Coriolis frequency. These are the units in which the "gsw" library (Library C, Appendix L) outputs PISH.

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 Θ (or potential temperature θ) are piecewise constant in the vertical, the geopotential

$$\Phi = \Phi^0 - \int\limits_0^p v(p') \, dp', \tag{3.32.1}$$

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

$$\Phi = \Phi^0 - \int\limits_0^p v(p') \, dp' = \Phi^0 - \sum_{i=1}^{n-1} \Big[\hat{h}\big(S_\mathrm{A}^i, \Theta^i, p^{i+1}\big) - \hat{h}\big(S_\mathrm{A}^i, \Theta^i, p^i\big) \Big]. \tag{3.32.2}$$

3.33 Freezing Temperature

The freezing temperature of seawater t_f is found by equating the chemical potential of water in seawater μ^W with the chemical potential of ice μ^{Ih}, so that it is found by solving implicitly the equation

$$\mu^W \left(S_A, t_f, p \right) = \mu^{Ih} \left(t_f, p \right) \qquad (3.33.1)$$

or equivalently, in terms of the two Gibbs functions,

$$g \left(S_A, t_f, p \right) - S_A \, g_{S_A} \left(S_A, t_f, p \right) = g^{Ih} \left(t_f, p \right). \qquad (3.33.2)$$

The Gibbs function for ice Ih, $g^{Ih} \left(t, p \right),$ is defined by IAPWS-06 and Feistel and Wagner (2006) and is summarized in Appendix H below. Thermodynamic arguments can also be used to calculate the isobaric latent heat of melting of ice.

3.34 Boiling Temperature

To be written.

Thermodynamic arguments can also be used to calculate the isobaric latent heat of evaporation of water.

4. CONCLUSIONS

The International Thermodynamic Equation of Seawater – 2010 (TEOS-10) allows all the thermodynamic properties of pure water, ice Ih and seawater to be evaluated in an internally self-consistent manner. Ice Ih is the naturally abundant form of ice, having hexagonal crystals. The related properties of water vapour and of moist air are also accessible by using the IAPWS-95 Helmholtz function for water vapour and code to evaluate these properties is included in the Libraries A and B discussed in the Introduction. 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 as large as ten times the precision of our 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 measure of the salinity of seawater. Importantly, Practical Salinity is retained as the salinity variable that is stored in data bases 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 (e. g. density and enthalpy) 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 and enthalpy 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. Just as potential temperature rather than *in situ* temperature is used (i) in ocean models, (ii) to plot data and (iii) for theoretical studies, so too Absolute Salinity should be used as the prognostic variable in ocean models, as an axis on $S_A - \Theta$ diagrams and in theoretical studies.

Conceptually we can categorize in situ temperature *t* and Practical Salinity S_P as the variables that are measured at sea, while absolute Salinity S_A and Conservative Temperature Θ (or less accurately potential temperature θ) are the variables that should be used as the prognostic variables of ocean models, as the axes of plots in publications (such as $S_A - \Theta$ diagrams) and for theoretical studies, since it is these variables that possess both the "potential" and "conservative" properties.

Ocean models already treat their prognostic variables as possessing the "conservative" property, and the interaction of the ocean with the ice and the atmosphere already proceeds in a manner consistent with the ocean model's salinity variable being Absolute Salinity (see Jackett et al. (2006)), with the caveat that the remineralization of particulate organic matter is a process that should be included as a source term in the Absolute Salinity conservation equation in ocean models. If this caveat can be ignored, then in order to make ocean models totally consistent with TEOS-10 they need to be initialized with Absolute Salinity and the salinity output of the models need to be compared with Absolute Salinity values derived from observations.

Similarly, 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 Θ. To complete the transition to Θ in ocean modeling, the models should be initialized with Θ rather than θ, the output temperature must be compared with observed Θ data rather than to θ 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 $\theta = \theta(S_A, \Theta)$. The final ingredient needed for an ocean model is a computationally efficient form of density in terms of the model variables, that is $\rho = \hat{\rho}(S_A, \Theta, p)$, such as that produced by McDougall et al. (2003) and Jackett et al. (2006), but in future based on the TEOS-10 description of the saline part of the Gibbs function of seawater (Feistel (2008), IAPWS-08). [Such an updated version of the $\hat{\rho}(S_A, \Theta, p)$ equation of Jackett et al. (2006) is expected to be available during 2009].

As a reminder, some of the relevant TEOS-10 papers and the gsw computer software can be downloaded from www.TEOS-10.org.

Acknowledgements

APPENDIX A: Background Theoretical Constructs 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.

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 $t/°C = T/K - 273.15$, and 1 °C is the same size as 1 K.

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) which was replaced 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°C), while in ITS-90 R_0 is R(0.01°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 $0\,°C < t_{90} < 968.71\,°C$, 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 $0\,°C < t_{90} < 40\,°C$ 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 and 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. It is therefore not possible to seek a unique and perfect conversion between IPTS-68 and ITS-90.

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.

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.

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

$$(T_{90} - T_{68})/\text{K} = -0.00025(T_{68}/\text{K} - 273.15) \tag{A.1.1}$$

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

$$(t_{90}/\text{°C}) = (t_{68}/\text{°C})/1.00024. \tag{A.1.2}$$

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_{68} for the boiling point of water was
100 °C while its t_{90} 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 oceanograohic temperature range within the
limitations of the temperature scales.

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_{90} (Rusby, pers. comm.), which may be as high as a couple of mK in the region of interest. This is being investigated by CCT, and may eventually lead to a new temperature scale ITS-20XX. However, there is no formal project to revise it yet, and no new scale will be defined before 2010.

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 either the uncertainty in thermodynamic temperature, or 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. 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 (A.1.3) thus

$$\left(t_{68}/°C\right) = 1.00024 \left(t_{90}/°C\right). \tag{A.1.3}$$

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, $P_0 \equiv 101\,325\,\text{Pa}$; that is $p \equiv P - P_0$. 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^{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.

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, $P_0 \equiv 101\,325\,\text{Pa}$. (When the CTD is lowered from the sea

surface, the monitoring software may display gauge pressure, indicating the distance from the surface.)

Since there is 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 mmHg = 1.000 000 142 466 321... torr. The torr is defined as exactly 1/760 of the Absolute Pressure of one standard atmosphere, so that one torr is equal to (101325/760) Pa.

Table A.2.1 Pressure unit conversion table

	Pascal (Pa)	bar (bar)	Technical atmosphere (at)	atmosphere (atm)	torr (Torr)	pound-force per square inch (psi)
1 Pa	$\equiv 1$ N/m^2	10^{-5}	10.197×10^{-6}	9.8692×10^{-6}	7.5006×10^{-3}	145.04×10^{-6}
1 bar	100 000	$\equiv 10^6$ dyn/cm^2	1.0197	0.986 92	750.06	14.503 7744
1 at	98 066.5	0.980 665	$\equiv 1$ kgf/cm^2	0.967 841	735.56	14.223
1 atm	101 325	1.013 25	1.0332	$\equiv 1$ atm	760	14.696
1 torr	133.322	1.3332×10^{-3}	1.3595×10^{-3}	1.3158×10^{-3}	$\equiv 1$ Torr	19.337×10^{-3}
1 psi	6 894.757	68.948×10^{-3}	70.307×10^{-3}	68.046×10^{-3}	51.715	$\equiv 1$ lbf/in^2

Example: 1 Pa = 1 N/m^2 = 10^{-5} bar = 10.197×10^{-6} at = 9.8692×10^{-6} atm, etc.

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. The Reference Composition is perfectly consistent with charge balance of ocean waters and the most recent atomic weights (Weiser (2006)). Seawater with this reference composition has Absolute Salinity S_A equal to the Reference-Composition Salinity S_R as defined below.

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 (2001), 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 32.435 6 g kg^{-1} when both are at the ITS-90 temperature $t =$ 14.996 °C and one standard atmosphere pressure, $P = 101\ 325$ 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 (Weiser (2006)).

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

$$S_{R12} = \frac{m_1 S_{R1} + m_2 S_{R2}}{m_1 + m_2}.$$
(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 chosen to normalize the seawater sample, then $S_{R12} = 35.165\ 04$ g kg^{-1} and the original Reference-Composition Salinity of sample 1 is given by

$$S_{R1} = [1 + (m_2 / m_1)] \times 35.165\ 04 \text{ g kg}^{-1}.$$
(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 note that in the above definitions a Practical Salinity of 35 is associated with a Reference Salinity of 35.16504 g kg^{-1}. This value was determined by Millero et al. (2008a) using the reference composition model, the most recent atomic weights (Weiser (2006)) and the relation $S = 1.80655\ Cl / (\text{g kg}^{-1})$ 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 for 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

$$S_R \approx u_{PS}\, S_P \qquad \text{where} \qquad u_{PS} \equiv (35.165\,04/35)\ \text{g kg}^{-1}. \qquad\qquad \text{(A.3.3)}$$

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 of a seawater sample, like the Reference Salinity, is intended to be precisely conservative during mixing and during changes in temperature and pressure without exchange of mass with its surroundings.

Clearly, a seawater sample whose Practical Salinity $S_P = 35$ has a Reference-Composition 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}. Thus the numerical difference is roughly 24 times larger than the uncertainty in using Reference Salinity as a measure of Absolute Salinity. The difference is also large compared to our ability to measure salinity at sea (which can be as precise as ± 0.002 g kg^{-1}). 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 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(‰) from measurements of Cl(‰) 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,

$$S(‰) = 0.03 + 1.805\ Cl(‰). \qquad\qquad \text{(A.3.4)}$$

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. To achieve this consistency while having salinity directly proportional to chlorinity, it was decided to determine the proportionality constant from Knudsen's formula at S = 35 ‰ (Cl = 19.3740 ‰). This resulted in the conversion formula

$$S(‰) = 1.80655\ Cl(‰) \qquad\qquad \text{(A.3.5)}$$

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 gives a best estimate of Absolute Salinity for Standard Seawater and 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 spatial variations of seawater composition into the procedure for estimating Absolute Salinity.

A.4 Absolute Salinity

Absolute Salinity S_A is defined to be the ratio of the mass of dissolved material in seawater to the total mass of seawater. Millero et al. (2008a) list the following six advantages of adopting Reference Salinity S_R 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 (g kg^{-1}), as a measure of Absolute Salinity. This approach could 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 Salinity with its known salt composition, but only uncertainly with respect to IAPSO Standard Seawater with unknown composition. These variations in the composition of seawater cause significant 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)),

$$34 \text{ g/kg} = 34 \text{ mg/g} = 0.034 \text{ kg/kg} = 0.034 = 3.4\ \% = 34\ 000 \text{ ppm} = 34\ 000 \text{ mg/kg.} \quad \text{(A.4.1)}$$

In particular, it is strictly correct to write the freshwater fraction of seawater as either $(1 - 0.001\ S_A/(\text{g kg}^{-1}))$ 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 g kg^{-1} as the preferred unit for S_A, (as in $S_A = 35.165\ 04$ 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 is the concentration variable that was used in the lab experiments for the fundamental determinations of the equation of state and other properties but was disregarded for field measurements with the definition of PSS-78 (Millero (2008)). Derived from its stoichiometric definition in the case of Reference Composition, Chlorinity Cl of Standard Seawater given in ‰ is converted to the Reference Salinity, $S_R = u_{Cl}\, Cl$, by the numerical factor $u_{Cl} = 1.806\,55\, u_{PS}$.

Regarding point number 6, the composition of the 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 closed 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. The thermodynamic properties of seawater are more accurately written as functions of Absolute Salinity (as well as of temperature and pressure) rather than as functions of Practical Salinity (Millero, 1974). This is the case because the properties of most dilute natural waters, including seawater containing added salts, are similar to the values of seawater at the same Absolute Salinity (Millero et al., 1978). All the physical 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. Some of the variable nonelectrolytes (e.g., SiO_2, CO_2 and dissolved organic material) do not have a conductivity signal. It is for this reason that the new thermodynamic definition of seawater (IAPWS-2008, Feistel (2008)) has the Gibbs function g of seawater expressed as a function of Absolute Salinity as $g\left(S_A, t, p\right)$ rather than as a function of Practical Salinity S_P or of Reference Salinity, S_R.

A.5 Spatial Variations in Seawater Composition: A First Algorithm for S_A

In a series of papers Millero et al. (1976a, 1978, 2000, 2008b) and McDougall et al. (2009) 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 (A.3.3), while the density measurement ρ^{meas} implies an Absolute Salinity S_A by using the equation of state and the equality $\rho^{\text{meas}} = \rho\left(S_A,\, 25\,°C,\, 0\,\text{dbar}\right)$. The difference between these two salinity measures is taken to be due to the composition of the sample being different to the Reference Composition. In these papers Millero established that the salinity difference $S_A - S_R$ could be estimated from knowledge of just the silicate concentration of the fluid sample. The reason for the good 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, 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.

This relationship between the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ and silicate concentration has been exploited by McDougall, Jackett and Millero (2009a) in a computer algorithm that uses an existing global data base of silicate 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 method of determining Absolute Salinity from readily measured quantities is the least mature aspect of the new thermodynamic description of seawater. It is expected, as new data (particularly density data) becomes available, that the determination of Absolute Salinity will improve. The computer software, in both FORTRAN and MATLAB, which evaluates Absolute Salinity S_A given the input variables Practical Salinity S_P, longitude φ, latitude λ and sea pressure p (in dbar) is available at www.TEOS-10.org.

A.6 The 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 Ih and seawater is described in Feistel et al. (2008).

The internationally accepted thermodynamic definition 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 °C $< t <$ 374 °C and 600 Pa $< p + P_0 <$ 1000 MPa) however it is a computationally expensive algorithm. 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 °C (specifically from $-\left[2.65 + (p+P_0) \times 0.0743 \text{ MPa}^{-1} \right]$ °C to 40 °C), and in the pressure range 0 $< p <$ 10^4 dbar we also recommend the use of the pure water part of the Gibbs function of Feistel (2003) which may soon also be released as an IAPWS Supplementary Release, perhaps as soon as 2009 as IAPWS-09.

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 essentially 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 m s^{-1} from Del Grosso's (1974) formula for seawater at high pressures and temperature below 5 $^{\circ}$C. Chen and Millero (1977) only measured the differences in the sound speed 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

$$\mathrm{d}h - v\,\mathrm{d}p = (T_0 + t)\mathrm{d}\eta + \mu\,\mathrm{d}S_{\mathrm{A}}. \qquad (A.7.1)$$

A readable derivation of the fundamental thermodynamic relation can be found in Warren (2006). The left-hand side of this equation is often written as $\mathrm{d}u + (p + P_0)\mathrm{d}v$ 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, η is the specific entropy and μ is the relative chemical potential. In fluid dynamics we usually deal with material derivatives, d/dt, that is, derivatives defined following the fluid motion, $\mathrm{d}/\mathrm{d}t = \partial/\partial t + \mathbf{u}\cdot\nabla$ where $\mathbf{u}$ is the fluid velocity. In terms of this type of derivative, and assuming local thermodynamic equilibrium, the fundamental thermodynamic relation is

$$\frac{\mathrm{d}h}{\mathrm{d}t} - \frac{1}{\rho}\frac{\mathrm{d}p}{\mathrm{d}t} = (T_0 + t)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}. \qquad (A.7.2)$$

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

$$(\rho C)_t + \nabla \cdot (\rho C \mathbf{u}) = \rho \frac{dC}{dt} = -\nabla \cdot \mathbf{F}^C. \tag{A.8.1}$$

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

Quantities that are conservative in the ocean are

(1) mass [$C = 1$ and $\mathbf{F}^C = \mathbf{0}$ in equation (A.8.1)],
(2) Absolute Salinity S_A,
(3) freshwater fraction $(1 - S_A)$, and
(4) Total Energy $\mathcal{E} = u + 0.5 \mathbf{u} \cdot \mathbf{u} + \Phi$ (see equation (B15)).

The middle part of (A.8.1) has used the continuity equation (which is the equation for the conservation of mass)

$$\partial \rho / \partial t \big|_{x, y, z} + \nabla \cdot (\rho \mathbf{u}) = 0. \tag{A.8.2}$$

Other variables such as potential temperature θ, enthalpy h, potential enthalpy h^0, Conservative Temperature Θ, internal energy u, entropy η, density ρ, potential density ρ_θ, specific volume anomaly δ and the Bernoulli function $\mathcal{B} = h + 0.5 \mathbf{u} \cdot \mathbf{u} + \Phi$ (see equation (B17)) are not conservative variables. Note that Θ and h^0 are however conservative variables at $p = 0$ (if the tiny dissipation of mechanical energy inside the control volume is ignored).

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 (1) mass, (2) Absolute Salinity S_A, (3) freshwater fraction $(1 - S_A)$ and total energy $\mathcal{E}$ are "isobaric conservative". In addition, the Bernoulli function $\mathcal{B}$ is also "isobaric conservative".

Some variables that are not "isobaric conservative" include potential temperature θ, potential enthalpy h^0, Conservative Temperature Θ, internal energy u, entropy η, density ρ, potential density ρ^Θ, and specific volume anomaly δ. Enthalpy h is not exactly "isobaric conservative" because enthalpy increases when the kinetic energy of fluid motion is dissipated by molecular viscosity inside the control volume. However, this is a tiny effect in the First Law of Thermodynamics and traditionally we regard enthalpy h as an "isobaric conservative" variable. Note that while h is "isobaric conservative", it is not a "conservative" variable.

McDougall (2003) showed that for all practical purposes we can treat Θ and h^0 as being both "conservative" and "isobaric conservative" variables (doing so ignores the dissipation of

mechanical energy and another term of comparable magnitude). Hence for all practical purposes in oceanography we have mass and five other variables that are both "conservative" and "isobaric conservative";

(1) Absolute Salinity S_A,

(2) freshwater fraction $(1 - S_A)$,

(3) Conservative Temperature Θ,

(4) potential enthalpy h^0 referenced to $p_r = 0$ and

(5) total energy $\mathcal{E}$.

Since the freshwater fraction is trivially related to Absolute Salinity, and since Θ is simply proportional to h^0, in essence we have mass and just three other variables, S_A, Θ and $\mathcal{E}$ that are both "conservative" and "isobaric conservative".

We note that for Absolute Salinity S_A the flux $\mathbf{F}^S$ in (A.8.1) is the molecular flux of salt and is given by equation (58.11) of Landau and Lifshitz (1959), consisting not only of the usual molecular diffusivity times $-\rho \nabla S_A$ but also 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 so-called 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.

If the ocean were in thermodynamic equilibrium, its temperature would be the same everywhere as would the chemical potential 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 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 Absolute Salinity S_A and entropy η. The constancy of entropy η can be seen from the First Law of Thermodynamics in (B19) below; with the right-hand side of (B19) 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^0, Conservative Temperature Θ and potential density ρ^Θ (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 $\mathcal{E}$ and the Bernoulli function $\mathcal{B}$. From eq. (B17) we notice that in the absence of molecular fluxes, the Bernoulli function $\mathcal{B}$ 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 $\mathcal{E}$ is explained in the discussion following eq. (B15).

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.

In Appendix A.8 above we concluded that only mass, and the three variables S_A, $\mathcal{E}$ and Θ (approximately) are both "conservative" and "isobaric conservative". Since $\mathcal{E}$ does not posses the "potential" property, we now conclude that only mass and the two variables S_A and Θ posses all three highly desired properties, namely that they are "conservative", "isobaric conservative" and "potential" variables. In the case of Conservative Temperature Θ, its "conservative" and "isobaric conservative" nature is approximate:- while Θ is not a 100% conservative variable, it is two orders of magnitude closer to being a totally conservative variable than are either potential temperature or entropy. Hence for all practical purposes we may take Θ to be both a "conservative" variable and an "isobaric conservative" variable. Also S_A and Θ are thermodynamic quantities, that is, they are functions of only (S_A, t, p) whereas $\mathcal{E}$ is a not a thermodynamic quantity.

In Table A.9.1 various oceanographic variables are categorized according to whether or not they posses the "potential" property, whether or not they are "conservative" variables, whether or not they are "isobaric conservative" variables, and whether or not they are thermodynamic quantities. Note that S_A and Θ (and h^0) are the only variables that achieve four "ticks" in this table.

Table A.9.1 The "Potential", "Conservative", "Isobaric Conservative" and
"Thermodynamic" nature of various Oceanographic Variables

Variable symbol	"Potential"?	"Conservative"?	"Isobaric Conservative"?	"Thermodynamic Variable"?
S_A	✓	✓	✓	✓
t	✗	✗	✗	✓
θ	✓	✗	✗	✓
η	✓	✗	✗	✓
h	✗	✗	✓[1]	✓
Θ, h^0	✓	✓[2]	✓[2]	✓
u	✗	✗	✗	✓
$\mathcal{B}$	✗	✗	✓	✗
$\mathcal{E}$	✗	✓	✓	✗
ρ, v	✗	✗	✗	✓
ρ_Θ	✓	✗	✗	✓
δ	✗	✗	✗	✓
ρ_v	✗	✗	✗	✓[3]
γ^n	✗	✗	✗	✗

[1] Taking ε to be negligible.

[2] Taking ε and other terms of similar size to be negligible (see the discussion following eq. (A.20.8).

[3] Once the reference sound speed function $c_0(p,\rho)$ has been decided upon.

A.10 Proof that $\theta = \theta(S_A,\eta)$ and $\Theta = \Theta(S_A,\theta)$

Consider changes occurring at the sea surface, (specifically at 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 μ to be functions of entropy η (in place of temperature t), that is, considering the functional form of h and μ to be $h = h(S_A,\eta,p)$ and $\mu = \mu(S_A,\eta,p)$, it follows from (A.7.1) that

$$h_\eta(S_A,\eta,0)\,\mathrm{d}\eta + h_{S_A}(S_A,\eta,0)\,\mathrm{d}S_A = (T_0+\theta)\mathrm{d}\eta + \mu(S_A,\eta,0)\,\mathrm{d}S_A, \qquad (A.10.1)$$

which shows that specific entropy η is simply a function of Absolute Salinity S_A and potential temperature θ, that is $\eta = \eta(S_A,\theta)$, with no separate dependence on pressure. It follows that $\theta = \theta(S_A,\eta)$. Similarly, from the definition of potential enthalpy and Conservative Temperature in (3.2.1) and (3.3.1), at $p = 0$ dbar it can be seen that (A.7.1) implies

$$c_p^0\,\mathrm{d}\Theta = (T_0+\theta)\mathrm{d}\eta + \mu(S_A,\theta,0)\,\mathrm{d}S_A. \qquad (A.10.2)$$

This shows that Conservative Temperature is also simply a function of Absolute Salinity and potential temperature, $\Theta = \Theta(S_A, \theta)$, with no separate dependence on pressure. It then follows that Θ may also be expressed as a function of only S_A and η.

A.11 The 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 η, θ and Θ as well as in situ temperature t.

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

$$\partial h / \partial S_A \big|_{T,p} = \mu(S_A, t, p) - (T_0 + t)\mu_T(S_A, t, p), \tag{A.11.1}$$

$$\partial h / \partial T \big|_{S_A, p} = c_p(S_A, t, p) = (T_0 + t)\eta_T(S_A, t, p), \tag{A.11.2}$$

and

$$\partial h / \partial p \big|_{S_A, T} = v(S_A, t, p) - (T_0 + t)v_T(S_A, t, p). \tag{A.11.3}$$

Now considering specific enthalpy to be a function of entropy (rather than of temperature t), that is, taking $h = \widehat{h}(S_A, \eta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\widehat{h}_\eta \, d\eta + \widehat{h}_{S_A} dS_A = (T_0 + t)d\eta + \mu dS_A \quad \text{while} \quad \partial\widehat{h}/\partial p \big|_{S_A, \eta} = v, \tag{A.11.4}$$

so that

$$\partial\widehat{h}/\partial\eta \big|_{S_A, p} = (T_0 + t) \quad \text{and} \quad \partial\widehat{h}/\partial S_A \big|_{\eta, p} = \mu. \tag{A.11.5}$$

Now taking specific enthalpy to be a function of potential temperature (rather than of temperature t), that is, taking $h = \tilde{h}(S_A, \theta, p)$, the fundamental thermodynamic relation (A.7.1) becomes

$$\tilde{h}_\theta \, d\theta + \tilde{h}_{S_A} dS_A = (T_0 + t)d\eta + \mu dS_A \quad \text{while} \quad \partial\tilde{h}/\partial p \big|_{S_A, \theta} = v. \tag{A.11.6}$$

To evaluate the $\tilde{h}_\theta$ partial derivative, it is first written in terms of the derivative with respect to entropy as

$$\tilde{h}_\theta \big|_{S_A, p} = \eta_\theta \big|_{S_A} \widehat{h}_\eta \big|_{S_A, p} = \eta_\theta \big|_{S_A} (T_0 + t), \tag{A.11.7}$$

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 $p = 0$)

$$\tilde{h}_\theta \big|_{S_A, p=0} = c_p(S_A, \theta, 0) = \eta_\theta \big|_{S_A} (T_0 + \theta). \tag{A.11.8}$$

These two equations are used to arrive at the desired expression for $\tilde{h}_\theta$ namely

$$\tilde{h}_\theta\big|_{S_A,p} = c_p(S_A,\theta,0)\frac{(T_0+t)}{(T_0+\theta)}. \tag{A.11.9}$$

To evaluate the $\tilde{h}_{S_A}$ 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

$$\tilde{h}_{S_A}\big|_{\theta,p} = \hat{h}_{S_A}\big|_{\eta,p} + \hat{h}_\eta\big|_{S_A,p}\,\eta_{S_A}\big|_\theta. \tag{A.11.10}$$

The partial derivative of specific entropy $\eta = -g_T$ with respect to Absolute Salinity, $\eta_{S_A} = -g_{S_A T}$, is also equal to $-\mu_T$ since chemical potential is defined by (18) as $\mu = g_{S_A}$. Since the partial derivative $\eta_{S_A}\big|_\theta$ in (A.11.10) is performed at fixed potential temperature (rather than at fixed in 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 $\tilde{h}_{S_A}$ namely

$$\tilde{h}_{S_A}\big|_{\theta,p} = \mu(S_A,t,p) - (T_0+t)\mu_T(S_A,\theta,0). \tag{A.11.11}$$

Notice that this expression contains some things that are evaluated at the general pressure p and one evaluated at the reference pressure $p = 0$.

We now move on to consider 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

$$\hat{h}_\Theta\,d\Theta + \hat{h}_{S_A}\,dS_A = (T_0+t)\,d\eta + \mu\,dS_A \quad \text{while} \quad \partial\hat{h}/\partial p\big|_{S_A,\Theta} = v. \tag{A.11.12}$$

The partial derivative $\hat{h}_\Theta$ follows directly form this equation as

$$\hat{h}_\Theta\big|_{S_A,p} = (T_0+t)\eta_\Theta\big|_{S_A,p} = (T_0+t)\eta_\Theta\big|_{S_A}. \tag{A.11.13}$$

At $p = 0$ this equation reduces to

$$\hat{h}_\Theta\big|_{S_A,p=0} = c_p^0 = (T_0+\theta)\eta_\Theta\big|_{S_A}, \tag{A.11.14}$$

and combining these two equations gives the desired expression for $\hat{h}_\Theta$ namely

$$\hat{h}_\Theta\big|_{S_A,p} = \frac{(T_0+t)}{(T_0+\theta)}\,c_p^0. \tag{A.11.15}$$

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 (using both parts of (A.11.5))

$$\tilde{h}_{S_A}\big|_{\Theta,p} = \mu(S_A,t,p) + (T_0+t)\eta_{S_A}\big|_\Theta. \tag{A.11.16}$$

The differential expression (A.11.12) can be evaluated at $p = 0$ where the left-hand side is simply $c_p^0 d\Theta$ so that from (A.11.12) we find that

$$\eta_{S_A}\big|_\Theta = -\frac{\mu(S_A,\theta,0)}{(T_0+\theta)}, \tag{A.11.17}$$

so that the desired expression for $\hat{h}_{S_A}$ is

$$\boxed{\hat{h}_{S_A}\Big|_{\Theta,p} = \mu(S_A,t,p) - \frac{(T_0+t)}{(T_0+\theta)}\mu(S_A,\theta,0).}$$ (A.11.18)

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 The Differential Relationships between η, θ and Θ

Evaluating the fundamental thermodynamic relation in the forms (A.11.6) and (A.11.12) using the four boxed equations in the above Appendix A.11, we find the relations

$$
\begin{aligned}
(T_0+t)\,d\eta + \mu(p)\,dS_A &= \frac{(T_0+t)}{(T_0+\theta)}\,c_p(0)\,d\theta + \left[\mu(p) - (T_0+t)\mu_T(0)\right]dS_A \\
&= \frac{(T_0+t)}{(T_0+\theta)}\,c_p^0\,d\Theta + \left[\mu(p) - \frac{(T_0+t)}{(T_0+\theta)}\mu(0)\right]dS_A .
\end{aligned}
$$ (A.12.1)

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

$$(T_0+\theta)\,d\eta = c_p(0)\,d\theta - (T_0+\theta)\mu_T(0)\,dS_A = c_p^0\,d\Theta - \mu(0)\,dS_A .$$ (A.12.2)

From this follows all the following partial derivatives between η, θ and Θ,

$$\Theta_\theta\big|_{S_A} = c_p(S_A,\theta,0)/c_p^0, \qquad \Theta_{S_A}\big|_\theta = \left[\mu(S_A,\theta,0) - (T_0+\theta)\mu_T(S_A,\theta,0)\right]/c_p^0,$$ (A.12.3)

$$\Theta_\eta\big|_{S_A} = (T_0+\theta)/c_p^0, \qquad \Theta_{S_A}\big|_\eta = \mu(S_A,\theta,0)/c_p^0,$$ (A.12.4)

$$\theta_\eta\big|_{S_A} = (T_0+\theta)/c_p(S_A,\theta,0), \qquad \theta_{S_A}\big|_\eta = (T_0+\theta)\mu_T(S_A,\theta,0)/c_p(S_A,\theta,0).$$ (A.12.5)

$$\theta_\Theta\big|_{S_A} = c_p^0/c_p(S_A,\theta,0), \qquad \theta_{S_A}\big|_\Theta = -\left[\mu(S_A,\theta,0) - (T_0+\theta)\mu_T(S_A,\theta,0)\right]/c_p(S_A,\theta,0).$$ (A.12.6)

$$\eta_\theta\big|_{S_A} = c_p(S_A,\theta,0)/(T_0+\theta), \qquad \eta_{S_A}\big|_\theta = -\mu_T(S_A,\theta,0).$$ (A.12.7)

$$\eta_\Theta\big|_{S_A} = c_p^0/(T_0+\theta), \qquad \eta_{S_A}\big|_\Theta = -\mu(S_A,\theta,0)/(T_0+\theta).$$ (A.12.8)

A.13 The First Law of Thermodynamics

The law of the conservation of energy for thermodynamic equilibrium states was discovered in the 19th century, formulated as a balance between internal energy, heat and work similar to the fundamental equation (A.7.1) by Gibbs (1873) and other early pioneers, 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" (A.13.1) (Landau and Lifshitz (1959), McDougall (2003), Griffies (2004)).

The First Law of Thermodynamics can therefore be written as (see also equation (B19) and the other equations (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)

$$\rho \left(\frac{\mathrm{d}h}{\mathrm{d}t} - \frac{1}{\rho} \frac{\mathrm{d}p}{\mathrm{d}t} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho\varepsilon \qquad (A.13.1)$$

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 equation (B24) below). Lastly, ε is the rate of dissipation of mechanical energy per unit mass, transformed into internal energy. 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, 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,

$$\partial(\rho h)/\partial t + \nabla \cdot (\rho\mathbf{u}h) - \frac{\mathrm{d}p}{\mathrm{d}t} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho\varepsilon. \qquad (A.13.2)$$

One then integrates over the volume that encompasses both fluid parcels while ignoring any radiative, boundary and molecular fluxes across the boundary of the control volume. The volume that encloses both original fluid parcels may change with time as the fluid moves (at constant pressure), mixes and contracts. The dissipation of mechanical energy by viscous friction is also commonly ignored during such mixing processes but in fact $\rho\varepsilon$ does cause a small increase in the enthalpy of the mixture with respect to that of the two original parcels. Apart from the dissipation term, under these assumptions (A.13.2) reduces to the statement that the volume integrated amount of ρh 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.

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

$$\rho\left((T_0+t)\frac{d\eta}{dt} + \mu\frac{dS_A}{dt} \right) = -\nabla\cdot\mathbf{F}^R - \nabla\cdot\mathbf{F}^Q + \rho\varepsilon \ . \tag{A.13.3}$$

The First Law of Thermodynamics (A.13.1) can also be written in terms of potential temperature θ (with respect to reference pressure p_r) as (from Bacon and Fofonoff (1996) and McDougall (2003), using equations (A.11.9) and (A.11.11) above)

$$\rho\left(\frac{(T_0+t)}{(T_0+\theta)}c_p(p_r)\frac{d\theta}{dt} + \left[\mu(p) - (T_0+t)\mu_T(p_r) \right]\frac{dS_A}{dt} \right) = -\nabla\cdot\mathbf{F}^R - \nabla\cdot\mathbf{F}^Q + \rho\varepsilon, \tag{A.13.4}$$

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

$$\rho\left(\frac{(T_0+t)}{(T_0+\theta)}c_p^0\frac{d\Theta}{dt} + \left[\mu(p) - \frac{(T_0+t)}{(T_0+\theta)}\mu(0) \right]\frac{dS_A}{dt} \right) = -\nabla\cdot\mathbf{F}^R - \nabla\cdot\mathbf{F}^Q + \rho\varepsilon \tag{A.13.5}$$

where c_p^0 is the fixed constant defined by the exact 15-digit number in equation (3.3.3) and Table D5 of Appendix D.

In the Appendix A.16, A.17 and A.18 the non-conservative production of entropy, potential temperature and Conservative Temperature will be quantified, both as Taylor series expansions that identify the relevant non-linear thermodynamic terms that cause the production of theses variables, and also on the $S_A - \Theta$ diagram where variables are contoured which graphically illustrate the non-conservation of these variables.

A quick ranking of these three variables, η, θ and Θ, 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 equations (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 μ in (A.13.3) vary at fixed pressure. Similarly the non-conservative production of potential temperature depends on the extent to which the coefficients $c_p(p_r)(T_0+t)/(T_0+\theta)$ and $\left[\mu(p) - (T_0+t)\mu_T(p_r) \right]$ in (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 (A.13.5) vary at fixed pressure. In this way the material derivative of entropy appears in (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 $d\theta/dt$ in (A.13.4) is dominated by the variations in the isobaric specific heat $c_p(S_A, t, p_r)$ which is mainly a function of S_A and which varies by 5% at the sea surface, while the material derivative of Conservative Temperature $d\Theta/dt$ in (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 considers only the variation of this ratio at each pressure level. This factor is unity at the sea surface and is also very close to unity in the deep ocean. In sections A.16, A.17 and A.18, we show that a realistic evaluation of the relative non-conservation of these variables $\eta : \theta : \Theta$ is approximately in the relative ratios 1 : 1 : 0.01.

On this basis one concludes that potential temperature is no more conserved in the ocean than is entropy; a thermodynamic variable which we know from the Second Law of Thermodynamics must be produced by irreversible mixing processes. Fortunately, Conservative Temperature is much more accurately conserved in the ocean and is 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 θ and Conservative Temperature Θ 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 eq. (3.3.3)), the neglect of the non-conservative source terms that should appear in the prognostic equation for θ 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 derived 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 Θ is absolutely unchanged (because of its "potential" nature) followed by a series of turbulent mixing events during which Θ is almost totally conserved. Hence it is clear that Θ 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.
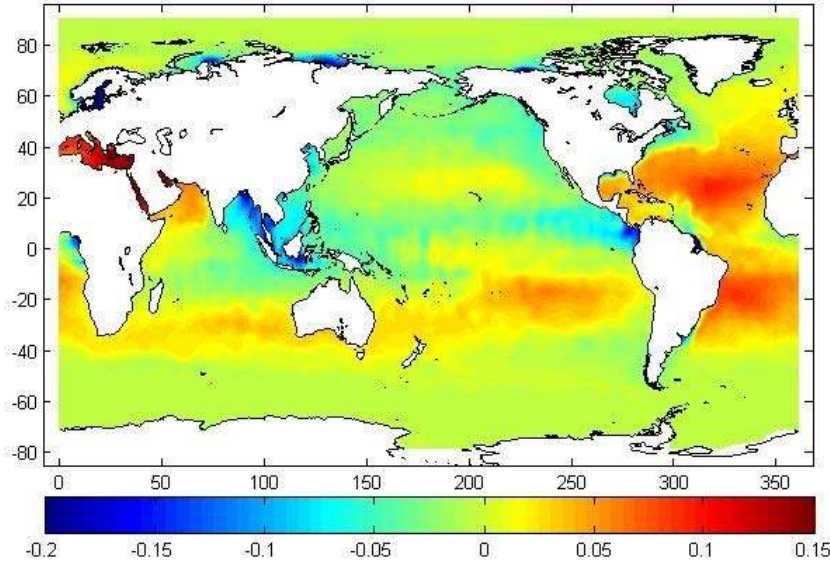
Figure A.13.1. Contours (in $°C$) of the difference $\theta - \Theta$ between potential temperature θ and Conservative Temperature Θ at the sea surface of the annually-averaged atlas of Gouretski and Koltermann (2004).

A.14 Advective and Diffusive "Heat" Fluxes

In section 3.23 and Appendix A.13 the First Law of Thermodynamics is shown to be practically equivalent to the conservation equation (A.20.10) for Conservative Temperature Θ. 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 less than 1% of the error in assuming that either $c_p^0 \theta$ or $c_p\left(S_A, \Theta, 0\,\text{dbar}\right)\theta$ is the "heat content" per unit mass of seawater.

The conservative form (A.20.10) 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 quantify the difference between these mean temperature gradients.

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

$$\left(\alpha^\theta / \beta^\theta\right)\nabla_n \theta = \nabla_n S_A = \left(\alpha^\Theta / \beta^\Theta\right)\nabla_n \Theta, \tag{A.14.1}$$

so that the epineutral gradients of θ and Θ are related by the ratios of their respective thermal expansion and saline contraction coefficients, namely

$$\nabla_n \theta = \frac{\left(\alpha^\Theta / \beta^\Theta\right)}{\left(\alpha^\theta / \beta^\theta\right)}\nabla_n \Theta. \tag{A.14.2}$$

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.

Using the functional form $\Theta = \Theta(S_A, \theta)$, the epineutral gradients of θ and Θ are related by

$$\nabla_n\Theta = \Theta_\theta\big|_{S_A} \nabla_n\theta + \Theta_{S_A}\big|_\theta \nabla_n S_A,$$ (A.14.3)

and using the neutral relationship $\nabla_n S_A = (\alpha^\theta/\beta^\theta)\nabla_n\theta$ we find

$$\nabla_n\Theta = \left(\Theta_\theta\big|_{S_A} + \frac{\alpha^\theta}{\beta^\theta}\Theta_{S_A}\big|_\theta\right)\nabla_n\theta.$$ (A.14.4)

Also, in section 3.13 we found that $T_b^\theta\nabla_n\theta = T_b^\Theta\nabla_n\Theta$, so that we can write the equivalent expressions

$$\frac{|\nabla_n\theta|}{|\nabla_n\Theta|} = \frac{(\alpha^\Theta/\beta^\Theta)}{(\alpha^\theta/\beta^\theta)} = \frac{T_b^\Theta}{T_b^\theta} = \left(\Theta_\theta\big|_{S_A} + \frac{\alpha^\theta}{\beta^\theta}\Theta_{S_A}\big|_\theta\right)^{-1}.$$ (A.14.5)

The two partial derivatives of Θ in the last part of this equation are both independent of pressure while the ratio $\alpha^\theta/\beta^\theta$ is a function of pressure. This ratio (A.14.5) of the epineutral gradients of θ and Θ is shown in Figure A.14.1.

Figure A.14.1 goes here

Figure A.14.1. Contours of the ratio $|\nabla_n\theta|/|\nabla_n\Theta|$ at $p = 0$ (panel (a)) and at $p = 2000$ dbar (panel (b)).

Comment on what this figure shows…. This figure can also be used to give an indication of the ratio of the vertical turbulent diffusive fluxes of θ and Θ, as follows. Similarly to (A.14.3) the vertical gradients are related by

$$\Theta_z = \Theta_\theta\big|_{S_A} \theta_z + \Theta_{S_A}\big|_\theta S_{A_z}, \tag{A.14.6}$$

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

$$\frac{\theta_z}{\Theta_z} \approx \left(\Theta_\theta\big|_{S_A} + \frac{1}{R_\rho} \frac{\alpha^\theta}{\beta^\theta} \Theta_{S_A}\big|_\theta \right)^{-1}. \tag{A.14.7}$$

For values of the stability ratio R_ρ close to unity, the ratio θ_z / Θ_z is close to the values of $|\nabla_n\theta|/|\nabla_n\Theta|$ shown in Figure A.14.1. For other values of the stability ratio, equation (A.14.7) can be calculated and plotted.

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 cabbeling. The ratio of the cabbeling dianeutral velocity calculated using potential temperature to that using Conservative Temperature is given by $\left(C_b^\theta \nabla_n\theta \cdot \nabla_n\theta \right)/\left(C_b^\Theta \nabla_n\Theta \cdot \nabla_n\Theta \right)$ (see section 3.9) which can be expressed as

$$\frac{C_b^\theta |\nabla_n\theta|^2}{C_b^\Theta |\nabla_n\Theta|^2} = \frac{C_b^\theta}{C_b^\Theta} \frac{\left(\alpha^\Theta/\beta^\Theta\right)^2}{\left(\alpha^\theta/\beta^\theta\right)^2} = \frac{C_b^\theta}{C_b^\Theta}\left(T_b^\Theta/T_b^\theta\right)^2 = \frac{C_b^\theta}{C_b^\Theta}\left(\Theta_\theta\big|_{S_A} + \frac{\alpha^\theta}{\beta^\theta} \Theta_{S_A}\big|_\theta \right)^{-2}, \tag{A.14.8}$$

and this is contoured in Figure A.14.2. Now talk about what is shown in this figure and why this ratio is not unity.

Figure A.14.2 goes here

Figure A.14.2. Contours of the ratio $\left(C_b^\theta |\nabla_n\theta|^2 \right)/\left(C_b^\Theta |\nabla_n\Theta|^2 \right)$ at $p = 0$ (panel (a)) and at $p = 2000$ dbar (panel (b)).

A.15 Derivation of the Expressions for α^θ, β^θ, α^Θ and β^Θ

This appendix derives the expressions in equations (2.18.2) – (2.18.3) and (2.19.2) – (2.19.3) for the thermal expansion coefficients α^θ and α^Θ and the haline contraction coefficients β^θ and β^Θ.

In order to derive equation (2.18.2) for α^θ we first need an expression for $\left.\partial\theta/\partial t\right|_{S_A,p}$.

This is found by differentiating with respect to in situ temperature the entropy equality $\eta(S_A,t,p) = \eta\left(S_A,\theta[S_A,t,p,p_r],p_r\right)$ which defines potential temperature, obtaining

$$\left.\frac{\partial\theta}{\partial t}\right|_{S_A,p} = \frac{\eta_T(S_A,t,p)}{\eta_T(S_A,\theta,p_r)} = \frac{g_{TT}(S_A,t,p)}{g_{TT}(S_A,\theta,p_r)}. \tag{A.15.1}$$

This is then used to obtain the desired expression (2.18.2) for α^θ as follows

$$\alpha^\theta = \left.\frac{1}{v}\frac{\partial v}{\partial\theta}\right|_{S_A,p} = \left.\frac{1}{v}\frac{\partial v}{\partial t}\right|_{S_A,p}\left(\left.\frac{\partial\theta}{\partial t}\right|_{S_A,p}\right)^{-1} = \frac{g_{Tp}(S_A,t,p)}{g_p(S_A,t,p)}\frac{g_{TT}(S_A,\theta,p_r)}{g_{TT}(S_A,t,p)}. \tag{A.15.2}$$

In order to derive equation (2.18.3) for α^Θ we first need an expression for $\left.\partial\Theta/\partial t\right|_{S_A,p}$.

This is found by differentiating with respect to in situ temperature the entropy equality $\eta(S_A,t,p) = \hat{\eta}\left(S_A,\Theta[S_A,t,p]\right)$ obtaining

$$\left.\frac{\partial\Theta}{\partial t}\right|_{S_A,p} = \eta_T(S_A,t,p)\left.\frac{\partial\Theta}{\partial\eta}\right|_{S_A} = -(T_0+\theta)g_{TT}(S_A,t,p)/c_p^0, \tag{A.15.3}$$

where the second part of this equation has used equation (A.12.4) for $\left.\Theta_\eta\right|_{S_A}$. This is then used to obtain the desired expression (2.18.3) for α^Θ as follows

$$\alpha^\Theta = \left.\frac{1}{v}\frac{\partial v}{\partial\Theta}\right|_{S_A,p} = \left.\frac{1}{v}\frac{\partial v}{\partial t}\right|_{S_A,p}\left(\left.\frac{\partial\Theta}{\partial t}\right|_{S_A,p}\right)^{-1} = -\frac{g_{Tp}(S_A,t,p)}{g_p(S_A,t,p)}\frac{c_p^0}{(T_0+\theta)g_{TT}(S_A,t,p)}. \tag{A.15.4}$$

In order to derive equation (2.19.2) for β^θ we first need an expression for $\left.\partial\theta/\partial S_A\right|_{T,p}$.

This is found by differentiating with respect to Absolute Salinity the entropy equality $\eta(S_A,t,p) = \eta\left(S_A,\theta[S_A,t,p,p_r],p_r\right)$ which defines potential temperature, obtaining

$$\begin{aligned}
\left.\frac{\partial\theta}{\partial S_A}\right|_{T,p} &= \left.\theta_\eta\right|_{S_A}\left[\eta_{S_A}(S_A,t,p) - \eta_{S_A}(S_A,\theta,p_r)\right] \\
&= \frac{(T_0+\theta)}{c_p(S_A,\theta,p_r)}\left[\mu_T(S_A,\theta,p_r) - \mu_T(S_A,t,p)\right] \\
&= \left[g_{S_AT}(S_A,t,p) - g_{S_AT}(S_A,\theta,p_r)\right]/g_{TT}(S_A,\theta,p_r),
\end{aligned} \tag{A.15.5}$$

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

$$\beta^\theta = \frac{1}{\rho}\frac{\partial \rho}{\partial S_A}\bigg|_{\theta, p} = \frac{1}{\rho}\frac{\partial \rho}{\partial S_A}\bigg|_{T, p} + \alpha^\theta \frac{\partial \theta}{\partial S_A}\bigg|_{T, p}, \tag{A.15.6}$$

and using (A.15.5) we arrive at the desired expression (2.19.2) for β^θ

$$\beta^\theta = -\frac{g_{S_A p}(S_A, t, p)}{g_p(S_A, t, p)} + \frac{g_{Tp}(S_A, t, p)\left[g_{S_A T}(S_A, t, p) - g_{S_A T}(S_A, \theta, p_r)\right]}{g_p(S_A, t, p)g_{TT}(S_A, t, p)}. \tag{A.15.7}$$

We 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 (A.15.5) and (A.15.7).

In order to derive equation (2.19.3) for β^Θ we first need an expression for $\partial\Theta/\partial S_A\big|_{T,p}$. This is found by differentiating with respect to Absolute Salinity the entropy equality $\eta(S_A, t, p) = \hat{\eta}(S_A, \Theta[S_A, t, p])$ obtaining

$$\begin{aligned}
\frac{\partial \Theta}{\partial S_A}\bigg|_{T, p} &= \Theta_\eta\big|_{S_A}\left[\eta_{S_A}(S_A, t, p) - \hat{\eta}_{S_A}\big|_\Theta\right] \\
&= \left[\mu(S_A, \theta, 0) - (T_0 + \theta)\mu_T(S_A, t, p)\right]/c_p^0 \tag{A.15.8}\\
&= \left[g_{S_A}(S_A, \theta, 0) - (T_0 + \theta)g_{S_A T}(S_A, t, p)\right]/c_p^0,
\end{aligned}$$

where equations (A.12.4) and (A.12.8) have been used. By differentiating $\rho = \hat{\rho}\left(S_A, \Theta[S_A, t, p], p\right)$ with respect to Absolute Salinity it can be shown that

$$\beta^\Theta = \frac{1}{\rho}\frac{\partial \rho}{\partial S_A}\bigg|_{\Theta, p} = \frac{1}{\rho}\frac{\partial \rho}{\partial S_A}\bigg|_{T, p} + \alpha^\Theta \frac{\partial \Theta}{\partial S_A}\bigg|_{T, p}, \tag{A.15.9}$$

and using (A.15.8) we arrive at the desired expression (2.19.3) for β^Θ namely

$$\beta^\Theta = -\frac{g_{S_A p}(S_A, t, p)}{g_p(S_A, t, p)} + \frac{g_{Tp}(S_A, t, p)\left[g_{S_A T}(S_A, t, p) - g_{S_A}(S_A, \theta, 0)/(T_0 + \theta)\right]}{g_p(S_A, t, p)g_{TT}(S_A, t, p)}. \tag{A.15.10}$$

A.16 The Non-conservative Production of Entropy η

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 ε term can be dropped from (A.13.1), this equation becoming

$$(\rho h)_t + \nabla\cdot(\rho\mathbf{u}h) = -\nabla\cdot\mathbf{F}^R - \nabla\cdot\mathbf{F}^Q. \qquad \textit{at constant pressure} \tag{A.16.1}$$

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 (A.16.1) is zero. Similarly the integral of $\nabla \cdot (\rho \mathbf{u}\, h)$ over the boundary is 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 of the two fluid parcels mass, salt content and enthalpy are conserved, that is

$$m_1 + m_2 = m, \tag{A.16.2}$$

$$m_1 S_{A1} + m_2 S_{A2} = m\, S_A, \tag{A.16.3}$$

$$m_1 h_1 + m_2 h_2 = m\, h, \tag{A.16.4}$$

while the non-conservative nature of entropy means that it obeys the equation,

$$m_1 \eta_1 + m_2 \eta_2 + m\, \delta\eta = m\eta. \tag{A.16.5}$$

Here S_A, h and η 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 η is now regarded as the functional form $\eta = \breve{\eta}(S_A, h, p)$ and is expanded in a Taylor series of S_A and h about the values of S_A and h of the mixed fluid, retaining terms to second order in $[S_{A2} - S_{A1}] = \Delta S_A$ and in $[h_2 - h_1] = \Delta h$. Then η_1 and η_2 are evaluated and (A.16.4) and (A.16.5) used to find

$$\delta\eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\partial^2 \breve{\eta}}{\partial h \partial h}(\Delta h)^2 + 2\frac{\partial^2 \breve{\eta}}{\partial h \partial S_A} \Delta h\, \Delta S_A + \frac{\partial^2 \breve{\eta}}{\partial S_A \partial S_A}(\Delta S_A)^2 \right\}. \tag{A.16.6}$$

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 $g(S_A, t, p)$ 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,

$$\breve{\eta}_{hh} < 0, \tag{A.16.7}$$

$$\breve{\eta}_{S_A S_A} < 0, \tag{A.16.8}$$

$$\left(\breve{\eta}_{hS_A}\right)^2 < \breve{\eta}_{hh}\, \breve{\eta}_{S_A S_A}, \tag{A.16.9}$$

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, $T = T_0 + t$)

$$\breve{\eta}_h = \left. \frac{\partial \eta}{\partial h} \right|_{S_A, p} = T^{-1} \tag{A.16.10}$$

$$\breve{\eta}_{S_A} = \left. \frac{\partial \eta}{\partial S_A} \right|_{h, p} = -\frac{\mu}{T}, \tag{A.16.11}$$

and from these relations the following expressions for the second order derivatives of can be found,

$$\breve{\eta}_{hh} = \left. \frac{\partial^2 \eta}{\partial h^2} \right|_{S_A, p} = \left. \frac{\partial T^{-1}}{\partial h} \right|_{S_A, p} = \frac{-T^{-2}}{c_p}, \tag{A.16.12}$$

$$\breve{\eta}_{S_A h} = \left. \frac{\partial^2 \eta}{\partial h \, \partial S_A} \right|_p = \left. \frac{\partial (-\mu/T)}{\partial h} \right|_{S_A, p} = -\frac{1}{c_p} \left(\frac{\mu}{T} \right)_T, \tag{A.16.13}$$

and

$$\breve{\eta}_{S_A S_A} = \left. \frac{\partial^2 \eta}{\partial S_A^2} \right|_{h, p} = \left. \frac{\partial (-\mu/T)}{\partial S_A} \right|_{T, p} - \left. \frac{\partial (-\mu/T)}{\partial h} \right|_{S_A, p} \left. \frac{\partial h}{\partial S_A} \right|_{T, p}$$

$$= -\frac{\mu_{S_A}}{T} - \frac{T^2}{c_p} \left[\left(\frac{\mu}{T} \right)_T \right]^2. \tag{A.16.14}$$

The last equation comes from regarding $\breve{\eta}_{S_A}$ as $\breve{\eta}_{S_A} = \breve{\eta}_{S_A} \left(S_A, h[S_A, t, p], p \right)$.

The constraint (A.16.7) that $\breve{\eta}_{hh} < 0$ 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 $\breve{\eta}_{S_A S_A} < 0$, requires (from (A.16.14)) that

$$g_{S_A S_A} > -\frac{T^3}{c_p} \left[\left(\frac{\mu}{T} \right)_T \right]^2, \tag{A.16.15}$$

that is, the second derivative of the Gibbs function with respect to Absolute Salinity $g_{S_A S_A}$ must exceed some negative number. The constraint (A.16.9) that $\left(\breve{\eta}_{hS_A} \right)^2 < \breve{\eta}_{hh} \, \breve{\eta}_{S_A S_A}$ requires that (substituting from (A.16.12), (A.16.13) and (A.16.14))

$$\frac{g_{S_A S_A}}{T^3 c_p} > 0, \tag{A.16.16}$$

and since the isobaric heat capacity must be positive, this requirement is that $g_{S_A S_A} > 0$, 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 $\eta = \breve{\eta}\left(S_A, h, p \right)$ 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 $g\left(S_A, t, p \right)$,

$$g_{TT} < 0 \tag{A.16.17}$$

and

$$g_{S_A S_A} > 0. \tag{A.16.18}$$

The Second Law of Thermodynamics does not impose any additional requirement on the cross derivatives $g_{S_A T}$ 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 $\mu(S_A, t, p)$ (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 $-\mu_{S_A} \nabla S_A$ and in order to avoid an unstable explosion of salt one must have $\mu_{S_A} = g_{S_A S_A} > 0$. 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))

$$g_{pp} < 0 \qquad (A.16.19)$$

and

$$\left(g_{Tp}\right)^2 < g_{pp} g_{TT}, \qquad (A.16.20)$$

recognizing that g_{TT} is negative (g_{Tp} 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 be also be regarded as a constraint on the thermal expansion coefficient α^t, implying that its square must be less than $g_p^2 g_{pp} g_{TT}$ or otherwise the relevant compressibility (κ) would be negative and the sound speed complex.

The constraints on the seawater Gibbs function $g(S_A, t, p)$ that have been discussed above are summarized as

$$g_p > 0, \quad g_{S_A S_A} > 0, \quad g_{pp} < 0, \quad g_{TT} < 0, \text{ and } \left(g_{Tp}\right)^2 < g_{pp} g_{TT}. \qquad (A.16.21)$$

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 Θ (since Θ is simply proportional to h at $p = 0$) as follows (now entropy is taken to be the functional form $\eta = \hat{\eta}(S_A, \Theta)$)

$$\delta\eta = -\frac{1}{2}\frac{m_1 m_2}{m^2}\left\{\frac{\partial^2 \hat{\eta}}{\partial \Theta^2}(\Delta\Theta)^2 + 2\frac{\partial^2 \hat{\eta}}{\partial \Theta \partial S_A}\Delta\Theta\,\Delta S_A + \frac{\partial^2 \hat{\eta}}{\partial S_A^2}(\Delta S_A)^2\right\}. \qquad (A.16.22)$$

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 $(S_A, \Theta) = (S_{SO}, 25\,°C)$ and then Θ is subtracted. The result is contoured in $S_A - \Theta$ space in Figure A.16.1. The fact that the variable in Figure A.16.1 is not zero over the whole $S_A - \Theta$ 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 $(S_A, \Theta) = (0\ \mathrm{g\,kg^{-1}}, 0\,°C)$ and the other at the warmest and saltiest corner of the figure, the non-conservative production of η on mixing parcels of equal mass is approximately $0.9\,°C$.
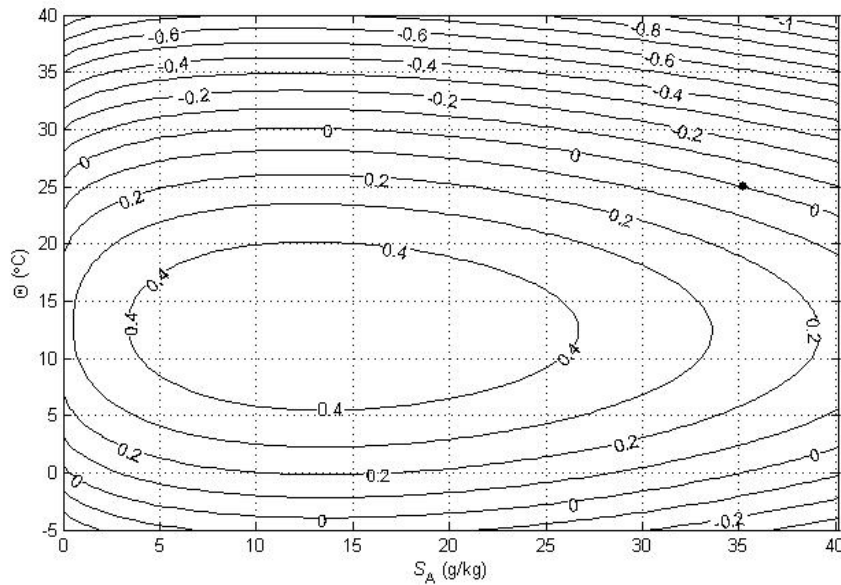
Figure A.16.1. Contours (in °C) of a variable that illustrates the non-conservative production of entropy η in the ocean.

Since entropy can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature $\eta = \hat{\eta}(S_A, \Theta)$, and since at any pressure in the ocean both S_A and Θ 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 Θ 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 The Non-conservative Production of Potential Temperature θ

When fluid parcels under go 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 equations (A.16.2) – (A.16.4). Potential temperature θ is not conserved during the mixing process and the production of potential temperature is given by

$$m_1\,\theta_1 + m_2\,\theta_2 + m\,\delta\theta \;=\; m\,\theta. \tag{A.17.1}$$

Enthalpy in the functional form $h = \tilde{h}\left(S_A, \theta, p\right)$ is expanded in a Taylor series of S_A and θ about the values S_A and θ of the mixed fluid, retaining terms to second order in $\left[S_{A2} - S_{A1}\right] = \Delta S_A$ and in $\left[\theta_2 - \theta_1\right] = \Delta\theta$. Then h_1 and h_2 are evaluated and (A.16.4) and (A.17.1) used to find

$$\delta\theta\,\tilde{h}_\theta \;=\; \tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{\tilde{h}_{\theta\theta}\left(\Delta\theta\right)^2 + 2\tilde{h}_{\theta S_A}\,\Delta\theta\,\Delta S_A + \tilde{h}_{S_A S_A}\left(\Delta S_A\right)^2\right\}. \tag{A.17.2}$$

The maximum production occurs when parcels of equal mass are mixed so that $\tfrac{1}{2}m_1 m_2\,m^{-2} = \tfrac{1}{8}$. The "heat capacity" $\tilde{h}_\theta$ is not a strong function of θ but is a much stronger function of S_A so the first term in the curly brackets in (A.17.2) is generally small compared with the second term. Also, the third term in (A.17.2), $\tilde{h}_{S_A S_A}\left(\Delta S_A\right)^2$, which causes the so-called "dilution heating", is usually small compared with the second term. A typical value of $\tilde{h}_{\theta S_A}$ is approximately -5.4 J kg^{-1} K^{-1} (g kg^{-1})$^{-1}$ (e.g. from Feistel and Hagen (1995)) so that an approximate expression for the production of potential temperature is

$$\delta\theta \approx \tfrac{1}{4}\tilde{h}_{\theta S_A}\,\Delta\theta\,\Delta S_A\big/\tilde{h}_\theta \approx -3.4x10^{-4}\left(\Delta\theta/\text{K}\right)\left(\Delta S_A\,/[\text{g kg}^{-1}]\right). \tag{A.17.3}$$

Since potential temperature $\theta = \hat{\theta}\left(S_A, \Theta\right)$ can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature, and since at any pressure in the ocean both S_A and Θ 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

$$\delta\theta \;=\; \tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{\frac{\Theta_{\theta\theta}}{\Theta_\theta}\left(\Delta\theta\right)^2 + 2\frac{\Theta_{\theta S_A}}{\Theta_\theta}\Delta\theta\,\Delta S_A + \frac{\Theta_{S_A S_A}}{\Theta_\theta}\left(\Delta S_A\right)^2\right\}. \tag{A.17.4}$$

where the exact proportionality between potential enthalpy and Conservative Temperature $h^0 \equiv c_p^0 \Theta$ 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 equation (A.17.4). The non-conservative production of potential temperature 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 reading off the production (in $^{\circ}C$) of θ from the figure. 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 θ 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 $^{\circ}C$.

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 θ 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 Conservative Temperature. 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 potential temperature. That is, the values contoured in Figures A.16.1 and A.17.1 are representative of the error, expressed in $^{\circ}C$, associated with assuming that η and θ respectively are conservative variables. These contoured values of temperature difference encapsulate the accumulated non-conservative production that occurred during all the many mixing processes that lead to the ocean's present state. The maximum such error for entropy is approximately -1.0 $^{\circ}C$ (from Figure A.16.1) while for potential temperature the maximum error is approximately -1.8 $^{\circ}C$ (from Figure A.17.1).
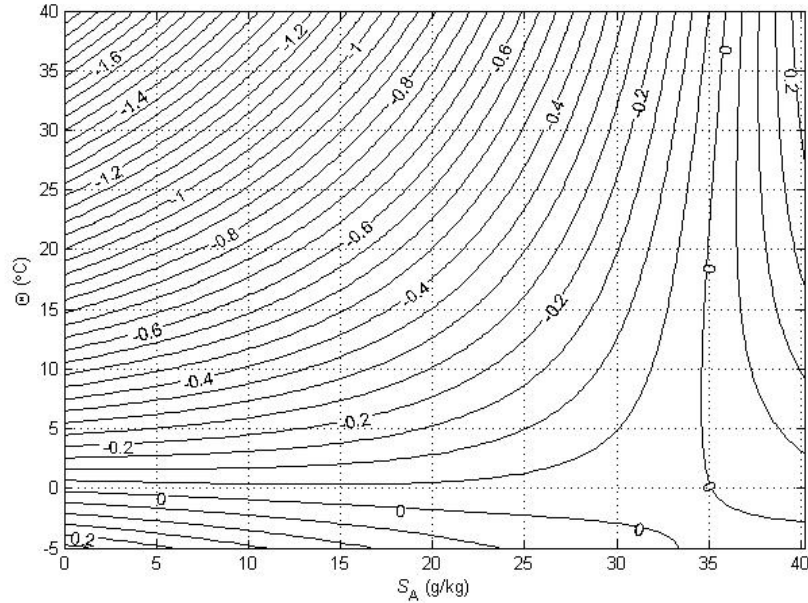
Figure A.17.1. Contours (in $°C$) of the difference between potential temperature and Conservative Temperature $\theta - \Theta$ which illustrates the non-conservative production of potential temperature θ in the ocean.

We know from the Second Law of Thermodynamics that entropy is a non-conservative variable and this knowledge has discouraged oceanographers from treating entropy as a conservative oceanographic variable. The conclusion that we reach by comparing Figures A.16.1 and A.17.1 is that potential temperature and entropy are approximately as non-conserved in the ocean as each other. This implies that θ is no better than η as an oceanographic variable with which to track water masses or as a variable to measure the "heat content" of seawater.

A.18 The Non-conservative Production of Conservative Temperature Θ

When fluid parcels under go 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 equations (A.16.2) – (A.16.4). Potential enthalpy h^0 and Conservative Temperature Θ are not exactly conserved during the mixing process and the production of Θ is given by

$$m_1 \Theta_1 + m_2 \Theta_2 + m\,\delta\Theta \; = \; m\,\Theta. \qquad (A.18.1)$$

Enthalpy in the functional form $h = \hat{h}(S_A, \Theta, p)$ is expanded in a Taylor series of S_A and Θ about the values S_A and Θ 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 (A.16.4) and (A.18.1) are used to find

$$\delta\Theta\,\hat{h}_{\Theta} \;=\; \tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{\hat{h}_{\Theta\Theta}\left(\Delta\Theta\right)^2 + 2\hat{h}_{\Theta S_A}\,\Delta\Theta\Delta S_A + \hat{h}_{S_A S_A}\left(\Delta S_A\right)^2\right\}. \tag{A.18.2}$$

In order to evaluate these partial derivatives, we first write enthalpy in terms of potential enthalpy (i. e. $c_p^0\,\Theta$) using (3.2.1), as

$$h \;=\; \hat{h}\left(S_A,\Theta,p\right) \;=\; c_p^0\,\Theta \;+\; \int_0^p \hat{v}\left(S_A,\Theta,p'\right)dp'. \tag{A.18.3}$$

This is differentiated with respect to Θ giving

$$h_\Theta\big|_{S_A,\,p} = \hat{h}_\Theta \;=\; c_p^0 \;+\; \int_0^p \alpha^\Theta/\rho\;dp'. \tag{A.18.4}$$

The right-hand side of (A.18.4) scales as $c_p^0 + \alpha^\Theta\,p/\rho$, which is more than c_p^0 by only about $0.0015\,c_p^0$ (for p of 4×10^7 Pa (4,000 dbar)). Hence, to a very good approximation, we may regard the left-hand side of (A.18.2) as simply the production of Conservative Temperature $\delta\Theta$. 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 equations (3.2.1) and (A.18.3), scales as $[p-p_r]/\rho$ which is as large as typical values of enthalpy itself. The reason is that the integral in (3.2.1) or (A.18.3) is dominated by the integral of the mean value of $1/\rho$, 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 (A.18.2), and these can be estimated in terms of the strength of cabbeling as follows. Equation (A.18.4) is differentiated with respect to Conservative Temperature, giving

$$\hat{h}_{\Theta\Theta} \;=\; \int_0^p \left(\alpha^\Theta/\rho\right)_\Theta dp' \;\approx\; \rho^{-1}\int_0^p \left(\alpha^\Theta\right)_\Theta dp', \tag{A.18.5}$$

so that we may write (A.18.2) approximately as (assuming $m_1 = m_2$)

$$\delta\Theta \;\approx\; \frac{p}{8\rho c_p^0}\left\{\alpha_\Theta^\Theta\left(\Delta\Theta\right)^2 + 2\alpha_{S_A}^\Theta\,\Delta\Theta\Delta S_A - \beta_{S_A}^\Theta\left(\Delta S_A\right)^2\right\}. \tag{A.18.6}$$

Equation (A.18.6) shows that the non-conservative production of Conservative Temperature is proportional to the non-conservative production of density (see equation (A.19.4) below) often refereed to loosely as "cabbeling" (McDougall, 1987b),

$$\begin{aligned}
\delta\rho_\theta &\approx \frac{\rho}{8}\left\{\alpha_\Theta^\Theta\left(\Delta\Theta\right)^2 + 2\alpha_{S_A}^\Theta\,\Delta\Theta\Delta S_A - \beta_{S_A}^\Theta\left(\Delta S_A\right)^2\right\}\\
&\approx \frac{\rho}{8}\left\{\alpha_\theta^\theta\left(\Delta\theta\right)^2 + 2\alpha_{S_A}^\theta\,\Delta\theta\Delta S - \beta_{S_A}^\theta\left(\Delta S_A\right)^2\right\}.
\end{aligned} \tag{A.18.7}$$

The production of Θ causes an increase (or decrease) in temperature and a consequent change in density of $-\rho\alpha^\Theta\delta\Theta$. The ratio of this increase in density (using (A.18.6)) to that caused by cabbeling (from (A.18.7)) is $-p\alpha^\Theta/\rho c_p^0$ which is about 0.0015 for a value of pressure p of 40 MPa (4,000 dbar). Hence it is clear that cabbeling has a much larger effect on density than does the non-conservation of Θ. Nevertheless, from equation (A.18.6) we see that the non-conservative production of Θ is proportional to the product of pressure and the strength of cabbeling.

McDougall (1987b) has shown that the first term in the bracket in (A.18.6) is usually about a factor of ten larger than the other two terms, so we may approximate the production of Conservative Temperature $\delta\Theta$ as a ratio of the contrast in Conservative Temperature $\Delta\Theta = \Theta_2 - \Theta_1$ as

$$\frac{\delta\Theta}{\Delta\Theta} \approx \frac{p\,\alpha_\Theta^\Theta(\Delta\Theta)}{8\rho c_p^0} \approx 3.3\times10^{-13}\,(p/\mathrm{Pa})(\Delta\Theta/\mathrm{K}). \qquad (A.18.8)$$

where α_Θ^Θ has been taken to be $1.1\times10^{-5}\,\mathrm{K}^{-2}$ (McDougall, 1987b).

At the sea surface Conservative Temperature Θ is totally conserved ($\delta\Theta = 0$). The non-conservative production of Conservative Temperature, $\delta\Theta$, increases linearly with pressure (see equation (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 $\delta\Theta$ decreases proportionally to the square of the temperature and salinity contrasts. McDougall (2003) concluded that the production $\delta\Theta$ between extreme seawater parcels at each pressure is largest at 600 dbar, and the magnitude of the non-conservative production of Conservative Temperature, $\delta\Theta$, is illustrated in Figure A.18.1 for data at this pressure. The quantity contoured on this figure is the difference between Θ 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 $(S_A = 0, \Theta = 0\,^\circ\mathrm{C})$ and at $(S_A = 35.165\,04\,\mathrm{g\,kg}^{-1}, \Theta = 0\,^\circ\mathrm{C})$. This quantity is then scaled so that it becomes $25\,^\circ\mathrm{C}$ at $(S_A = 35.165\,04\,\mathrm{g\,kg}^{-1}, \Theta = 25\,^\circ\mathrm{C})$. In this manner the quantity that is contoured in Figure A.18.1 represents the amount by which Conservative Temperature Θ 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 $4\times10^{-3}\,^\circ\mathrm{C}$ and 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 Θ in the real ocean is a factor of more than one hundred less than the maximum non-conservative production of potential temperature θ. The material in appendices A.16 to A.18 follows closely the paper of McDougall (2003).
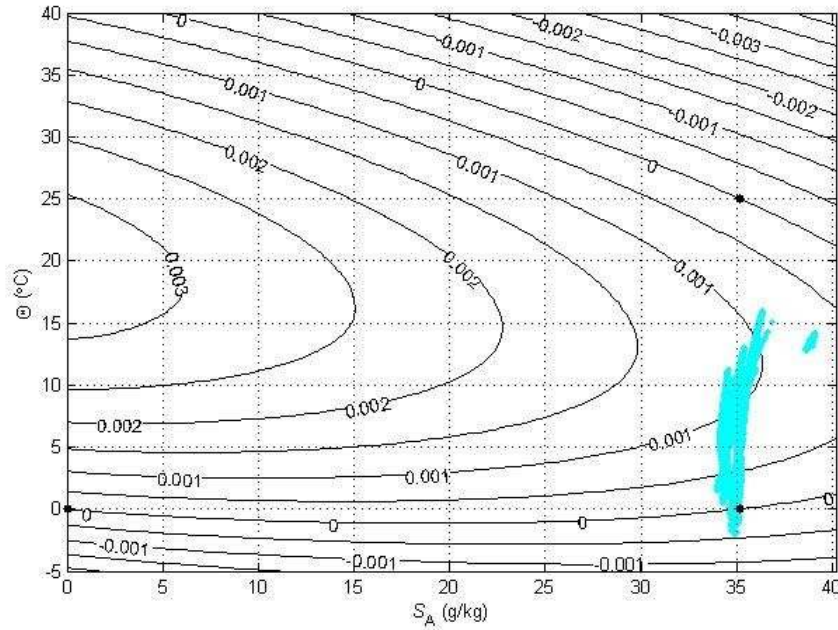
Figure A.18.1. Contours (in $°C$) of a variable that is used to illustrate the non-conservative production of Conservative Temperature Θ at $p = 600$ dbar. The cloud of points show where most of the oceanic data reside at $p = 600$ dbar (6 Mpa).

A.19 The Non-conservative Production of Density ρ and of Potential Density ρ^{Θ}

For the purpose of calculating the non-conservative production of density we take Conservative Temperature Θ to be 100% conservative (see Appendix A.19 above). Density is written in the functional form

$$\rho = \hat{\rho}(S_A, \Theta, p) \qquad (A.19.1)$$

and the same mixing process between two fluid parcels is considered as in the previous appendices. Mass and Absolute Salinity are conserved during the mixing process (equations (A.16.2) and (A.16.3)) as is Conservative Temperature, that is

$$m_1 \Theta_1 + m_2 \Theta_2 = m \Theta, \qquad (A.19.2)$$

while the non-conservative nature of density means that it obeys the equation,

$$m_1 \rho_1 + m_2 \rho_2 + m \delta\rho = m \rho. \qquad (A.19.3)$$

Density is expanded in a Taylor series of S_A and Θ about the values of S_A and Θ 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 ρ_1 and ρ_2 are evaluated and (A.19.3) is used to find

$$\delta\rho = -\tfrac{1}{2}\frac{m_1 m_2}{m^2}\left\{ \hat{\rho}_{\Theta\Theta}(\Delta\Theta)^2 + 2\hat{\rho}_{S_A\Theta}\Delta\Theta\Delta S_A + \hat{\rho}_{S_A S_A}(\Delta S_A)^2 \right\}. \qquad (A.19.4)$$

This non-conservative production of density $\delta\rho$ 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 ρ^{Θ}. The quantity contoured on this figure is formed as follows. First the linear function of S_A is found that is equal

to ρ^{Θ} at $\left(S_{A} = 0, \Theta = 0 \text{ °C}\right)$ and at $\left(S_{A} = 35.165\,04\,\text{g kg}^{-1}, \Theta = 0 \text{ °C}\right)$. This linear function of S_{A} is

subtracted from ρ^{Θ} and the result is scaled to equal 25 °C at $\left(S_{A} = 35.165\,04\,\text{g kg}^{-1}, \Theta = 25 \text{ °C}\right)$.

The variable that is contoured in Figure A.19.1 is the difference between this scaled linear combination of ρ^{Θ} 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 Θ is a factor of approximately 4000 smaller than this.
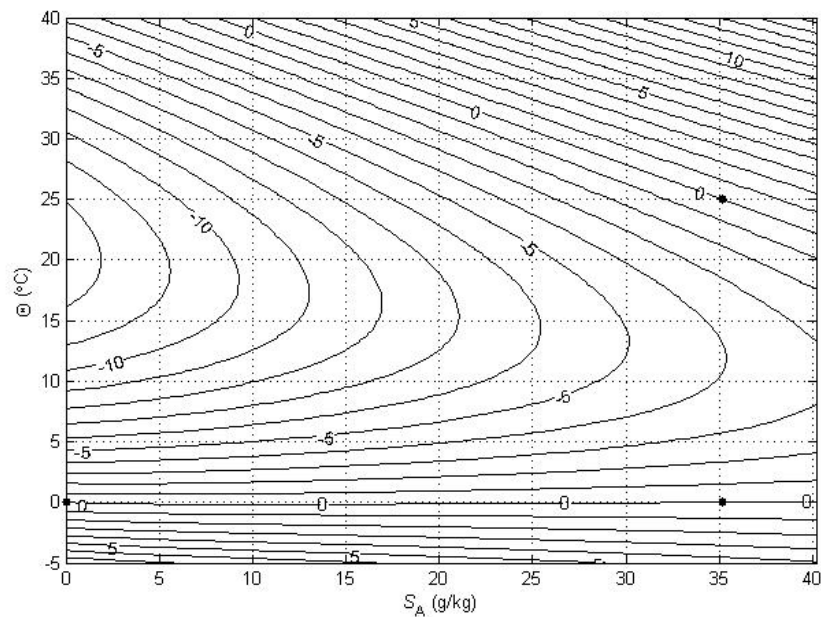
Figure A.19.1. Contours (in °C) of a variable that is used to illustrate the non-conservative production of potential density ρ^{Θ}. The three dots that are forced to be zero are shown with black dots.

A.20 The Material Derivatives of S_A and Θ in a Turbulent Ocean

Absolute Salinity obeys the instantaneous conservation equation (eq. (A.8.1), see the discussion in Appendix A.8)

$$\left(\rho S_A\right)_t + \nabla\cdot\left(\rho S_A \mathbf{u}\right) \;=\; \rho\frac{dS_A}{dt} \;=\; -\nabla\cdot\mathbf{F}^S, \tag{A.20.1}$$

where $\mathbf{F}^S$ is composed of the several contributions to the molecular flux of salt (expressions for which can be seen at equation (58.11) of Landau and Lifshitz (1959)). For completeness, we repeat the continuity equation (A.8.2) here as

$$\rho_t + \nabla\cdot\left(\rho\mathbf{u}\right) \;=\; 0. \tag{A.20.2}$$

Temporally averaging this equation in Cartesian coordinates (i. e. at fixed x, y, z) gives

$$\bar{\rho}_t + \nabla\cdot\left(\overline{\rho\mathbf{u}}\right) \;=\; 0, \tag{A.20.3}$$

which we choose to write in the following form, after division by a constant density ρ_0 (usually taken to be 1035 kg m^{-3}, see Griffies (2004))

$$\left(\bar{\rho}/\rho_0\right)_t + \nabla\cdot\tilde{\bar{\mathbf{u}}} \;=\; 0 \quad \text{where} \quad \tilde{\bar{\mathbf{u}}} \equiv \overline{\rho\mathbf{u}}/\rho_0. \tag{A.20.4}$$

This velocity $\tilde{\bar{\mathbf{u}}}$ is actually proportional to the average mass flux per unit area.

The conservation equation for Absolute Salinity (A.20.1) is now averaged in the corresponding manner obtaining (McDougall et al, 2002)

$$\left(\frac{\bar{\rho}}{\rho_0}\overline{S_A}^{\rho}\right)_t + \nabla\cdot\left(\overline{S_A}^{\rho}\,\tilde{\bar{\mathbf{u}}}\right) \;=\; \frac{\bar{\rho}}{\rho_0}\frac{\partial\overline{S_A}^{\rho}}{\partial t} + \tilde{\bar{\mathbf{u}}}\cdot\nabla\overline{S_A}^{\rho} \;=\; -\frac{1}{\rho_0}\nabla\cdot\overline{\mathbf{F}^S} - \frac{1}{\rho_0}\nabla\cdot\left(\overline{\rho S_A'' \mathbf{u}''}\right). \tag{A.20.5}$$

Here the Absolute Salinity has been density-weighted averaged, that is, $\overline{S_A}^{\rho} \equiv \overline{\rho S_A}/\bar{\rho}$, 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 (A.20.5) 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 Absolute Salinity

$$\left(\frac{\tilde{\rho}}{\rho_0}\hat{S}_A\right)_{t}\bigg|_n + \nabla_n\cdot\left(\frac{\tilde{\rho}}{\rho_0}\hat{S}_A\,\hat{\mathbf{v}}\right) + \left(\frac{\tilde{\rho}}{\rho_0}\tilde{e}\,\hat{S}_A\right)_z \;=\; \frac{\tilde{\rho}}{\rho_0}\frac{\partial\hat{S}_A}{\partial t}\bigg|_n + \frac{\tilde{\rho}}{\rho_0}\hat{\mathbf{v}}\cdot\nabla_n\hat{S}_A + \frac{\tilde{\rho}}{\rho_0}\tilde{e}\frac{\partial\hat{S}_A}{\partial z}$$
$$= \frac{1}{h}\nabla_n\cdot\left(hK\nabla_n\hat{S}_A\right) + \left(D\frac{\partial\hat{S}_A}{\partial z}\right)_z. \tag{A.20.6}$$

Here the over-hat means that the variable has been averaged in a thickness-and-density-weighted manner between a pair of "neutral surfaces" a small distance h apart in the vertical, $\hat{\mathbf{v}}$

is the thickness-and-density-weighted lateral horizontal velocity, e is the dianeutral velocity (the vertical velocity that penetrates through the neutral tangent plane) and $\tilde{e}$ is the average of e along the "neutral surface" (that is, $\tilde{e}$ is not thickness-weighted). The turbulent fluxes are parameterized by the epineutral diffusivity K and the dianeutral (or vertical) diffusivity D.

Having derived this evolution equation (A.20.6) for Absolute Salinity without invoking the Boussinesq approximation, we now follow common practice and invoke this approximation, finding the simpler expression

$$\left. \frac{\partial \hat{S}_A}{\partial t} \right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{S}_A + \tilde{e} \frac{\partial \hat{S}_A}{\partial z} = \frac{1}{h} \nabla_n \cdot \left(h K \nabla_n \hat{S}_A \right) + \left(D \frac{\partial \hat{S}_A}{\partial z} \right)_z . \quad \text{(A.20.7)}$$

The left-hand side is the material derivative of the thickness-weighted Absolute Salinity with respect to the thickness-weighted velocity of density coordinates. The right-hand side is the divergence of the turbulent fluxes of Absolute Salinity (the fact that this is in fact the divergence of a flux can be seen when the right-hand side is written in Cartesian coordinates).

We turn now to consider the material derivative of Conservative Temperature. From equation (A.13.5) the instantaneous material derivative of Θ is, without approximation,

$$\rho c_p^0 \frac{d\Theta}{dt} = \frac{(T_0 + \theta)}{(T_0 + t)} \left(-\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \right) + \left[\frac{(T_0 + \theta)}{(T_0 + t)} \mu(p) - \mu(0) \right] \nabla \cdot \mathbf{F}^S . \quad \text{(A.20.8)}$$

The fact that the right-hand side of (A.20.8) is not the divergence of a flux means that Θ 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-ideal nature of the molecular fluxes of heat and salt appearing on the right-hand side of (A.20.8) is of no practical consequence. These non-ideal terms on the right-hand side of (A.20.8) are no larger than the dissipation term $\rho \varepsilon$ which is also justifiably neglected in oceanography (McDougall (2003)).

Hence with negligible error, the right-hand side of (A.20.8) may be regarded as the sum of the ideal molecular flux of heat term $-\nabla \cdot \mathbf{F}^Q$ 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 θ 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 $c_p^0 \Theta$. There is an issue at the sea floor where the boundary heat flux (the geothermal heat flux) affects Conservative Temperature through the "heat capacity" $(T_0 + t) c_p^0 / (T_0 + \theta)$ rather than simply c_p^0. That is, the input of a certain amount of geothermal heat will cause a local change in Θ as though the seawater had the "specific heat capacity" $(T_0 + t) c_p^0 / (T_0 + \theta)$ rather than c_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 to the geothermal heat flux was ever considered important, it could probably be allowed for in an ocean model by an artificial proportional change to the geothermal heat flux at the ocean model boundary.

We conclude that it is sufficiently accurate to assume that Conservative Temperature is in fact conservative and that the instantaneous conservation equation is

$$c_p^0 \left(\rho \Theta \right)_t + c_p^0 \nabla \cdot \left(\rho \Theta \mathbf{u} \right) = \rho c_p^0 \frac{d\Theta}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q . \tag{A.20.9}$$

Now we perform the same two-stage averaging procedure as outlined above in the case of Absolute Salinity. The Boussinesq form of the mesoscale-averaged equation is (analogous to (A.20.7)

$$\left. \frac{\partial \hat{\Theta}}{\partial t} \right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} + \tilde{e} \frac{\partial \hat{\Theta}}{\partial z} = \frac{1}{h} \nabla_n \cdot \left(hK \nabla_n \hat{\Theta} \right) + \left(D\hat{\Theta}_z - F^{\text{bound}} \right)_z . \tag{A.20.10}$$

As in the case of the Absolute Salinity equation, 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, and the radiative and geothermal heat fluxes remain in (A.20.10) in the vertical heat flux F^{bound} which is the sum of these boundary heat fluxes divided by $\rho_0 c_p^0$.

The material derivatives of Absolute Salinity (A.20.7) and Conservative Temperature (A.20.10) are the underpinning evolution equations for these variables and for passive tracers in ocean models. An important issue for ocean models is how to relate $\hat{\mathbf{v}}$ to the Eulerian-mean horizontal velocity $\bar{\mathbf{v}}$. This area of research involves residual-mean theory. We will not discuss this topic here. Suffice it to say that the mean advection can be expressed in Cartesian coordinates with for example, (A.20.10) becoming

$$\frac{d\hat{\Theta}}{dt} = \left. \hat{\Theta}_t \right|_z + \hat{\mathbf{v}} \cdot \nabla_z \hat{\Theta} + w^* \hat{\Theta}_z = \frac{1}{h} \nabla_n \cdot \left(hK \nabla_n \hat{\Theta} \right) + \left(D\hat{\Theta}_z - F^{\text{bound}} \right)_z , \tag{A.20.11}$$

where the vertical velocity w^* is related to $\tilde{e}$ by

$$w^* = \left. z_t \right|_n + \hat{\mathbf{v}} \cdot \nabla_n z + \tilde{e} . \tag{A.20.12}$$

A.21 The Material Derivatives of Density and of Locally-Referenced Potential Density; the Dianeutral Velocity $\tilde{e}$

Regarding density to be a function of Conservative Temperature (i. e. $\rho = \hat{\rho}\left(S_A, \Theta, p\right)$) and taking the material derivative of the natural logarithm of density following the mesoscale-thickness-weighted-averaged mean flow (as in (A.20.10) or (A.20.11)), we have

$$\rho^{-1} \frac{d\rho}{dt} = \beta^\Theta \frac{d\hat{S}_A}{dt} - \alpha^\Theta \frac{d\hat{\Theta}}{dt} + \kappa \frac{d\hat{p}}{dt} . \tag{A.21.1}$$

One can continue to consider the material derivative of in situ density, and in so doing, one carries along the last term in (A.21.1), namely the isentropic compressibility κ times the material derivative of pressure, but it is more relevant and more interesting to consider the material derivative of the logarithm of the *locally-referenced potential density*, ρ^l, since this

variable is locally constant in the neutral tangent plane. The material derivative of ρ^l is given by

$$\rho^{-1}\frac{d\rho^l}{dt} = \rho^{-1}\frac{d\rho}{dt} - \kappa\frac{d\hat{p}}{dt} = \beta^\Theta\frac{d\hat{S}_A}{dt} - \alpha^\Theta\frac{d\hat{\Theta}}{dt}. \tag{A.21.2}$$

Substituting from equations (A.20.7) and (A.20.10) above, and noting that both the temporal and the lateral gradients of ρ^l vanish along the neutral tangent plane ($\alpha^\Theta\nabla_n\hat{\Theta} - \beta^\Theta\nabla_n\hat{S}_A = \mathbf{0}$ and $\alpha^\Theta\hat{\Theta}_t\big|_n - \beta^\Theta\hat{S}_{A_t}\big|_n = 0$), the material derivative of ρ^l amounts to the following equation for the dianeutral velocity $\tilde{e}$ (note that the boundary heat flux F^{bound} also needs to be included for fluid volumes that abut the sea surface)

$$\begin{aligned}\tilde{e}\left(\alpha^\Theta\hat{\Theta}_z - \beta^\Theta\hat{S}_{A_z}\right) &= \alpha^\Theta h^{-1}\nabla_n\cdot\left(hK\nabla_n\hat{\Theta}\right) - \beta^\Theta h^{-1}\nabla_n\cdot\left(hK\nabla_n\hat{S}_A\right) \\ &\quad + \alpha^\Theta\left(D\hat{\Theta}_z\right)_z - \beta^\Theta\left(D\hat{S}_{A_z}\right)_z.\end{aligned} \tag{A.21.3}$$

The left-hand side is equal to $\tilde{e}\,g^{-1}N^2$ and the first two terms on the right hand side would amount 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 equations (3.8.2) and (3.9.2) for the definitions of C_b^Θ and T_b^Θ)

$$\boxed{\tilde{e}\,g^{-1}N^2 = -K\left(C_b^\Theta\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + T_b^\Theta\nabla_n\hat{\Theta}\cdot\nabla_n\hat{p}\right) + \alpha^\Theta\left(D\hat{\Theta}_z\right)_z - \beta^\Theta\left(D\hat{S}_{A_z}\right)_z.} \tag{A.21.4}$$

The cabbeling nonlinearity (the C_b^Θ term) always causes "densification", that is, it always causes a negative dianeutral velocity $\tilde{e}$, while the thermobaric nonlinearity (the T_b^Θ term) can cause either diapycnal upwelling or downwelling.

To summarize this appendix A.21 so far; we have found that the material derivative of in situ density (A.21.1), when adjusted for the dynamically passive compressibility term, becomes the material derivative of locally-referenced potential density (A.21.2) which can be interpreted as an expression (A.21.4) for $\tilde{e}$, the temporally-averaged vertical velocity through the local neutral tangent plane. This dianeutral velocity $\tilde{e}$ 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 cabbeling and thermobaric nonlinearities of the equation of state. Note that a common diapycnal mixing mechanism, double-diffusive convection (which actually comes in two separate flavours, a salt-fingering type and a "diffusive" type of double-diffusive convection) is omitted from the conservation equations (A.20.7) and (A.20.10) and also from the mean dianeutral velocity equation (A.21.4). It is however straight-forward to include these processes in these conservation equations (see for example McDougall (1994, 1997b)).

A.22 The Water-Mass Transformation Equation

It is instructive to substitute equation (A.21.4) for $\tilde{e}$ into the expression (A.20.10) for the material derivative of $\hat{\Theta}$, thus eliminating $\tilde{e}$ and obtaining the following equation for the temporal and spatial evolution of $\hat{\Theta}$ along the neutral tangent plane (McDougall (1984))

$$
\left. \frac{\partial \hat{\Theta}}{\partial t} \right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} = \frac{1}{h} \nabla_n \cdot \left(hK\nabla_n\hat{\Theta} \right) + KgN^{-2}\hat{\Theta}_z \left(C_b^{\Theta} \nabla_n\hat{\Theta} \cdot \nabla_n\hat{\Theta} + T_b^{\Theta} \nabla_n\hat{\Theta} \cdot \nabla_n\hat{p} \right)
$$
$$
+ D\beta^{\Theta} gN^{-2}\hat{\Theta}_z^3 \frac{d^2\hat{S}_A}{d\hat{\Theta}^2} \ .
$$

(A.22.1)

The last term has been written as proportional to the curvature of the $\hat{S}_A - \hat{\Theta}$ diagram of a vertical cast; this term can also be written as $D\beta^{\Theta} gN^{-2}\left(\hat{\Theta}_z\hat{S}_{A_{zz}} - \hat{S}_{A_z}\hat{\Theta}_{zz} \right)$. The form of equation (A.22.1) 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, cabbeling and thermobaricity, (ii) are affected by diapycnal turbulent mixing only to the extent that the vertical $\hat{S}_A - \hat{\Theta}$ 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.20.7) and (A.20.10) are the fundamental conservation equations of salinity and Conservative Temperature in a turbulent ocean, and the pair of equations (A.21.4) and (A.22.1) are simply derived as linear combinations of (A.20.7) and (A.20.10). The "density" conservation equation (A.21.4) and the "water-mass transformation" equation (A.22.1) are in some sense the "normal modes" of (A.20.7) and (A.20.10). That is, (A.21.4) expresses how mixing processes contribute to the mean vertical velocity $\tilde{e}$ through the neutral tangent plane, while (A.22.1) 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 (A.22.1) is

$$
\left. \frac{\partial \hat{S}_A}{\partial t} \right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{S}_A = \frac{1}{h} \nabla_n \cdot \left(hK\nabla_n\hat{S}_A \right) + KgN^{-2}\hat{S}_{A_z} \left(C_b^{\Theta} \nabla_n\hat{\Theta} \cdot \nabla_n\hat{\Theta} + T_b^{\Theta} \nabla_n\hat{\Theta} \cdot \nabla_n\hat{p} \right)
$$
$$
+ D\alpha^{\Theta} gN^{-2}\hat{\Theta}_z^3 \frac{d^2\hat{S}_A}{d\hat{\Theta}^2} \ ,
$$

(A.22.2)

and it easy to show that α^{Θ} times the right-hand side of (A.22.1) is equal to β^{Θ} times the right-hand side of (A.22.2).

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.23.1) using (A.21.4) giving (from McDougall (1984))

$$\left.\frac{\partial \hat{C}}{\partial t}\right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{C} = \frac{1}{h} \nabla_n \cdot \left(hK \nabla_n \hat{C} \right) + K g N^{-2} \hat{C}_z \left(C_b^{\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + T_b^{\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{p} \right)$$

$$+ D \left(\hat{S}_{A_z} \right)^2 \frac{d^2 \hat{C}}{d\hat{S}_A^2} + \frac{\hat{C}_z}{\hat{S}_{A_z}} D\alpha^{\Theta} g N^{-2} \hat{\Theta}_z^3 \frac{d^2 \hat{S}_A}{d\hat{\Theta}^2} . \tag{A.22.3}$$

This equation shows that vertical turbulent mixing processes affect the tracer on neutral tangent planes according to the curvature of vertical casts as displayed on both the $\hat{S}_A - \hat{C}$ and the $\hat{S}_A - \hat{\Theta}$ curves. The last two terms in (A.22.3) can also be written as

$$D \left(\hat{S}_{A_z} \right)^2 \frac{d^2 \hat{C}}{d\hat{S}_A^2} + \frac{\hat{C}_z}{\hat{S}_{A_z}} D\alpha^{\Theta} g N^{-2} \hat{\Theta}_z^3 \frac{d^2 \hat{S}_A}{d\hat{\Theta}^2} =$$

$$D \left(\hat{S}_{A_z} \hat{C}_{zz} - \hat{S}_{A_{zz}} \hat{C}_z \right) \Big/ \hat{S}_{A_z} + D\hat{C}_z \alpha^{\Theta} g N^{-2} \left(\hat{\Theta}_z \hat{S}_{A_{zz}} - \hat{S}_{A_z} \hat{\Theta}_{zz} \right) \Big/ \hat{S}_{A_z} . \tag{A.22.4}$$

A.23 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 (A.20.7), and (A.20.10))

$$\left.\frac{\partial \hat{C}}{\partial t}\right|_z + \hat{\mathbf{v}} \cdot \nabla_z \hat{C} + w^* \frac{\partial \hat{C}}{\partial z} = \left.\frac{\partial \hat{C}}{\partial t}\right|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{C} + \tilde{e} \hat{C}_z$$

$$= \left.\frac{\partial \hat{C}}{\partial t}\right|_\sigma + \hat{\mathbf{v}} \cdot \nabla_\sigma \hat{C} + \tilde{e}^d \hat{C}_z \tag{A.23.1}$$

$$= \frac{1}{h} \nabla_n \cdot \left(hK \nabla_n \hat{C} \right) + \left(D \hat{C}_z \right)_z ,$$

where $\tilde{e}^d$ is the vertical component of the total transport velocity that moves through the potential density surface. Notice that in each case 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))

$$\alpha^{\Theta}(p_r) \left. \hat{\Theta}_t \right|_\sigma - \beta^{\Theta}(p_r) \left. \hat{S}_{A_t} \right|_\sigma = 0 \quad \text{and} \quad \alpha^{\Theta}(p_r) \nabla_\sigma \hat{\Theta} - \beta^{\Theta}(p_r) \nabla_\sigma \hat{S}_A = \mathbf{0}, \tag{A.23.2}$$

where $\alpha^{\Theta}(p_r)$ and $\beta^{\Theta}(p_r)$ are shorthand notations for $\alpha^{\Theta}\left(\hat{S}_A, \hat{\Theta}, p_r\right)$ and $\beta^{\Theta}\left(\hat{S}_A, \hat{\Theta}, p_r\right)$ respectively, and p_r is the reference pressure of the potential density. Using equations (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.20.10) for Conservative Temperature can be derived (see equation (26) of McDougall (1991))

$$\left.\frac{\partial \hat{\Theta}}{\partial t}\right|_\sigma + \hat{\mathbf{v}} \cdot \nabla_\sigma \hat{\Theta} + \tilde{e}^{\mathrm{d}} \frac{\partial \hat{\Theta}}{\partial z} = \frac{1}{h^\sigma} \nabla_\sigma \cdot \left(h^\sigma K \nabla_\sigma \hat{\Theta} \right) + \left(D \hat{\Theta}_z \right)_z$$

$$- \frac{1}{h} \nabla_n \cdot \left(\left[G^\Theta - 1 \right] h K \nabla_n \hat{\Theta} \right) \tag{A.23.3}$$

$$- \left(G^\Theta \left[G^\Theta - 1 \right] K \frac{\nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta}}{\hat{\Theta}_z} \right)_z ,$$

where the "isopycnal temperature gradient ratio" G^Θ is defined as $G^\Theta = r \left[R_\rho - 1 \right] / \left[R_\rho - r \right]$. The corresponding equation for Absolute Salinity is

$$\left.\frac{\partial \hat{S}_{\mathrm{A}}}{\partial t}\right|_\sigma + \hat{\mathbf{v}} \cdot \nabla_\sigma \hat{S}_{\mathrm{A}} + \tilde{e}^{\mathrm{d}} \frac{\partial \hat{S}_{\mathrm{A}}}{\partial z} = \frac{1}{h^\sigma} \nabla_\sigma \cdot \left(h^\sigma K \nabla_\sigma \hat{S}_{\mathrm{A}} \right) + \left(D \hat{S}_{\mathrm{A}_z} \right)_z$$

$$- \frac{1}{h} \nabla_n \cdot \left(\left[\frac{G^\Theta}{r} - 1 \right] h K \nabla_n \hat{S}_{\mathrm{A}} \right) \tag{A.23.4}$$

$$- \left(\frac{G^\Theta}{r} \left[G^\Theta - 1 \right] K \frac{\nabla_n \hat{\Theta} \cdot \nabla_n \hat{S}_{\mathrm{A}}}{\hat{\Theta}_z} \right)_z .$$

The terms in the second and third lines of (A.23.3) and (A.23.4) arise from the fact that in the first line of these equations, the lateral diffusion is written as occurring 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 (A.23.4) by $\beta^\Theta(p_{\mathrm{r}})$ and subtracting $\alpha^\Theta(p_{\mathrm{r}})$ times (A.23.3) we find the corresponding expression for the diapycnal velocity $\tilde{e}^{\mathrm{d}}$ (following McDougall (1991))

$$\tilde{e}^{\mathrm{d}} \frac{1}{\hat{\rho}_\Theta} \frac{\partial \hat{\rho}_\Theta}{\partial z} = \frac{\beta^\Theta(p_{\mathrm{r}})}{h^\sigma} \nabla_\sigma \cdot \left(h^\sigma K \nabla_\sigma \hat{S}_{\mathrm{A}} \right) - \frac{\alpha^\Theta(p_{\mathrm{r}})}{h^\sigma} \nabla_\sigma \cdot \left(h^\sigma K \nabla_\sigma \hat{\Theta} \right)$$

$$+ \beta^\Theta(p_{\mathrm{r}}) \left(D \hat{S}_{\mathrm{A}_z} \right)_z - \alpha^\Theta(p_{\mathrm{r}}) \left(D \hat{\Theta}_z \right)_z$$

$$+ \alpha^\Theta(p_{\mathrm{r}})(r-1) \frac{1}{h} \nabla_n \cdot \left(h K \nabla_n \hat{\Theta} \right) + \alpha^\Theta(p_{\mathrm{r}}) \frac{G^\Theta}{r} K \nabla_n r \cdot \nabla_n \hat{\Theta} \tag{A.23.5}$$

$$- \beta^\Theta(p_{\mathrm{r}}) \left(\frac{\alpha^\Theta(p_{\mathrm{r}})}{\beta^\Theta(p_{\mathrm{r}})} \right)_z G^\Theta \left[G^\Theta - 1 \right] K \frac{\nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta}}{\hat{\Theta}_z}$$

$$- \frac{\beta^\Theta(p_{\mathrm{r}})}{\beta^\Theta(p)} \left[\frac{G^\Theta}{r} - 1 \right] K \left(C_b^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + T_b^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{p} \right).$$

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 $T_b^\Theta K \nabla_n \hat{\Theta} \cdot \nabla_n \hat{p}$ 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 (A.23.5) can also be written as (c.f. the last line of (A.26.2) below) $C_b^\Theta(p_r) K \nabla_\sigma \hat{\Theta} \cdot \nabla_\sigma \hat{\Theta}$.

A.24 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.20.7) and (A.20.10) for Absolute Salinity and Conservative Temperature are now written with respect to this general "a" coordinate as

$$\left.\frac{\partial \hat{S}_A}{\partial t}\right|_a + \hat{\mathbf{v}} \cdot \nabla_a \hat{S}_A + \tilde{e}^a \frac{\partial \hat{S}_A}{\partial z} = \frac{1}{h} \nabla_n \cdot \left(h K \nabla_n \hat{S}_A\right) + \left(D \frac{\partial \hat{S}_A}{\partial z}\right)_z \qquad (A.24.1)$$

and

$$\left.\frac{\partial \hat{\Theta}}{\partial t}\right|_a + \hat{\mathbf{v}} \cdot \nabla_a \hat{\Theta} + \tilde{e}^a \frac{\partial \hat{\Theta}}{\partial z} = \frac{1}{h} \nabla_n \cdot \left(h K \nabla_n \hat{\Theta}\right) + \left(D \hat{\Theta}_z\right)_z. \qquad (A.24.2)$$

Cross-multiplying these equations by $\beta^\Theta = \beta^\Theta\left(\hat{S}_A, \hat{\Theta}, p\right)$ and $\alpha^\Theta = \alpha^\Theta\left(\hat{S}_A, \hat{\Theta}, p\right)$ and subtracting gives

$$\tilde{e}^a = -g N^{-2} K \left(C_b^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + T_b^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{p}\right) + \alpha^\Theta \left(D \hat{\Theta}_z\right)_z - \beta^\Theta \left(D \hat{S}_{A_z}\right)_z$$

$$+ g N^{-2} \hat{\mathbf{v}} \cdot \left[\beta^\Theta \nabla_n \hat{S}_A - \alpha^\Theta \nabla_n \hat{\Theta}\right] + g N^{-2} \left[\beta^\Theta \left.\frac{\partial \hat{S}_A}{\partial t}\right|_a - \alpha^\Theta \left.\frac{\partial \hat{\Theta}}{\partial t}\right|_a\right]. \qquad (A.24.3)$$

The terms in the second line of this equation can be shown to be (from Klocker and McDougall (2010a) and from (3.14.1) above)

$$g N^{-2} \hat{\mathbf{v}} \cdot \left[\beta^\Theta \nabla_n \hat{S}_A - \alpha^\Theta \nabla_n \hat{\Theta}\right] = -\hat{\mathbf{v}} \cdot \frac{\nabla_a \hat{\rho}^l}{\hat{\rho}_z^l} = \hat{\mathbf{v}} \cdot \left(\nabla_n z - \nabla_a z\right) = \hat{\mathbf{v}} \cdot \mathbf{s} \qquad (A.24.4)$$

and

$$g N^{-2} \left[\beta^\Theta \left.\frac{\partial \hat{S}_A}{\partial t}\right|_a - \alpha^\Theta \left.\frac{\partial \hat{\Theta}}{\partial t}\right|_a\right] = -\frac{\hat{\rho}_t^l\big|_a}{\hat{\rho}_z^l} = z_t\big|_n - z_t\big|_a \qquad (A.24.5)$$

where $\hat{\rho}^l$ is the (thickness-weighted) locally-referenced potential density.

Combining these results with (A.21.4) we have the rather simple kinematic result that

$$\tilde{e}^a = \tilde{e} + \hat{\mathbf{v}} \cdot \mathbf{s} + \left(z_t\big|_n - z_t\big|_a\right), \qquad (A.24.6)$$

showing that the vertical velocity through a general "a" surface, $\tilde{e}^a$, is that through the neutral tangent plane $\tilde{e}$ 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 neural tangent plane, $z_t\big|_n - z_t\big|_a$.

A.25 The Material Derivative of Potential Density

Using the relationships (A.23.2) that relate the gradients of Absolute Salinity and Conservative Temperature in potential density surfaces, the material derivative of the natural logarithm of potential density is $\beta^{\Theta}(p_{\mathrm{r}})$ times the material derivative (A.20.7) of Absolute salinity minus $\alpha^{\Theta}(p_{\mathrm{r}})$ times the material derivative (A.20.10) of Conservative Temperature. Performing these operations with the advection being taken 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 $\tilde{e}^{\mathrm{d}}$ as follows

$$
\begin{aligned}
\tilde{e}^{\mathrm{d}}\frac{1}{\hat{\rho}^{\Theta}}\frac{\partial\hat{\rho}^{\Theta}}{\partial z} &= \beta^{\Theta}(p_{\mathrm{r}})\tfrac{1}{h}\nabla_n\cdot\left(hK\nabla_n\hat{S}_{\mathrm{A}}\right) - \alpha^{\Theta}(p_{\mathrm{r}})\tfrac{1}{h}\nabla_n\cdot\left(hK\nabla_n\hat{\Theta}\right) \\
&\quad + \beta^{\Theta}(p_{\mathrm{r}})\left(D\hat{S}_{\mathrm{A}_z}\right)_z - \alpha^{\Theta}(p_{\mathrm{r}})\left(D\hat{\Theta}_z\right)_z,
\end{aligned}
\tag{A.25.1}
$$

where the following exact expression for the vertical gradient of potential density has been used,

$$
\frac{1}{\hat{\rho}^{\Theta}}\frac{\partial\hat{\rho}^{\Theta}}{\partial z} = \beta^{\Theta}(p_{\mathrm{r}})\hat{S}_{\mathrm{A}_z} - \alpha^{\Theta}(p_{\mathrm{r}})\hat{\Theta}_z.
\tag{A.25.2}
$$

Equation (A.25.1) can be written more informatively as (following McDougall, 1991)

$$
\begin{aligned}
\tilde{e}^{\mathrm{d}}\frac{1}{\hat{\rho}^{\Theta}}\frac{\partial\hat{\rho}^{\Theta}}{\partial z} &= \left(\frac{D}{\hat{\rho}^{\Theta}}\frac{\partial\hat{\rho}^{\Theta}}{\partial z}\right)_z \\
&\quad + D\left\{\alpha_{\Theta}^{\Theta}(p_{\mathrm{r}})\hat{\Theta}_z^2 + 2\alpha_{S_{\mathrm{A}}}^{\Theta}(p_{\mathrm{r}})\hat{\Theta}_z\hat{S}_{\mathrm{A}_z} - \beta_{S_{\mathrm{A}}}^{\Theta}(p_{\mathrm{r}})\hat{S}_{\mathrm{A}_z}^2\right\} \\
&\quad + \alpha^{\Theta}(p_{\mathrm{r}})[r-1]\tfrac{1}{h}\nabla_n\cdot\left(hK\nabla_n\hat{\Theta}\right) \\
&\quad + \frac{\beta^{\Theta}(p_{\mathrm{r}})}{\beta^{\Theta}(p)}K\left(C_b^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{\Theta} + T_b^{\Theta}\nabla_n\hat{\Theta}\cdot\nabla_n\hat{p}\right),
\end{aligned}
\tag{A.25.3}
$$

where r is defined in equation (3.17.2) 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 term would be present on the right of (A.25.3).

A.26 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 $\tilde{e}^{\mathrm{d\_model}}$ in this class of model obeys the equation (c.f. equation (A.25.1) above)

$$\tilde{e}^{\text{d\_model}} \frac{1}{\hat{\rho}^{\Theta}} \frac{\partial \hat{\rho}^{\Theta}}{\partial z} = \beta^{\Theta}(p_{\text{r}}) \frac{1}{h^{\sigma}} \nabla_{\sigma} \cdot \left(h^{\sigma} K^{\sigma} \nabla_{\sigma} \hat{S}_{\text{A}} \right) - \alpha^{\Theta}(p_{\text{r}}) \frac{1}{h^{\sigma}} \nabla_{\sigma} \cdot \left(h^{\sigma} K^{\sigma} \nabla_{\sigma} \hat{\Theta} \right)$$
$$+ \beta^{\Theta}(p_{\text{r}}) \left(D \hat{S}_{\text{A}_z} \right)_z - \alpha^{\Theta}(p_{\text{r}}) \left(D \hat{\Theta}_z \right)_z \,, \tag{A.26.1}$$

where ∇_{σ} is the gradient operator along the potential density coordinate, K^{σ} is the lateral diffusivity along the layers and h^{σ} is the thickness between a pair of potential density surfaces in the vertical. This equation can be rewritten as

$$\tilde{e}^{\text{d\_model}} \frac{1}{\hat{\rho}^{\Theta}} \frac{\partial \hat{\rho}^{\Theta}}{\partial z} = \left(\frac{D}{\hat{\rho}^{\Theta}} \frac{\partial \hat{\rho}^{\Theta}}{\partial z} \right)_z$$
$$+ D \left\{ \alpha_{\Theta}^{\Theta}(p_{\text{r}}) \hat{\Theta}_z^2 + 2\alpha_{S_{\text{A}}}^{\Theta}(p_{\text{r}}) \hat{\Theta}_z \hat{S}_{\text{A}_z} - \beta_{S_{\text{A}}}^{\Theta}(p_{\text{r}}) \hat{S}_{\text{A}_z}^2 \right\} \tag{A.26.2}$$
$$+ K^{\sigma} C_b^{\Theta}(p_{\text{r}}) \nabla_{\sigma} \hat{\Theta} \cdot \nabla_{\sigma} \hat{\Theta} \,.$$

The terms in the vertical turbulent diffusivity D are identical to those in the correct equation (A.25.3) while the diapycnal velocity due to cabbeling is quite similar to that in the correct expression (A.25.3); the difference 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 $\alpha^{\Theta}(p_{\text{r}})[r-1]h^{-1}\nabla_n \cdot \left(hK\nabla_n \hat{\Theta} \right)$ in (A.25.3) is missing from (A.26.2). 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 (A.26.2); that is, the term proportional to $K T_b^{\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{p}$ in (A.25.3) is absent from (A.26.2). The thermobaric diapycnal advection is probably significant in the Southern Ocean (Klocker and McDougall (2010b)) 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 in done in height-coordinate ocean models.

A.27 The Material Derivative of Orthobaric Density

Orthobaric density $\rho_v(p, \rho)$ 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 (McDougall and Jackett (2005a)). The material derivative of ρ_v can be expressed with respect to orthobaric density surfaces as

$$\left. \frac{\partial \rho_v}{\partial t} \right|_{\rho_v} + \hat{\mathbf{v}} \cdot \nabla_{\rho_v} \rho_v + \tilde{e}^{\rho_v} \frac{\partial \rho_v}{\partial z} = \tilde{e}^{\rho_v} \frac{\partial \rho_v}{\partial z} \,, \tag{A.27.1}$$

where the temporally averaged vertical velocity through the ρ_v surface is given by (from McDougall and Jackett, 2005a)

$$\tilde{e}^{\rho_v} = gN^{-2}\left(\alpha^{\Theta}\dot{\Theta} - \beta^{\Theta}\dot{S}\right) + (\psi-1)\left(\hat{p}_t\big|_{\rho_v} + \hat{\mathbf{v}}\cdot\nabla_{\rho_v}\hat{p}\right)\Big/\hat{p}_z,$$ (A.27.2)

where

$$(\psi-1) \approx 2g^2N^{-2}c_0^{-3}\Delta c \approx -\rho g^2 T_b^{\Theta}N^{-2}\left[\hat{\Theta} - \Theta_0(p,\rho)\right],$$ (A.27.3)

and Δc 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 approximation to the sound speed is equivalent to the difference between the actual Conservative Temperature of a water parcel and the reference value $\Theta_0(p,\rho)$. Here $\dot{S}_A$ is shorthand for the material derivative of $\hat{S}_A$ and is expressed in terms of mixing processes by the right-hand side of (A.20.7); $\dot{\Theta}$ is similarly shorthand for the material derivative of $\hat{\Theta}$ and is given by the right-hand side of equation (A.20.10).

The first term on the right of (A.27.2) represents the effects of irreversible mixing processes on the flow though orthobaric density surfaces, and this contribution to $\tilde{e}^{\rho_v}$ is exactly the same as the flow through neutral tangent planes, $\tilde{e}$ (equation (A.21.4)). The second term in (A.27.2) 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.28 The Material Derivative of Neutral Density

Neutral Density γ^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 these two seawater parcels. The material derivative of γ^n can be expressed with respect to Neutral Density surfaces as

$$\frac{\partial \gamma^n}{\partial t}\bigg|_{\gamma} + \hat{\mathbf{v}}\cdot\nabla_{\gamma}\gamma^n + \tilde{e}^{\gamma}\gamma_z^n = \tilde{e}^{\gamma}\gamma_z^n,$$ (A.28.1)

where the temporally averaged vertical velocity through the γ^n surface is given by (from McDougall and Jackett (2005b))

$$\tilde{e}^{\gamma} \approx \frac{\left(\alpha^{\Theta}(\overline{p})\dot{\Theta} - \beta^{\Theta}(\overline{p})\dot{S}_{A}\right)}{\left(\alpha^{\Theta}(\overline{p})\Theta_{z}^{r} - \beta^{\Theta}(\overline{p})S_{A_{z}}^{r}\right)} + \hat{\mathbf{v}} \cdot \mathbf{s}^{r}$$

$$+ \left(\psi^{\gamma} - 1\right)\left(\hat{p}_{t}|_{\gamma} + \hat{\mathbf{v}} \cdot \nabla_{\gamma}\hat{p}\right)\left(\hat{p}_{z}\right)^{-1}$$

$$+ \left(\psi^{\gamma} - 1\right)\left(\hat{\mathbf{v}} \cdot \nabla_{\gamma}p^{r} - \frac{(\hat{p} - p^{r})}{(\hat{\Theta} - \Theta^{r})}\hat{\mathbf{v}} \cdot \nabla_{\gamma}\Theta^{r}\right)\left(p_{z}\right)^{-1} \qquad \text{(A.28.2)}$$

$$+ 2(\psi^{\gamma} - 1)\frac{\left(\alpha^{\Theta}(\overline{p})\dot{\Theta} - \beta^{\Theta}(\overline{p})\dot{S}_{A}\right)}{\left(\alpha^{\Theta}(\overline{p})\Theta_{z}^{r} - \beta^{\Theta}(\overline{p})S_{A_{z}}^{r}\right)}$$

$$+ \left(\psi^{\gamma} - 1\right)\hat{\mathbf{v}} \cdot \mathbf{s}^{r}.$$

Here $\dot{S}_{A}$ is shorthand for the material derivative of $\hat{S}_{A}$ following the appropriate mean velocity and is expressed in terms of mixing processes by the right-hand side of (A.20.7), $\dot{\Theta}$ is similarly shorthand for the material derivative of $\hat{\Theta}$ and is given by equation (A.20.10), and $\left(\psi^{\gamma} - 1\right)$ is defined by

$$\left(\psi^{\gamma} - 1\right) = \frac{-\frac{1}{2}\rho g^{2}T_{b}^{\Theta}(\hat{\Theta} - \Theta^{r})}{\left[N^{2} + \rho g^{2}T_{b}^{\Theta}(\hat{\Theta} - \Theta^{r}) - \frac{1}{2}\rho g^{2}T_{b}^{\Theta}(\hat{p} - p^{r})\Theta_{p}^{r}\right]}. \qquad \text{(A.28.3)}$$

Hence $\left(\psi^{\gamma} - 1\right)$ is nonzero to the extent that there is a water mass contrast $(\Theta - \Theta^{r})$ 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 $(\hat{\Theta} - \Theta^{r})$ and $(\hat{p} - p^{r})$ the denominator in (A.28.3) is close to N^{2} and $\left(\psi^{\gamma} - 1\right)$ is small. In these expressions the thermal expansion coefficient $\alpha^{\Theta}(\overline{p})$ and saline contraction coefficient $\beta^{\Theta}(\overline{p})$ 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, $\alpha^{\Theta}(\overline{p})$ and $\beta^{\Theta}(\overline{p})$ are shorthand for $\alpha^{\Theta}\left(\overline{S}_{A}, \overline{\Theta}, \overline{p}\right)$ and $\beta^{\Theta}\left(\overline{S}_{A}, \overline{\Theta}, \overline{p}\right)$.

The first term in (A.28.2) is expected in the sense that when there are irreversible mixing processes so that $\dot{\Theta}$ and $\dot{S}$ are non-zero, one expects that neutral density would change. The next term in (A.28.2), $\hat{\mathbf{v}} \cdot \mathbf{s}^{r}$, is the mean vertical motion through the γ^{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 four terms in (A.28.2) arise because of the non-quasi-material (non-potential) nature of Neutral Density. The second line of (A.28.2) represents the vertical advection arising from the seemingly innocuous sliding motion along the sloping Neutral Density surface and form the vertical heaving of these surfaces. The lateral gradients of properties in the reference data set also affect the mean flow $\tilde{e}^{\gamma}$ through the Neutral Density surface. Note that as $(\hat{\Theta} - \Theta^{r})$ tends to zero, $\left(\psi^{\gamma} - 1\right)$ also tends to zero so that the third line of (A.28.2) is well-behaved and becomes proportional to $(\hat{p} - p^{r})\hat{\mathbf{v}} \cdot \nabla_{\gamma}\Theta^{r}$.

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 δQ 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 ρ, and δQ per unit volume, δq, as

$$\rho \left(\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} \right) = \frac{\delta q}{dt}. \qquad \textit{for pure water} \quad (B1)$$

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, $\mathbf{F}^{\mathrm{R}}$, and minus the divergence of the molecular flux of heat $\mathbf{F}^{\mathrm{q}} = -k^T \nabla T$ (where k^T is the molecular diffusivity of heat), so that the First Law of Thermodynamics for pure water is

$$\rho \left(\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} \right) = \frac{\delta q}{dt} = -\nabla \cdot \mathbf{F}^{\mathrm{R}} + \nabla \cdot \left(k^T \nabla T \right) + \rho \varepsilon. \qquad \textit{for pure water} \quad (B.2)$$

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))

$$dH - Vdp = \delta Q + \left(\mu - [T_0 + t] \mu_T \right) M \, dS_{\mathrm{A}}. \qquad (B.3)$$

where M is the mass of the fluid parcel. When integrated over the surface of a finite volume of fluid of fixed mass, the last term in (B.3) becomes the area integral of the normal component of $-\left(\mu - [T_0 + t] \mu_T \right) \mathbf{F}^S$ through the boundary of that volume so that the material derivative form of (B.3) is

$$\rho \left(\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} \right) = \frac{\delta q}{dt} - \nabla \cdot \left[\left(\mu - [T_0 + t] \mu_T \right) \mathbf{F}^S \right]. \qquad (B.4)$$

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 $\delta q / \mathrm{d}t$ 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.22) or (B.24)) for the molecular flux $\mathbf{F}^Q$). The two versions of the First Law of Thermodynamics are different by the divergence of the flux

$$\left(T_0 + t\right)\left(\mu_T + b\frac{\mu_{S_A}}{\rho k^S}\right)\mathbf{F}^S. \tag{B.5}$$

This inconsistency in fluxes means that the rather poorly defined "rate of heating" $\delta q / \mathrm{d}t$ must be different in the saline case than in the pure water situation. 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" $\delta q / \mathrm{d}t$ is doomed to failure.

Since there appears to be no way of deriving the First Law of Thermodynamics that involves the "heating" term $\delta q / \mathrm{d}t$, we follow Landau and Lifshitz (1959) and Griffies (2004) 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 conservation equation for total energy must have the conservative form, and so we insist that the forcing terms in this equation must 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) terms of material derivatives following the instantaneous motion of a fluid parcel

$$\mathrm{d}/\mathrm{d}t = \partial/\partial t\big|_{x,y,z} + \mathbf{u}\cdot\nabla,$$

$$\frac{dh}{dt} - \frac{1}{\rho}\frac{dp}{dt} = \frac{du}{dt} + (p + P_0)\frac{dv}{dt} = (T_0 + t)\frac{d\eta}{dt} + \mu\frac{dS_A}{dt} . \qquad (B.6)$$

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 $h = u + (p + P_0)v$ 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 Φ with respect to some fixed height z_0 is defined by

$$\Phi = \int_{z_0}^{z} g(z')\, dz'. \qquad (B.7)$$

At a fixed location in space Φ 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 Φ is then readily constructed as

$$(\rho\Phi)_t + \nabla\cdot(\rho\Phi\mathbf{u}) = \rho\frac{d\Phi}{dt} = \rho gw, \qquad (B.8)$$

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.

The 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 v^{visc} and the velocity divergence $\nabla\cdot\mathbf{u}$ (following Gill (1982)), so arriving at

$$\rho\frac{d\mathbf{u}}{dt} + f\,\mathbf{k}\times\rho\mathbf{u} = -\nabla p - \rho g\mathbf{k} + \nabla\cdot\left(\rho v^{\text{visc}}\widehat{\nabla\mathbf{u}}\right), \qquad (B.9)$$

where f is the Coriolis frequency, v^{visc} is the viscosity and $\widehat{\nabla\mathbf{u}}$ is twice the symmetrized velocity shear, $\widehat{\nabla\mathbf{u}} = \left(\partial u_i/\partial x_j + \partial u_j/\partial x_i\right)$. 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)).

The kinetic energy evolution equation

The kinetic energy evolution equation is found by taking the scalar product of equation (B.9) with $\mathbf{u}$ giving

$$\left(\rho\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right)$$
$$= \rho\,\mathrm{d}\!\left(\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)\!\big/\mathrm{d}t \;\; = \;\; -\mathbf{u}\cdot\nabla p - \rho gw + \nabla\cdot\left(\rho v^{\mathrm{visc}}\nabla\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right) - \rho\varepsilon,$$

(B.10)

where the dissipation of mechanical energy ε is the positive definite quantity

$$\varepsilon \;\equiv\; \tfrac{1}{2}v^{\mathrm{visc}}\left(\widehat{\nabla\mathbf{u}}\cdot\widehat{\nabla\mathbf{u}}\right).$$

(B.11)

The evolution equation for the sum of kinetic and gravitational potential energies

The evolution equation for total mechanical energy $0.5\mathbf{u}\cdot\mathbf{u} + \Phi$ is found by adding equations (B8) and (B10) giving

$$\left(\rho\left[\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right]\right)_t + \nabla\cdot\left(\rho\mathbf{u}\left[\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right]\right)$$
$$= \rho\,\mathrm{d}\!\left(\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right)\!\big/\mathrm{d}t \;\; = \;\; -\mathbf{u}\cdot\nabla p + \nabla\cdot\left(\rho v^{\mathrm{visc}}\nabla\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right) - \rho\varepsilon.$$

(B.12)

Notice that the term ρgw which has the role of exchanging energy between the kinetic and gravitational potential forms has cancelled when these two evolution equations were added.

The 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), both the specific entropy s 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 $\mathrm{d}u/\mathrm{d}t = -(p+P_0)\mathrm{d}v/\mathrm{d}t$ 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 equation (A.8.1) in the form $\mathrm{d}\rho/\mathrm{d}t + \rho\nabla\cdot\mathbf{u} = 0$, $\mathrm{d}u/\mathrm{d}t$ can be expressed in this situation of no molecular, radiative or boundary fluxes as $\mathrm{d}u/\mathrm{d}t = -\rho^{-1}(p+P_0)\nabla\cdot\mathbf{u}$. Adding this equation to the inviscid, non-dissipative version of (B.12) gives

$$\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t \;\; = \;\; -\nabla\cdot\left([p+P_0]\mathbf{u}\right), \qquad \textit{no molecular fluxes} \;\; \text{(B.13)}$$

where the total energy

$$\mathcal{E} = u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$$

(B.14)

is defined as the sum of the internal, kinetic and gravitational potential energies.

The conservation equation for total energy in the presence of molecular fluxes

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 $\boldsymbol{\sigma}$, and the interior flux of energy due to this stress tensor is $\mathbf{u} \cdot \boldsymbol{\sigma}$ so that there needs to be the additional term $-\nabla \cdot (\mathbf{u} \cdot \boldsymbol{\sigma})$ added to the right-hand side of the total energy conservation equation. Consistently with equation (B.9) above we take the stress tensor to be $\boldsymbol{\sigma} = -\rho v^{\text{visc}} \widehat{\nabla \mathbf{u}}$ so that the extra term is $\nabla \cdot \left(\rho v^{\text{visc}} \nabla \tfrac{1}{2} [\mathbf{u} \cdot \mathbf{u}] \right)$. Also heat fluxes at the ocean boundaries and by radiation $\mathbf{F}^R$ and molecular diffusion $\mathbf{F}^Q$ necessitate the additional terms $-\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q$. At this stage we have not specified the form of the molecular diffusive flux of heat $\mathbf{F}^Q$ in terms of gradients of temperature and Absolute Salinity; this is done below in Eq (B.24). The total energy conservation equation in the presence of molecular, radiative and boundary fluxes is then

$$
\begin{aligned}
(\rho \mathcal{E})_t + \nabla \cdot (\rho \mathbf{u} \mathcal{E}) \\
= \rho \, d\mathcal{E}/dt = -\nabla \cdot ([p + P_0]\mathbf{u}) - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \nabla \cdot \left(\rho v^{\text{visc}} \nabla \tfrac{1}{2} [\mathbf{u} \cdot \mathbf{u}] \right)
\end{aligned}
\tag{B.15}
$$

The right-hand side of the $\mathcal{E}$ conservation equation (B15) is certainly the divergence of a flux, ensuring that the volume integral of total energy is well-behaved and ensuring that total energy $\mathcal{E}$ is 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 $\rho \mathcal{E} = \rho \left(u + \tfrac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi \right)$ while the divergence part of the left-hand side based on a <u>different</u> quantity, namely the Bernoulli function $\mathcal{B} = h + \tfrac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi$. This form of the total energy equation is

$$
(\rho \mathcal{E})_t + \nabla \cdot (\rho \mathbf{u} \mathcal{B}) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \nabla \cdot \left(\rho v^{\text{visc}} \nabla \tfrac{1}{2} [\mathbf{u} \cdot \mathbf{u}] \right).
\tag{B.16}
$$

In an ocean modeling context, it is rather strange to contemplate the energy variable that is advected through the face of a model grid, $\mathcal{B}$, 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 $\mathcal{B} = h + \tfrac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi$ so that the prognostic equation for the Bernoulli function is

$$
(\rho \mathcal{B})_t + \nabla \cdot (\rho \mathbf{u} \mathcal{B}) = \rho \, d\mathcal{B}/dt = p_t - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \nabla \cdot \left(\rho v^{\text{visc}} \nabla \tfrac{1}{2} [\mathbf{u} \cdot \mathbf{u}] \right).
\tag{B.17}
$$

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 $\mathcal{B}$ is conserved following the fluid motion in the absence of radiative, boundary and molecular fluxes. Subject to this steady-state assumption, the Bernoulli function $\mathcal{B}$ possesses the "potential" property. The negative aspect of this $\mathcal{B}$ evolution equation (B.17) is that in the more general

situation where the flow is unsteady, the presence of the p_t 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 $\mathcal{B}$ 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 $\mathcal{E} = \mathcal{B} - (p + P_0)/\rho$ and continuing to consider the situation where the whole ocean is in a steady state so that $\mathcal{B}$ 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 $p_t = 0$ everywhere, then $\mathcal{B}$ remains constant while the parcel's $\mathcal{E}$ changes by the difference in the quantity $-(p + P_0)/\rho$ 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

$$(\rho u)_t + \nabla \cdot (\rho \mathbf{u}\, u) = \rho\, du/dt = -(p + P_0)\nabla \cdot \mathbf{u} - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho\varepsilon. \qquad (B.18)$$

Using the continuity equation in the form $d\rho/dt + \rho\nabla \cdot \mathbf{u} = 0$ and the fundamental thermodynamic relation (A.7.2), this equation can be written as

$$\boxed{\begin{aligned} \rho\left(\frac{dh}{dt} - \frac{1}{\rho}\frac{dp}{dt}\right) &= \rho\left(\frac{du}{dt} + (p + P_0)\frac{dv}{dt}\right) = \\ \rho\left((T_0 + t)\frac{d\eta}{dt} + \mu\frac{dS_A}{dt}\right) &= -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho\varepsilon, \end{aligned}} \qquad (B.19)$$

which is the First Law of Thermodynamics. The corresponding equation expressing the conservation of Absolute Salinity is

$$\boxed{\rho\frac{dS_A}{dt} = (\rho S_A)_t + \nabla \cdot (\rho \mathbf{u}\, S_A) = -\nabla \cdot \mathbf{F}^S,} \qquad (B.20)$$

where $\mathbf{F}^S$ is the molecular flux of salt. 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, equations (B.23) and (B.24) below list these molecular fluxes in terms of the spatial gradients of these quantities.

At first sight equation (B.19) has little to recommend it; there is a non-conservative source term $\rho\varepsilon$ on the right-hand side and the left-hand side is not ρ 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 equations (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. This is essential; total energy cannot be allowed to spontaneously appear or disappear. 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 the appendix involved the poorly defined "rate of heating" $\delta q/\mathrm{d}t$ and did not lead us to the First Law. For completeness, the molecular fluxes $\mathbf{F}^Q$ and $\mathbf{F}^S$ are now written in terms of the gradients of Absolute Salinity, temperature and pressure.

Landau and Lifshitz (1959) (their section 58) show that the molecular fluxes $\mathbf{F}^Q$ and $\mathbf{F}^S$ are given in terms of the chemical potential μ and the gradients of temperature and of chemical potential by

$$\mathbf{F}^S = -a\nabla\mu - b\nabla T \qquad (B.21)$$

and

$$\mathbf{F}^Q = -b(T_0+t)\nabla\mu - \gamma\nabla T + \mu\mathbf{F}^S, \qquad (B.22)$$

where a, b and γ 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

$$\mathbf{F}^S = -\rho k^S\nabla S_A - \left(\frac{\rho k^S\mu_T}{\mu_{S_A}} + b\right)\nabla T + \frac{k^S\beta^t}{\mu_{S_A}}\nabla p \qquad (B.23)$$

(using the relation $\beta^t = -\rho\mu_p$ that follows from the definition of both β^t and μ in terms of the Gibbs function) and

$$\mathbf{F}^Q = \left(\mu + b\frac{[T_0+t]\mu_{S_A}}{\rho k^S}\right)\mathbf{F}^S - k^T\nabla T. \qquad (B.24)$$

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 Gibbs 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.

Appendix C: Papers Describing the TEOS-10 Thermodynamic Definition of Seawater

Primary Standard Documents

IAPWS, 1995: 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. Fredericia, Denmark, September 1996, available at http://www.iapws.org/relguide/IAPWS95.pdf

IAPWS, 2006: Release on an Equation of State for H_2O Ice Ih, The International Association for the Properties of Water and Steam, Witney, UK, September 2006, available at http://www.iapws.org/relguide/Ice.pdf

IAPWS 2008: 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 at http://www.iapws.org

Millero, F.J., Feistel, R., Wright, D.G., and McDougall, T.J., 2008: The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale, *Deep-Sea Res. I,* **55**, 50-72.

Secondary Standard Documents

IAPWS, 2009: Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use, The International Association for the Properties of Water and Steam, Arnhem, Netherlands, September 2009, proposed Release.

IOC Manuals and Guides No. xx, 2010: *The International Thermodynamic Equation Of Seawater 2010 (TEOS-10): Calculation and Use of Thermodynamic Properties,* UNESCO (English), 150pp.

Tertiary Standard Documents

McDougall, T. J., D. R. Jackett and F. J. Millero, 2009: An algorithm for estimating Absolute Salinity in the global ocean. *Ocean Sci. Discuss.*, **6**, 215-242. http://www.ocean-sci-discuss.net/6/215/2009/osd-6-215-2009.html and from www.TEOS-10.org. [This paper and its computer algorithm contain the state of the art today for estimating Absolute Salinity from field measurements of Practical Salinity. As more measurements become available in coming years, it is expected this algorithm will be updated, after such improvements appear in the refereed literature.]

Background papers to the declared standards

Wagner, W. and Pruß, A., 2002: The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data,* **31**, 387-535.

McDougall, T.J., 2003: Potential enthalpy: A conservative oceanic variable for evaluating heat content and heat fluxes. *Journal of Physical Oceanography*, **33**, 945-963.

Feistel, R. and W. Wagner, 2006: A New Equation of State for H_2O Ice Ih. *J. Phys. Chem. Ref. Data,* **35**, 2, 1021-1047.

Feistel, R., 2003: A new extended Gibbs thermodynamic potential of seawater. *Progr. Oceanogr.*, **58**, 43-114.

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.

Feistel, R., D. G. Wright, K. Miyagawa, A. H. Harvey, J. Hruby, D. R. Jackett, T. J. McDougall and W. Wagner, 2008: Mutually consistent thermodynamic potentials for fluid water, ice and seawater: a new standard for oceanography. *Ocean Science*, **4**, 275-291. http://www.ocean-sci.net/4/275/2008/os-4-275-2008.html

Marion, G.M., F. J. Millero, and R. Feistel, 2009: Precipitation of solid phase calcium carbonates and their effect on application of seawater $S_A - T - P$ models, *Ocean Sci.*, 5, 285-291. www.ocean-sci.net/5/285/2009/

Millero, F.J., 2000. Effect of changes in the composition of seawater on the density-salinity relationship. *Deep-Sea Res. I* **47**, 1583-1590.

Millero, F. J., F. Huang, N. Williams, J. Waters and R. Woosley, 2009: The effect of composition on the density of South Pacific Ocean waters, *Mar. Chem.*, **114**, 56-62.

Millero, F.J., J. Waters, R. Woosley, F. Huang, and M. Chanson, 2008: The effect of composition on the density of Indian Ocean waters, *Deep-Sea Res. I*, **55**, 460-470.

McDougall, T.J., R. Feistel, F. J. Millero, D. R. Jackett, D. G. Wright, B. A. King, G. M. Marion, C.-T. A. Chen and P. Spitzer, 2009: *The International Thermodynamic Equation Of Seawater 2010 (TEOS-10): Calculation and Use of Thermodynamic Properties*, Global Ship-based Repeat Hydrography Manual, IOCCP Report No. 14, ICPO Publication Series no. 134, 150pp.

Papers describing computer software

Feistel, R., D. G. Wright, D. R. Jackett, K. Miyagawa, W. Wagner, U. Overhoff, C. Guder, G. M. Marion, V. Tchijov, A. Feistel, J. H. Reissmann, 2009: Numerical implementation and oceanographic application of the thermodynamic potentials of water, vapour, ice, and seawater. Part I: Background and equations. *Ocean Science*, in preparation.

Wright, D. G., R. Feistel, D. R. Jackett, K. Miyagawa, A. Feistel, C. Guder, G. M. Marion, U. Overhoff, J. H. Reissmann, V. Tchijov, and W. Wagner, 2009a: Numerical implementation and oceanographic application of the thermodynamic potentials of water, vapour, ice, and seawater. Part II: The library routines. *Ocean Science*, in preparation.

TEOS-10 web site

We have created and are maintaining the web site www.TEOS-10.org which serves many of the TEOS-10 papers and the TEOS-10 manual as well as key computer software.

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 D1. Selected properties of pure water were taken from IAPWS (1996, 1997, 2005, 2006) as listed in Table D2. The chemical Reference Composition of seawater from Millero et al. (2008a) is given in Table D3. Selected seawater constants derived from the Reference Composition are listed in Table D4. The exact value of the isobaric "heat capacity" c_p^0 is given in Table D5.

Table D1. Fundamental constants from CODATA 2006 (Mohr et al. (2008)) and ISO (1993).

Symbol	Value	Uncertainty	Unit	Comment
R	8.314 472	0.000 015	J mol^{-1} K^{-1}	molar gas constant
P_0	101 325	exact	Pa	normal pressure
T_0	273.15	exact	K	Celsius zero point

Table D2. Selected properties of liquid water from IAPWS (1996, 1997, 2005, 2006) and Feistel (2003).

Symbol	Value	Uncertainty	Unit	Comment
M_W	18.015 268	0.000 002	g mol^{-1}	molar mass
T_{MD}	3.978 121	0.04	°C	maximum density , temperature
ρ_{MD}	999.974 95	0.000 84	kg m^{-3}	maximum density at P_0
ρ^0	999.8431	0.001	kg m^{-3}	density at T_0 and P_0, $\rho^0 = 1/v^0$
$\left(\partial\rho^0/\partial T\right)_P$	$6.774\ 876 \times 10^{-2}$	0.06×10^{-2}	kg m^{-3} K^{-1}	$\left(\partial\rho/\partial T\right)_P$ at T_0 and P_0
T_t	273.16	exact	K	triple point temperature
P_t	611.657	0.01	Pa	triple point pressure
ρ_t	999.793	0.01	kg m^{-3}	triple point density
η_t	0	exact	J kg^{-1} K^{-1}	triple point entropy
u_t	0	exact	J kg^{-1}	triple point internal energy
T_f^0	273.152 519	0.000 002	K	freezing point at P_0

Table D3. The sea salt composition definition for reference salinity of the standard ocean at 25°C and 101325 Pa. X – mole fractions, Z – valences, W – mass fractions (Millero et al. 2008). Molar masses M from Wieser (2006) with their uncertainties given in the brackets. The mass fractions are with respect to the mass of solution rather than the mass of pure water in solution.

Solute j	Z_j	M_j g mol^{-1}	X_j 10^{-7}	$X_j \times Z_j$ 10^{-7}	W_j
Na$^+$	+1	22.989 769 28(2)	4188071	4188071	0.3065958
Mg^{2+}	+2	24.305 0(6)	471678	943356	0.0365055
Ca^{2+}	+2	40.078(4)	91823	183646	0.0117186
K$^+$	+1	39.098 3(1)	91159	91159	0.0113495
Sr^{2+}	+2	87.62(1)	810	1620	0.0002260
Cl$^-$	−1	35.453(2)	4874839	−4874839	0.5503396
SO$_4^{2-}$	−2	96.062 6(50)	252152	−504304	0.0771319
HCO$_3^-$	−1	61.016 84(96)	15340	−15340	0.0029805
Br$^-$	−1	79.904(1)	7520	−7520	0.0019134
CO$_3^{2-}$	−2	60.008 9(10)	2134	−4268	0.0004078
B(OH)$_4^-$	−1	78.840 4(70)	900	−900	0.0002259
F$^-$	−1	18.998 403 2(5)	610	−610	0.0000369
OH$^-$	−1	17.007 33(7)	71	−71	0.0000038
B(OH)$_3$	0	61.833 0(70)	2807	0	0.0005527
CO$_2$	0	44.009 5(9)	86	0	0.0000121
Sum			1 000 000 0	0	1.0

Table D4. Selected properties of the KCl-normalised reference seawater (Millero et al. 2008), and proposals of the WG127 (2006).

Symbol	Value	Uncertainty	Unit	Comment
M_S	31.403 8218	0.001	g mol^{-1}	reference salinity molar mass $M_S = \sum_j X_j M_j$
Z^2	1.245 2898	exact[a]	-	reference salinity valence factor $Z^2 = \sum_j X_j Z_j^2$
N_S	$1.917\ 6461 \times 10^{22}$	6×10^{17}	g^{-1}	reference salinity particle number $N_S = N_A / M_S$
u_{PS}	1.004 715…	exact[a]	g kg^{-1}	unit conversion factor, 35.165 04 g kg^{-1} / 35
S_{SO}	35.165 04	exact[a]	g kg^{-1}	standard ocean reference salinity, 35 u_{PS}
T_{SO}	273.15	exact	K	standard ocean temperature $T_{SO} = T_0$
t_{SO}	0	exact	°C	standard ocean temperature $t_{SO} = T_{SO} - T_0$
P_{SO}	101 325	exact	Pa	standard ocean surface pressure $P_{SO} = P_0$
p_{SO}	0	exact	Pa	standard ocean surface sea pressure $p_{SO} = P_{SO} - P_0$
h_{SO}	0	exact	J kg^{-1}	standard ocean surface enthalpy $h_{SO} = u_t$
η_{SO}	0	exact	J kg^{-1} K^{-1}	standard ocean surface entropy $\eta_{SO} = \eta_t$
S_u	40.188 617…	exact[a]	g kg^{-1}	unit-related scaling constant, 40 u_{PS}
t_u	40	exact	°C	unit-related scaling constant
p_u	10^8	exact	Pa	unit-related scaling constant
g_u	1	exact	J kg^{-1}	unit-related scaling constant

[a] by definition of Reference Salinity and reference composition

Table D5. The exact definition of the isobaric "heat capacity" that relates potential enthalpy to Conservative Temperature Θ.

Symbol	Value	Uncertainty	Unit	Comment
c_p^0	3991.867 957 119 63	exact	J kg^{-1} K^{-1}	See eq. (3.3.3)

Coriolis Parameter

The rotation rate of the earth Ω is (Griffies (2004))

$$\Omega = 7.2921 x 10^{-5} \text{ s}^{-1} \tag{D.1}$$

and the Coriolis parameter f is

$$f = 2\Omega \sin\phi = 1.45842 x 10^{-4} \sin\phi \text{ s}^{-1} \tag{D.2}$$

where ϕ is latitude.

Gravitational Acceleration

The gravitational acceleration g is (Moritz (2000))

$$
\begin{aligned}
g &= 9.780\ 327 \left[1 + 5.3024 x 10^{-3} \sin^2\phi - 5.8 x 10^{-6} \sin^2 2\phi \right] \text{m s}^{-2} \\
&= 9.780\ 327 \left[1 + 5.2792 x 10^{-3} \sin^2\phi + 2.32 x 10^{-5} \sin^4\phi \right] \text{m s}^{-2},
\end{aligned}
\tag{D.3}
$$

where ϕ is latitude. This is the gravitational acceleration on the surface of an ellipsoid which is an approximation to the geoid. The average value of g over the earth's surface at mean sea level is 9.7976 m s^{-2} (this value needs recalculating without a reference to Gill) but a more relevant average value of g for oceanography is that averaged over the surface of the ocean, namely (this needs checking now) 9.7963 m s^{-2}. Gill (1982) (page 597) also gives a height dependence of g but his formula seems to apply to the atmosphere, not to the ocean.

Appendix E: Algorithm for calculating Practical Salinity S_P

E.1 Calculation of Practical Salinity S_P 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 $t_{68} = 15\,°C$ and pressure equal to one standard atmosphere ($p = 0$ dbar and absolute pressure P equal to $101\,325$ 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 32.4356×10^{-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

$$S_P = \sum_{i=0}^{5} a_i \left(K_{15}\right)^{i/2} \quad \text{where} \quad K_{15} = \frac{C\left(S_P, t_{68} = 15°C, 0\right)}{C\left(35, t_{68} = 15°C, 0\right)}, \tag{E.1.1}$$

and the coefficients a_i are given in the following table. Note that the sum of the six a_i coefficients is precisely 35, that is $\sum_{i=0}^{5} a_i = 35$, while the sum of the six b_i coefficients is precisely zero, that is, $\sum_{i=0}^{5} b_i = 0$. Equation (E.1.1) is valid in the range $2 < S_P < 42$.

i	a_i	b_i	c_i	d_i	e_i
0	0.0080	0.0005	6.766097×10^{-1}		
1	- 0.1692	- 0.0056	2.00564×10^{-2}	3.426×10^{-2}	2.070×10^{-5}
2	25.3851	- 0.0066	1.104259×10^{-4}	4.464×10^{-4}	$- 6.370 \times 10^{-10}$
3	14.0941	- 0.0375	$- 6.9698 \times 10^{-7}$	4.215×10^{-1}	3.989×10^{-15}
4	- 7.0261	0.0636	1.0031×10^{-9}	$- 3.107 \times 10^{-3}$	
5	2.7081	- 0.0144			

E.2 Calculation of Practical Salinity S_P at oceanographic temperature and pressure

The following formulae from Unesco (1983) are valid over the range $-2\,°C \le t \le 35\,°C$ and $0 \le p \le 10\,000\,dbar$. Measurements of salinity in the field generally measure the conductivity ratio R

$$R = \frac{C\left(S_P, t_{68}, p\right)}{C\left(35, t_{68} = 15\,°C, 0\right)} = \frac{C\left(S_P, t_{68}, p\right)}{C\left(S_P, t_{68}, 0\right)} \frac{C\left(S_P, t_{68}, 0\right)}{C\left(35, t_{68}, 0\right)} \frac{C\left(35, t_{68}, 0\right)}{C\left(35, t_{68} = 15\,°C, 0\right)} \tag{E.2.1}$$

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

$$R = \frac{C\left(S_P, t_{68}, p\right)}{C\left(35, t_{68} = 15\,°C, 0\right)} = R_p R_t r_t. \tag{E.2.2}$$

The last factor r_t has been fitted to experimental data as the polynomial in temperature (t_{68})

$$r_t = \sum_{i=0}^{4} c_i \left(t_{68} / °C \right)^i \tag{E.2.3}$$

and the factor R_p has been fitted to experimental data as a function of p, t_{68} and R as

$$R_p = 1 + \frac{\sum_{i=1}^{3} e_i p^i}{1 + d_1 \left(t_{68} / °C \right) + d_2 \left(t_{68} / °C \right)^2 + R \left[d_3 + d_4 \left(t_{68} / °C \right) \right]}. \tag{E.2.4}$$

Thus for any sample measurement of R it is possible to evaluate r_t and R_p and hence calculate

$$R_t = \frac{R}{R_p r_t}. \tag{E.2.5}$$

At a temperature of $t_{68} = 15\ °C$, R_t is simply K_{15} and Practical Salinity S_P can be determined form (E.1.1). For temperatures other than $t_{68} = 15\ °C$, Practical Salinity S_P is given by the following function of R_t with $k = 0.0162$,

$$S_P = \sum_{i=0}^{5} a_i \left(R_t \right)^{i/2} + \frac{\left(t_{68} / °C - 15 \right)}{\left[1 + k \left(t_{68} / °C - 15 \right) \right]} \sum_{i=0}^{5} b_i \left(R_t \right)^{i/2}. \tag{E.2.6}$$

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 equation (2.4.1), namely $S_R \approx u_{PS} S_P$ to estimate Reference Salinity S_R.

The temperatures in equations (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 equation (A.1.3) of appendix A.1. This is done as the first line of the computer code described in the "gsw" software library (Library C, Appendix L). 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 S_P

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 equation (E.2.6) is first performed to evaluate R_t. Because r_t is a function only of temperature, at this stage both R_t and r_t are known so that equation (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 "gsw" algorithm library (Library C, Appendix L). 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 S_P 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_{15-90} instead of K_{15}, where K_{15-90} is defined

$$K_{15-90} = \frac{C\left(S_P, t_{90} = 15\ °C, 0\right)}{C\left(35, t_{90} = 15\ °C, 0\right)}.$$
(E.4.1)

The magnitude of the difference $K_{15-90} - K_{15}$ can be calculated and is found to be less than 6.8×10^{-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_{15-90} in (E.1.1) instead of K_{15} incurs a change in Practical Salinity of less than 3×10^{-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 $t_{90} = 15\ °C$, the same mass fraction 32.4356×10^{-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 equation (E.1.1) can equivalently refer to a ratio of conductivities at $t_{90} = 14.996\ °C$.

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 $t_{68} = 1.00024\, t_{90}$ 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 climatic change taking place in the world ocean on the global scale over decades or centuries requires measurement techniques that permit 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 are 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, e.g. 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. 2008). 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). This implies the risk that readings taken today may possess an enlarged uncertainty when being compared with observations taken in 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" (VIM, 2008). 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. In a comparison of measured quantity values they 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 built up. National Metrological Institutes (NMIs) have developed primary reference procedures to realise these 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. 2008) 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 can be seen as a primary standard. Its production procedure, 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. Both these solutions are artefacts 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 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 decade or century time scales, there is an uncertainty of its K_{15} 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 a conductivity ratio. Unfortunately the related uncertainty of absolute conductivity measurements with present-day state-of-the-art technology is one order of magnitude lower 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. 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 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. Remember that it is the quantity value that is traceable, not the method to achieve this value. The method in use is essential only 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 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 the 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 the IAPSO Standard Seawater samples added to the labels of these bottles when they are manufactured.

Appendix F: Coefficients of the Pure Water Gibbs Function of IAPWS 2009

The pure water part of the Gibbs function of Feistel (2003) is expected to be soon approved by IAPWS (IAPWS-09) as an alternative thermodynamic description of pure water in the oceanographic ranges of temperature and pressure. Non-zero coefficients g_{ij} of the pure water specific Gibbs energy $g^W(t, p)$ as a function of the independent variables ITS-90 Celsius temperature, $t = t_u \times y$, and sea pressure, $p = p_u \times z$.

$$g^W(t, p) = g_u \sum_{j=0}^{7} \sum_{k=0}^{6} g_{jk}\, y^j z^k \,, \tag{F.1}$$

with the reduced temperature $y = t/t_u$ and the reduced pressure $z = p / p_u$. The constants t_u, p_u and g_u are given in Table X. The reduced quantities y and z vary from 0 to 1 in the oceanographic standard range. Coefficients not contained in this table have the value $g_{jk} = 0$. Two of these 41 parameters (g_{00} and g_{10}) are arbitrary and are computed from the reference-state conditions of vanishing specific entropy, s, and specific internal energy, u, of liquid H$_2$O at the triple point,

$$s(T_t, p_t) = 0, \tag{F.2}$$

$$u(T_t, p_t) = 0. \tag{F.3}$$

Note that the values of g_{00} and g_{10} in the table below are taken from Feistel et al. (2008) 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 (F.2) and (F.3) (see Feistel et al (2008) for a discussion of this point).

j	k	g_{jk}	j	k	g_{jk}
0	0	$0.101\ 342\ 743\ 139\ 674 \times 10^3$	3	2	$0.499\ 360\ 390\ 819\ 152 \times 10^3$
0	1	$0.100\ 015\ 695\ 367\ 145 \times 10^6$	3	3	$-0.239\ 545\ 330\ 654\ 412 \times 10^3$
0	2	$-0.254\ 457\ 654\ 203\ 630 \times 10^4$	3	4	$0.488\ 012\ 518\ 593\ 872 \times 10^2$
0	3	$0.284\ 517\ 778\ 446\ 287 \times 10^3$	3	5	$-0.166\ 307\ 106\ 208\ 905 \times 10$
0	4	$-0.333\ 146\ 754\ 253\ 611 \times 10^2$	4	0	$-0.148\ 185\ 936\ 433\ 658 \times 10^3$
0	5	$0.420\ 263\ 108\ 803\ 084 \times 10$	4	1	$0.397\ 968\ 445\ 406\ 972 \times 10^3$
0	6	$-0.546\ 428\ 511\ 471\ 039$	4	2	$-0.301\ 815\ 380\ 621\ 876 \times 10^3$
1	0	$0.590\ 578\ 347\ 909\ 402 \times 10$	4	3	$0.152\ 196\ 371\ 733\ 841 \times 10^3$
1	1	$-0.270\ 983\ 805\ 184\ 062 \times 10^3$	4	4	$-0.263\ 748\ 377\ 232\ 802 \times 10^2$
1	2	$0.776\ 153\ 611\ 613\ 101 \times 10^3$	5	0	$0.580\ 259\ 125\ 842\ 571 \times 10^2$
1	3	$-0.196\ 512\ 550\ 881\ 220 \times 10^3$	5	1	$-0.194\ 618\ 310\ 617\ 595 \times 10^3$
1	4	$0.289\ 796\ 526\ 294\ 175 \times 10^2$	5	2	$0.120\ 520\ 654\ 902\ 025 \times 10^3$
1	5	$-0.213\ 290\ 083\ 518\ 327 \times 10$	5	3	$-0.552\ 723\ 052\ 340\ 152 \times 10^2$
2	0	$-0.123\ 577\ 859\ 330\ 390 \times 10^5$	5	4	$0.648\ 190\ 668\ 077\ 221 \times 10$
2	1	$0.145\ 503\ 645\ 404\ 680 \times 10^4$	6	0	$-0.189\ 843\ 846\ 514\ 172 \times 10^2$
2	2	$-0.756\ 558\ 385\ 769\ 359 \times 10^3$	6	1	$0.635\ 113\ 936\ 641\ 785 \times 10^2$
2	3	$0.273\ 479\ 662\ 323\ 528 \times 10^3$	6	2	$-0.222\ 897\ 317\ 140\ 459 \times 10^2$
2	4	$-0.555\ 604\ 063\ 817\ 218 \times 10^2$	6	3	$0.817\ 060\ 541\ 818\ 112 \times 10$
2	5	$0.434\ 420\ 671\ 917\ 197 \times 10$	7	0	$0.305\ 081\ 646\ 487\ 967 \times 10$
3	0	$0.736\ 741\ 204\ 151\ 612 \times 10^3$	7	1	$-0.963\ 108\ 119\ 393\ 062 \times 10$
3	1	$-0.672\ 507\ 783\ 145\ 070 \times 10^3$			

Appendix G: Coefficients of the Saline Gibbs Function for Seawater of IAPWS 2008

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, $p = p_u \times z$:

$$g^S(S_A, t, p) = g_u \sum_{j,k} \left\{ g_{1jk} x^2 \ln x + \sum_{i>1} g_{ijk} x^i \right\} y^j z^k .$$
(G.1)

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 equations (2.6.7) and (2.6.8) when the pure water Gibbs function was that of IAPWS-95.

i	j	k	g_{ijk}	i	j	k	g_{ijk}	i	j	k	g_{ijk}
1	0	0	5812.81456626732	2	5	0	–21.6603240875311	3	2	2	–54.1917262517112
1	1	0	851.226734946706	4	5	0	2.49697009569508	2	3	2	–204.889641964903
2	0	0	1416.27648484197	2	6	0	2.13016970847183	2	4	2	74.7261411387560
3	0	0	–2432.14662381794	2	0	1	–3310.49154044839	2	0	3	–96.5324320107458
4	0	0	2025.80115603697	3	0	1	199.459603073901	3	0	3	68.0444942726459
5	0	0	–1091.66841042967	4	0	1	–54.7919133532887	4	0	3	–30.1755111971161
6	0	0	374.601237877840	5	0	1	36.0284195611086	2	1	3	124.687671116248
7	0	0	–48.5891069025409	2	1	1	729.116529735046	3	1	3	–29.4830643494290
2	1	0	168.072408311545	3	1	1	–175.292041186547	2	2	3	–178.314556207638
3	1	0	–493.407510141682	4	1	1	–22.6683558512829	3	2	3	25.6398487389914
4	1	0	543.835333000098	2	2	1	–860.764303783977	2	3	3	113.561697840594
5	1	0	–196.028306689776	3	2	1	383.058066002476	2	4	3	–36.4872919001588
6	1	0	36.7571622995805	2	3	1	694.244814133268	2	0	4	15.8408172766824
2	2	0	880.031352997204	3	3	1	–460.319931801257	3	0	4	–3.41251932441282
3	2	0	–43.0664675978042	2	4	1	–297.728741987187	2	1	4	–31.6569643860730
4	2	0	–68.5572509204491	3	4	1	234.565187611355	2	2	4	44.2040358308000
2	3	0	–225.267649263401	2	0	2	384.794152978599	2	3	4	–11.1282734326413
3	3	0	–10.0227370861875	3	0	2	–52.2940909281335	2	0	5	–2.62480156590992
4	3	0	49.3667694856254	4	0	2	–4.08193978912261	2	1	5	7.04658803315449
2	4	0	91.4260447751259	2	1	2	–343.956902961561	2	2	5	–7.92001547211682
3	4	0	0.875600661808945	3	1	2	83.1923927801819				
4	4	0	–17.1397577419788	2	2	2	337.409530269367				

Appendix H: Coefficients of the Gibbs function of Ice Ih of IAPWS 2006

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 has been adopted as an IAPWS Release in 2006, here referred to as IAPWS-06. This equation of state for ice Ih is given by Eq. (H.1) as a function of temperature, with two of its coefficients being polynomial functions of sea pressure, p, ($p = P - P_0$)

$$g^{\text{Ih}}(t,p) = g_0 - s_0 T_{\text{t}} \cdot \tau + T_{\text{t}} \operatorname{Re} \sum_{k=1}^{2} r_k \left[(t_k - \tau)\ln(t_k - \tau) + (t_k + \tau)\ln(t_k + \tau) - 2t_k \ln t_k - \frac{\tau^2}{t_k} \right]$$

$$g_0(p) = \sum_{k=0}^{4} g_{0k} \cdot \left(\frac{p}{P_{\text{t}}}\right)^k \tag{H.1}$$

$$r_2(p) = \sum_{k=0}^{2} r_{2k} \cdot \left(\frac{p}{P_{\text{t}}}\right)^k,$$

with the reduced temperature $\tau = (T_0 + t)/T_{\text{t}}$ and T_{t} and P_{t} are given in Table H.1. 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 H.2.

TABLE H.1 Special constants and values used in the ice Ih Gibbs function.

Quantity	Symbol	Value	Unit
Experimental triple-point pressure	P_{t}	611.657	Pa
Numerical triple-point pressure	$P_{\text{t}}^{\text{num}}$	611.654 771 007 894	Pa
Normal pressure	P_0	101325	Pa
Triple-point temperature	T_{t}	273.16	K

TABLE H.2 Coefficients of the equation of state (Gibbs potential function) as given by Eq. (H.1).

Coefficient	Real part	Imaginary part	Unit
g_{00}	$-0.632\,020\,233\,335\,886 \times 10^6$		J kg^{-1}
g_{01}	$0.655\,022\,213\,658\,955$		J kg^{-1}
g_{02}	$-0.189\,369\,929\,326\,131 \times 10^{-7}$		J kg^{-1}
g_{03}	$0.339\,746\,123\,271\,053 \times 10^{-14}$		J kg^{-1}
g_{04}	$-0.556\,464\,869\,058\,991 \times 10^{-21}$		J kg^{-1}
s_0 (absolute)	$0.189\,13 \times 10^3$		$\text{J kg}^{-1}\,\text{K}^{-1}$
s_0 (IAPWS-95)	$-0.332\,733\,756\,492\,168 \times 10^4$		$\text{J kg}^{-1}\,\text{K}^{-1}$
t_1	$0.368\,017\,112\,855\,051 \times 10^{-1}$	$0.510\,878\,114\,959\,572 \times 10^{-1}$	
r_1	$0.447\,050\,716\,285\,388 \times 10^2$	$0.656\,876\,847\,463\,481 \times 10^2$	$\text{J kg}^{-1}\,\text{K}^{-1}$
t_2	$0.337\,315\,741\,065\,416$	$0.335\,449\,415\,919\,309$	
r_{20}	$-0.725\,974\,574\,329\,220 \times 10^2$	$-0.781\,008\,427\,112\,870 \times 10^2$	$\text{J kg}^{-1}\,\text{K}^{-1}$
r_{21}	$-0.557\,107\,698\,030\,123 \times 10^{-4}$	$0.464\,578\,634\,580\,806 \times 10^{-4}$	$\text{J kg}^{-1}\,\text{K}^{-1}$
r_{22}	$0.234\,801\,409\,215\,913 \times 10^{-10}$	$-0.285\,651\,142\,904\,972 \times 10^{-10}$	$\text{J kg}^{-1}\,\text{K}^{-1}$

The numerical triple point pressure P_t^{num} listed in Table H.1 was derived in Feistel et al. (2008) as the absolute pressure at which the three phases of water were in thermodynamic equilibrium at the triple point temperature, using the definitions 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 $-\pi < \text{Im}\left[\ln(z)\right] \leq +\pi$. 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 H.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 H.2 is the value in the revised IAPWS-2006 Ice Ih Release which improves the numerical consistency (Feistel et al. (2009)) with the IAPWS-1995 for the fluid phase of water.

Appendix I: Recommended Nomenclature, Symbols and Units in Oceanography

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 adopted in the software Libraries A and B for the input variables for all the software as well as for the outputs of all the subroutines. 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 (Library C, Appendix L) 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 consistent with this choice of units, with the one exception being the units of the various geostrophic streamfunctions.

It seems impractical to recommend that the field of oceanography fully adopt strict basic SI units. It is very valuable to have the field adopt the same units for the variables that are used 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 (Library C, Appendix L).

Table H1. Suggested Symbols and Units in Oceanography

Quantity	Symbol	Units	Comments
Chlorinity	Cl	g kg^{-1}	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 we use mass fraction units for Chlorinity.
Standard Ocean Reference Salinity	S_{SO}	g kg^{-1}	35.165 04 g kg^{-1} being exactly $35\,u_{PS}$, corresponding to the standard ocean Practical Salinity of 35.
Freezing temperatures	t^f, θ^f, Θ^f	$°C$	In situ, potential and conservative values, each as a function of S_A and p.
Absolute pressure	P	Pa	When absolute pressure is used it should always be in Pa, not in Mpa nor in dbar.
Sea pressure. Sea pressure is the pressure argument to all software in the "gsw" library.	p	dbar	Equal to $P - P^0$ and expressed in dbar not Pa.
Gauge pressure. Gauge pressure (also called applied pressure) is sometimes reported from ship-born instruments.	p^{gauge}	dbar	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^{gauge}, as p is the argument to the seawater Gibbs function.
Reference pressure	p_r	dbar	The value of the sea pressure p to which potential temperature and/or potential density are referenced.

One standard atmosphere	P_0	Pa	exactly 101 325 Pa
Isopycnal slope ratio	r	1	$r = \dfrac{\alpha^\Theta(p)/\beta^\Theta(p)}{\alpha^\Theta(p_\mathrm{r})/\beta^\Theta(p_\mathrm{r})}$
Stability Ratio	R_ρ	1	$R_\rho = \alpha^\Theta \Theta_z / \beta^\Theta (S_\mathrm{A})_z \approx \alpha^\theta \theta_z / \beta^\theta (S_\mathrm{A})_z$.
Isopycnal Temperature Gradient Ratio	G^Θ	1	$G^\Theta = r[R_\rho - 1]/[R_\rho - r]$
Practical Salinity	S_P	1	Defined in the range $2 < S_\mathrm{P} < 42$ by PSS-78 based on measured conductivity ratios.
Reference Salinity	S_R	g kg^{-1}	Reference-Composition Salinity (or Reference Salinity for short) is the Absolute Salinity of seawater samples that have Reference Composition. At $S_\mathrm{P} = 35$, S_R is exactly $u_\mathrm{PS} S_\mathrm{P}$ while in the range $2 < S_\mathrm{P} < 42$ $S_\mathrm{R} \approx u_\mathrm{PS} S_\mathrm{P}$.
Absolute Salinity (This is the salinity argument to all the "gsw" library functions.)	S_A	g kg^{-1}	$S_\mathrm{A} = S_\mathrm{R} + \delta S_\mathrm{A} \approx u_\mathrm{PS} S_\mathrm{P} + \delta S_\mathrm{A}$
Absolute Salinity Anomaly	δS_A	g kg^{-1}	$\delta S_\mathrm{A} = S_\mathrm{A} - S_\mathrm{R}$, the difference between Absolute Salinity and Reference-Composition Salinity.
Temperature	t	°C	
Absolute Temperature	T	K	$T/\mathrm{K} \equiv T_0/\mathrm{K} + t/(°\mathrm{C}) = 273.15 + t/(°\mathrm{C})$
temperature derivatives	T	K	When a quantity is differentiated with respect to in situ temperature, the symbol T is used in order to distinguish this variable from time.
Celsius zero point	T_0	K	$T_0 \equiv 273.15$ K
Potential temperature	θ	°C	Defined implicitly by equation (3.1.2)
Conservative Temperature	Θ	°C	Defined in equation (3.3.1) as exactly potential enthalpy divided by c_p^0 .
A constant "specific heat", for use with Conservative Temperature	c_p^0	J kg^{-1} K^{-1}	$c_p^0 \equiv 3991.867\ 957\ 119\ 63$ J kg^{-1} K^{-1}. This 15-digit number is defined to be the exact value of c_p^0 .
Combined standard uncertainty	u_c	Varies	
Enthalpy	H	J	
Specific enthalpy	h	J kg^{-1}	$h = u + (p + P_0)v$. Here p must be in Pa not dbar.
Specific potential enthalpy	h^0	J kg^{-1}	Specific enthalpy referenced to zero sea pressure. $h^0 = h(S_\mathrm{A}, \theta[S_\mathrm{A}, t, p, p_r = 0], p_r = 0)$
Specific isobaric heat capacity	c_p	J kg^{-1} K^{-1}	$c_p = \partial h / \partial T\big|_{S_\mathrm{A}, p}$
Internal energy	U	J	
Specific internal energy	u	J kg^{-1}	
Specific isochoric heat capacity	c_v	J kg^{-1} K^{-1}	$c_v = \partial u / \partial T\big|_{S_\mathrm{A}, v}$
Gibbs function (Gibbs energy)	G	J	
Specific Gibbs function (Gibbs energy)	g	J kg^{-1}	
Specific Helmholtz Energy	f	J kg^{-1}	

Unit conversion factor for salinities	u_{PS}	$\mathrm{g\,kg^{-1}}$	$u_{PS} \equiv (35.16504/35)\,\mathrm{g\,kg^{-1}} \approx 1.004\,715...\,\mathrm{g\,kg^{-1}}$ The first part of this expression is exact.
Entropy	Σ	$\mathrm{J\,K^{-1}}$	
Specific entropy	η	$\mathrm{J\,kg^{-1}\,K^{-1}}$	In other publications the symbol s is used for specific entropy.
Density	ρ	$\mathrm{kg\,m^{-3}}$	
Density anomaly	σ^t	$\mathrm{kg\,m^{-3}}$	$\rho(S_A,t,0) - 1000\,\mathrm{kg\,m^{-3}}$
Potential density anomaly referenced to a sea pressure of 10 MPa	σ_1	$\mathrm{kg\,m^{-3}}$	$\rho(S_A, \theta[S_A,t,p,p_r],p_r) -$ $1000\,\mathrm{kg\,m^{-3}}$ where $p_r = 10\,\mathrm{MPa}$
Potential density anomaly referenced to a sea pressure of 40 MPa	σ_4	$\mathrm{kg\,m^{-3}}$	$\rho(S_A, \theta[S_A,t,p,p_r],p_r) -$ $1000\,\mathrm{kg\,m^{-3}}$ where $p_r = 40\,\mathrm{MPa}$
Thermal expansion coefficient with respect to *in situ* temperature	α^t	$\mathrm{K^{-1}}$	$v^{-1}\partial v/\partial T\big|_{S_A,p} = -\rho^{-1}\partial\rho/\partial T\big|_{S_A,p}$
Thermal expansion coefficient with respect to potential temperature θ	α^θ	$\mathrm{K^{-1}}$	$v^{-1}\partial v/\partial \theta\big|_{S_A,p} = -\rho^{-1}\partial\rho/\partial \theta\big|_{S_A,p}$
Thermal expansion coefficient with respect to Conservative Temperature Θ	α^Θ	$\mathrm{K^{-1}}$	$v^{-1}\partial v/\partial \Theta\big|_{S_A,p} = -\rho^{-1}\partial\rho/\partial \Theta\big|_{S_A,p}$
Haline contraction coefficient at constant *in situ* temperature	β^t	$\mathrm{kg\,g^{-1}}$	$-v^{-1}\partial v/\partial S_A\big|_{T,p} = \rho^{-1}\partial\rho/\partial S_A\big|_{T,p}$ Note that the units for β^t are consistent with S_A being in $\mathrm{g\,kg^{-1}}$.
Haline contraction coefficient at constant potential temperature	β^θ	$\mathrm{kg\,g^{-1}}$	$-v^{-1}\partial v/\partial S_A\big|_{\theta,p} = \rho^{-1}\partial\rho/\partial S_A\big|_{\theta,p}$ Note that the units for β^θ are consistent with S_A being in $\mathrm{g\,kg^{-1}}$.
Haline contraction coefficient at constant Conservative Temperature	β^Θ	$\mathrm{kg\,g^{-1}}$	$-v^{-1}\partial v/\partial S_A\big|_{\Theta,p} = +\rho^{-1}\partial\rho/\partial S_A\big|_{\Theta,p}$ Note that the units for β^Θ are consistent with S_A being in $\mathrm{g\,kg^{-1}}$.
Haline contraction coefficient at constant Conservative Temperature	β^Θ	$\mathrm{kg\,g^{-1}}$	$-v^{-1}\partial v/\partial S_A\big|_{\Theta,p} = +\rho^{-1}\partial\rho/\partial S_A\big|_{\Theta,p}$ Note that the units for β^Θ are consistent with S_A being in $\mathrm{g\,kg^{-1}}$.
Isothermal compressibility	κ^t	$\mathrm{dbar^{-1}}$	
Isentropic and isohaline compressibility	κ	$\mathrm{dbar^{-1}}$	
Chemical potential of water in seawater	μ^W	$\mathrm{J\,g^{-1}}$	
Chemical potential of sea salt in seawater	μ^S	$\mathrm{J\,g^{-1}}$	
Relative chemical potential of (sea salt and water in) seawater	μ	$\mathrm{J\,g^{-1}}$	$(\partial g/\partial S_A)_{t,p} = \mu^S - \mu^W$
Dissipation rate of kinetic energy per unit mass	ε	$\mathrm{J\,kg^{-1}\,s^{-1}}$ $= \mathrm{m^2\,s^{-3}}$	
Adiabatic lapse rate	Γ	$\mathrm{K\,dbar^{-1}}$	$\Gamma = \dfrac{\partial t}{\partial p}\bigg|_{S_A,\theta} = \dfrac{\partial t}{\partial p}\bigg|_{S_A,\Theta} = \dfrac{\partial t}{\partial p}\bigg|_{S_A,\eta}$

Sound speed	c	$\mathrm{m\ s^{-1}}$	
Specific volume	v	$\mathrm{m^3\ kg^{-1}}$	$v = \rho^{-1}$
Specific volume anomaly	δ	$\mathrm{m^3\ kg^{-1}}$	
Thermobaric coefficient based on θ	T_b^θ	$\mathrm{K^{-1}dbar^{-1}}$	$T_b^\theta = \beta^\theta\,\partial\left(\alpha^\theta/\beta^\theta\right)/\partial p\big|_{S_A,\theta}$
Thermobaric coefficient based on Θ	T_b^Θ	$\mathrm{K^{-1}dbar^{-1}}$	$T_b^\Theta = \beta^\Theta\,\partial\left(\alpha^\Theta/\beta^\Theta\right)/\partial p\big|_{S_A,\Theta}$
Cabbeling coefficient based on θ	C_b^θ	$\mathrm{K^{-2}}$	$C_b^\theta = \partial\alpha^\theta/\partial\theta\big|_{S_A,p} + 2\frac{\alpha^\theta}{\beta^\theta}\partial\alpha^\theta/\partial S_A\big|_{\theta,p} - \left(\frac{\alpha^\theta}{\beta^\theta}\right)^2\partial\beta^\theta/\partial S_A\big|_{\theta,p}$
Cabbeling coefficient based on Θ	C_b^Θ	$\mathrm{K^{-2}}$	$C_b^\Theta = \partial\alpha^\Theta/\partial\Theta\big|_{S_A,p} + 2\frac{\alpha^\Theta}{\beta^\Theta}\partial\alpha^\Theta/\partial S_A\big|_{\Theta,p} - \left(\frac{\alpha^\Theta}{\beta^\Theta}\right)^2\partial\beta^\Theta/\partial S_A\big|_{\Theta,p}$
Buoyancy frequency	N	$\mathrm{s^{-1}}$	$N^2 = g\left(\alpha^\Theta\Theta_z - \beta^\Theta S_{A_z}\right) = g\left(\alpha^\theta\theta_z - \beta^\theta S_{A_z}\right)$
Neutral helicity	H^n	$\mathrm{m^{-3}}$	Defined by (3.13.1) and (3.13.2)
Neutral density	γ^n	$\mathrm{kg\ m^{-3}}$	A density variable whose iso-surfaces are designed to be approximately neutral, i. e. $\alpha^\Theta\nabla_\gamma\Theta \approx \beta^\Theta\nabla_\gamma S_A$.
Neutral-Surface-Potential-Vorticity	NSPV	$\mathrm{s^{-3}}$	$\mathrm{NSPV} = -g\rho^{-1}f\gamma_z^n$ where f is the Coriolis parameter.
Dynamic height anomaly	Φ'	$\mathrm{m^2\ s^{-2}}$	$\mathrm{Pa\ m^3\ kg^{-1}} = \mathrm{m^2\ s^{-2}}$
Montgomery potential	π	$\mathrm{m^2\ s^{-2}}$	$\mathrm{Pa\ m^3\ kg^{-1}} = \mathrm{m^2\ s^{-2}}$
Montgomery potential	$\tilde{\pi}$	$\mathrm{m^2\ s^{-2}}$	$\mathrm{Pa\ m^3\ kg^{-1}} = \mathrm{m^2\ s^{-2}}$
PISH (Pressure-Integrated Steric Height)	Ψ'	$\mathrm{kg\ s^{-2}}$	Streamfunction for f times the depth-integrated relative mass flux, see eq. (3.31.1) – (3.31.5).
Coriolis parameter	f	$\mathrm{s^{-1}}$	$1.45842\,x10^{-4}\sin\phi\ \mathrm{s^{-1}}$
Molality	m	$\mathrm{mol\ kg^{-1}}$	$m = \sum_i m_i = \frac{1}{\langle A\rangle}\frac{S_A}{(1-S_A)}$ where $<A>$ is the mole-weighted average atomic weight of the elements of sea salt, $<A> = 31.403\,8218\ldots\mathrm{g\ mol^{-1}}$
ionic strength	I	$\mathrm{mol\ kg^{-1}}$	$I = \tfrac{1}{2}m\left\langle Z^2\right\rangle = \tfrac{1}{2}\sum_i m_i z_i^2$ $= 0.622\,644\,9\times m$ $\approx \frac{622.644\,9}{31.403\,821\,8}\mathrm{mol\ kg^{-1}}\times\frac{S_A}{(1-S_A)}$
osmotic coefficient	ϕ	1	$\varphi(S_A,T,p) = \frac{g(0,t,p) - \mu^W(S_A,t,p)}{mR(T_0+t)}$ where the molar gas constant, $R = 8.314\,472\ \mathrm{J\ mol^{-1}\ K^{-1}}$

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 μmol/kg and not $\mathrm{cm^3dm^{-3}}$, ml/l or μmol/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).

Table I.2. Suggested Symbols when variables are functions of η, θ and Θ

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. This table lists the suggested markings on the variables that arise commonly in this context. The thermodynamic variables are related to the thermodynamic potentials $h = \hat{h}(S_A, \eta, p)$, $h = \tilde{h}(S_A, \theta, p)$ and $h = \hat{h}(S_A, \Theta, p)$ by the expressions in Appendix N.

quantity	function of	symbol for this functional form
enthalpy, h specific volume, v density, ρ entropy, η	(S_A, t, p)	$h = h(S_A, t, p)$ $v = v(S_A, t, p)$ $\rho = \rho(S_A, t, p)$ $\eta = \eta(S_A, t, p)$
enthalpy, h specific volume, v density, ρ potential temperature, θ	(S_A, η, p)	$h = \hat{h}(S_A, \eta, p)$ $v = \hat{v}(S_A, \eta, p)$ $\rho = \hat{\rho}(S_A, \eta, p)$ $\theta = \hat{\theta}(S_A, \eta)$
enthalpy, h specific volume, v density, ρ entropy, η	(S_A, θ, p)	$h = \tilde{h}(S_A, \theta, p)$ $v = \tilde{v}(S_A, \theta, p)$ $\rho = \tilde{\rho}(S_A, \theta, p)$ $\eta = \tilde{\eta}(S_A, \theta)$
enthalpy, h specific volume, v density, ρ entropy, η	(S_A, Θ, p)	$h = \hat{h}(S_A, \Theta, p)$ $v = \hat{v}(S_A, \Theta, p)$ $\rho = \hat{\rho}(S_A, \Theta, p)$ $\eta = \hat{\eta}(S_A, \Theta)$

Appendix J: Software in Library A; the Official Thermodynamic Description of Seawater

This software library, Library A, contains the official TEOS-10 subroutines for evaluating all the thermodynamic properties of pure water (using IAPWS-95), seawater (using IAPWS-08 for the saline part) and for ice Ih (using IAPWS-06). All of the inputs and all of the outputs of the algorithms in Library A are strictly 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 0.035 165 04 kg kg^{-1} [not 35.165 04 g kg^{-1}]), *in situ* temperature is Absolute Temperature T in K and pressure is Absolute Pressure P in Pa. Use of these basic SI units greatly simplifies the calculation of theoretical expressions in thermodynamics.

The only exceptions to this rule for the units for the inputs in Library A are

- the function that calculates Practical Salinity S_P from conductivity ratio (PSS-78),
- the function that calculates Absolute Salinity (in kg kg^{-1}), which has Practical Salinity S_P (which is unitless and takes numbers like 35 not 0.035) as its salinity input variable, along with longitude φ (°E) latitude λ (°N) and Absolute Pressure P (Pa),
- the inverse function $S_P = S_P(S_A, \varphi, \lambda, P)$.

Because the IAPWS-95 description of pure water substance (both liquid and vapour) is the world-wide standard for pure water substance, Library A is the official description of seawater. This IAPWS-95 thermodynamic potential of pure water substance 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 ESO80 with which oceanographers are familiar. Second, the IAPWS-95 thermodynamic potential is a Helmholtz function which expresses pressure as a function of density and temperature; that is, IAPWS-95 has the form $P = f(T, \rho)$. Since IAPWS-95 describes not only liquid water but also water vapour, this Helmholtz form of the thermodynamic potential is natural. In Library B we present an alternative thermodynamic description of seawater based on the IAPWS-09 description of the pure liquid water part as a Gibbs function.

The thermodynamic potentials of pure water, ice and the saline part of seawater have been carefully adjusted by Feistel (2008) to make them fully compatible with each other. 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).

It is intended that Library A will be served from the Ocean Science web site, pending the Feistel et al. (2009) and Wright et al. (2009a) papers being published by that journal.

Appendix K: Software in Library B; the fast library in SI units

This software library, Library B, contains the TEOS-10 subroutines for evaluating all the thermodynamic properties of pure water (using <u>IAPWS-09</u>), seawater (using IAPWS-08 for the saline part) and for ice Ih (using IAPWS-06). All of the inputs and all of the outputs of the algorithms in Library B (as in Library A) are strictly 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 0.035 165 04 kg kg^{-1} [not 35.165 04 g kg^{-1}]), *in situ* temperature T is Absolute Temperature in K and pressure is Absolute Pressure P in Pa. Use of these basic SI units greatly simplifies the calculation of theoretical expressions in thermodynamics.

The only exceptions to this rule for the units for the inputs in Library B are

- the function that calculates Practical Salinity S_P from conductivity ratio (PSS-78),
- the function that calculates Absolute Salinity (in kg kg^{-1}), which has Practical Salinity S_P (which is unitless and takes numbers like 35 not 0.035) as its salinity input variable, along with longitude φ (°E) latitude λ (°N) and Absolute Pressure P (Pa),
- the inverse function $S_P = S_P\left(S_A, \varphi, \lambda, P\right)$.

Since the IAPWS-95 description of pure water substance (both liquid and vapour) is the world-wide standard for pure water substance, Library A is the official description of seawater. Because the oceanographically relevant ranges of temperature and pressure are relatively limited (compared with the corresponding range of validity of IAPWS-95) Feistel (2003) was able to fit a Gibbs function $g\left(T, P\right)$ to the corresponding Gibbs function derived from IAPWS-95. This Feistel (2003) Gibbs function of pure water is a much more computationally efficient description of pure water in the oceanographic parameter ranges than IAPWS-95 and yet all the underlying thermodynamic data are fitted to much better than the standard errors of those data. This has been confirmed by our checks (see Appendix M). The pure water part of Feistel (2003) is currently undergoing evaluation by IAPWS for possible release as an IAPWS-blessed description of pure liquid water in the oceanographic ranges of temperature pressure. This draft Release is referred to here as IAPWS-09. Library B is intended to be a duplication of Library A, with the same units for input and outputs, with the only difference being exchanging the Helmholtz thermodynamic potential of pure liquid water of IAPWS-95 with the Gibbs function of IAPWS-09. Since the error involved in this substitution is many times less than the uncertainty in our knowledge of all measureable thermodynamic properties, oceanographers can use this Library B with confidence, so gaining a substantial factor in computational efficiency and without having to navigate the unfamiliar theoretical territory associated with the Helmholtz function.

It is intended that Library B will be served from the Ocean Science web site, pending the Feistel et al. (2009) and Wright et al. (2009a) papers being published by that journal.

Appendix L: Software in Library C, the gsw Library;
the fast library in oceanographic units

(**gsw**, "Gibbs SeaWater" library; an implementation of IAPWS-09 + IAPWS-06 + IAPWS-08)

This software library, Library C, contains the TEOS-10 subroutines for evaluating all the thermodynamic properties of pure water (using IAPWS-09), seawater (using IAPWS-08 for the saline part) and for ice Ih (using IAPWS-06). Unlike Libraries A and B, in this gsw library we do 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 that the pure water fraction (the so-called "freshwater fraction") is $(1 - S_A)$ only when Absolute Salinity 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.

The outputs of all the algorithms in this gsw library are identical to those in Library B, since they are based on the same three Gibbs functions of pure water, of ice Ih, and the saline Gibbs function. The only difference between Libraries B and C is in the units of the input parameters and of the outputs.

This gsw library (short for the Gibbs-SeaWater library) has inputs in "oceanographic" units, namely Absolute Salinity S_A in g kg^{-1} (so that for example standard ocean reference salinity is 35.165 04 g kg^{-1} [not 0.035 165 04 kg kg^{-1}]), *in situ* temperature t in °C and pressure as sea pressure p in dbar.

The only exceptions to this rule for the units for the inputs
- 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 φ (°E) latitude λ (°N) and pressure p (dbar),
- the inverse function $S_P = S_P(S_A, \varphi, \lambda, p)$.

Library C, the "gsw" library is available from the web site at www.TEOS-10.org.

Table L.1. A Selection of Function Names in the gsw Library at www.TEOS-10.org.

Thermodynamic Property	Function name	Units of the output	Remarks
Practical Salinity S_P	gsw_PSal	unitless	PSal from PSS-78
Absolute Salinity S_A	gsw_ASal	g kg^{-1}	The McDougall, Jackett and Millero (2009a) algorithm
Practical Salinity S_P	gsw_PSal_from_ASal	Unitless $2 < S_P < 42$	Inverse function of gsw_ASal
Gibbs function g and its 1st and 2nd derivatives	gsw_g	various units	
specific volume v	gsw_specvol	m^3 kg^{-1}	
density ρ	gsw_dens	kg m^{-3}	
specific entropy η	gsw_entropy	J kg^{-1} K^{-1}	
specific enthalpy h	gsw_enthalpy	J kg^{-1}	
isothermal compressibility κ^t	gsw_kappa_t	dbar^{-1}	
isentropic compressibility κ	gsw_kappa	dbar^{-1}	
sound speed	gsw_svel	m s^{-1}	
thermal expansion coefficient with respect to in situ temperature t	gsw_alpha_t	K^{-1}	
thermal expansion coefficient with respect to potential temperature θ	gsw_alpha_ptmp	K^{-1}	
thermal expansion coefficient with respect to Conservative Temperature Θ	gsw_alpha_ctmp	K^{-1}	
saline contraction coefficient at constant in situ temperature t	gsw_beta_t	kg g^{-1}	
saline contraction coefficient at constant potential temperature θ	gsw_beta_ptmp	kg g^{-1}	
saline contraction coefficient at constant Conservative Temperature Θ	gsw_beta_ctmp	kg g^{-1}	
isobaric heat capacity c_p	gsw_cp	J kg^{-1} K^{-1}	
potential temperature θ	gsw_ptmp	°C	$\theta\left(S_A, t, p, p_r\right)$
Conservative Temperature Θ	gsw_ctmp	°C	$\Theta\left(S_A, \theta\right)$ where θ is potential temperature with $p_r = 0$.
potential temperature θ	gsw_ptmp0_from_ctmp	°C	Inverse function of gsw_ctmp
potential density ρ^Θ	gsw_pden	kg m^{-3}	$\rho^\Theta\left(S_A, t, p, p_r\right)$

Appendix M: Checking $g(S_A, t, p)$ 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 M.1 here, this estimate is the column labeled "Resulting r.m.s.". All the data in Table M.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 L.1) included density ρ, isobaric specific heat capacity c_p, thermal expansion coefficient α^t, sound speed *c*, specific volume *v*, freezing temperature t_f, mixing heat Δh. This dataset included 1834 observations. Column 2 of Table M.1 are the data sources that are listed in the references. The r.m.s. values were calculated with the equation:

$$\text{r.m.s} = \left[\frac{1}{n} \sum_n \left(\text{F03 - expt.datum} \right)^2 \right]^{0.5} \tag{M.1}$$

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 M.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 $S_P = 20.062$, $t = 25\ °C$, 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 M.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 M.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 M.2) included isobaric specific heat capacity c_p, mixing heat Δh, freezing point depression t_f, water vapor pressure p^{vap}, and the Debye-Hückel limiting law g^{LL}. This salinity dataset included 602 observations. Column 2 of Table M.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 M.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 water in the oceanographic ranges of temperature and pressure.

Table M.1. Summary of data used in the regression to determine the coefficients of the Feistel (2003) Gibbs potential.

Quantity	Source	$S_A/\left(\mathrm{g\ kg^{-1}}\right)$	t /°C	p/MPa	Points	Required r.m.s.	Resulting r.m.s.	Verifying r.m.s.
ρ	MGW76c	0.5-40	0-40	0	122	4 ppm	4.1 ppm	4.2 ppm
ρ	PBB80	5-42	0-30	0	345	4 ppm	4.0 ppm	4.2 ppm
ρ	PG93	34-50	15-30	0	81	10 ppm	12.0[i] ppm	11.9 ppm
c_p	BDSW70	10-50	0-40	0	25	2 J/kg K)	1.45[ii] J/(kg K)	1.43 J/(kg K)
c_p	MPD73	1-40	5-35	0	48	0.5 J/(kg K)	0.52 J/(kg K)	0.45 J/(kg K)
α^t	C78	10-30	-6-1	0.7-33	31	0.6 ppm/K	0.73 ppm/K	0.74 ppm/K
c	D74(I-III)	29-43	0-35	0-2	92	5 cm/s	1.7 cm/s	1.6 cm/s
c	D74(IVa-d)	29-43	0-30	0.1-5	32	5 cm/s	1.2 cm/s	1.2 cm/s
c	D74(V-VI)	33-37	0-5	0-100	128	5 cm/s	3.5 cm/s	3.5 cm/s
v	CM76	5-40	0-40	0-100	558	10 ppm	11.0 ppm	11.2 ppm
v^S	BS70	30-40	-2-30	1-100	221	4 ppm	2.6 ppm	2.6 ppm
t_f	DK74	4-40	-2-0	0	32	2 J/kg	1.8 J/kg	1.9 J/kg
Δh	B68	0-33	25	0	24	4 J	2.4 J	2.4 J
Δh	MHH73	1-41	0-30	0	95	0.4 J/kg	0.5 J/kg	0.5 J/kg

[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 M.2. Summary of extra datasets used in the regression to determine the coefficients of the Feistel (2008) Gibbs potential.

Quantity	Source	$S_A/\left(\mathrm{g\ kg^{-1}}\right)$	t /°C	p/MPa	Points	Resulting r.m.s.	Verifying r.m.s.
c_p	BDCW67	11-117	2-80	0	221	3.46 J/(kg K)	3.46 J/(kg K)
c_p^S	MPD73	1-40	5-35	0	48	0.57 J/(kg K)	0.57 J/(kg K)
c_p	MP05	1-35	10-40	0	41	1.30 J/(kg K)	1.30 J/(kg K)
Δh	B68	0-97	25	0	33	0.75 J/kg	0.75 J/kg
Δh	C70	35-36	2-25	0	19	7.2 J/kg	7.1 J/kg
Δh	MHH73	1-35	0-30	0	120	3.3 J/kg	3.3 J/kg
t_f	DK74	4-40	-0.2-(-2.2)	0	32	1.6 mK	1.6 mK
t_f	FM07	5-109	-0.3-(-6.9)	0	22	1.2 mK	1.0 mK
p^{vap}	R54	18-40	25	0	13	2.8 J/kg	2.8 J/kg
t_{boil}	BSRSR74	6-70	60-80	0	32	9.1 J/kg	9.3 J/kg
g^{LL}	F08	35	-5-95	0	21	0.091 J/kg	0.092 J/kg

Appendix N: Thermodynamic properties based on $\widehat{h}(S_A,\eta,p)$, $\tilde{h}(S_A,\theta,p)$ 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 $h = \widehat{h}(S_A,\eta,p)$. It proves theoretically convenient to consider the additional functional forms $h = \tilde{h}(S_A,\theta,p)$ 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 $\eta = \tilde{\eta}(S_A,\theta)$ and $\eta = \hat{\eta}(S_A,\Theta)$ for entropy, they do form complete thermodynamic potentials. Table N.1 lists expressions for some common thermodynamic quantities in terms of these potential functions. The results in this table for $\widehat{h}(S_A,\eta,p)$ mostly come from Feistel (2008) and Feistel et al. (2009) while those for $\tilde{h}(S_A,\theta,p)$ and $\hat{h}(S_A,\Theta,p)$ are from McDougall et al. (2009b).

In addition to Table N.1 we have the following expressions for the thermobaric and cabbeling coefficients (of Eqs. (3.8.1) – (3.9.2))

$$T_b^{\theta} = \frac{\tilde{h}_{pp\theta}}{\hat{h}_p} - \frac{\tilde{h}_{p\theta}}{\tilde{h}_{pS_A}}\frac{\tilde{h}_{ppS_A}}{\tilde{h}_p} = \frac{\tilde{v}_{p\theta}}{\tilde{v}} - \frac{\tilde{v}_{\theta}}{\tilde{v}_{S_A}}\frac{\tilde{v}_{pS_A}}{\tilde{v}} = -\frac{\tilde{\rho}_{p\theta}}{\tilde{\rho}} + \frac{\tilde{\rho}_{\theta}}{\tilde{\rho}_{S_A}}\frac{\tilde{\rho}_{pS_A}}{\tilde{\rho}}, \tag{N.1}$$

$$T_b^{\Theta} = \frac{\hat{h}_{pp\Theta}}{\hat{h}_p} - \frac{\hat{h}_{p\Theta}}{\hat{h}_{pS_A}}\frac{\hat{h}_{ppS_A}}{\hat{h}_p} = \frac{\hat{v}_{p\Theta}}{\hat{v}} - \frac{\hat{v}_{\Theta}}{\hat{v}_{S_A}}\frac{\hat{v}_{pS_A}}{\hat{v}} = -\frac{\hat{\rho}_{p\Theta}}{\hat{\rho}} + \frac{\hat{\rho}_{\Theta}}{\hat{\rho}_{S_A}}\frac{\hat{\rho}_{pS_A}}{\hat{\rho}}, \tag{N.2}$$

$$\begin{aligned}
C_b^{\theta} &= \frac{\tilde{h}_{p\theta\theta}}{\hat{h}_p} - 2\frac{\tilde{h}_{p\theta}}{\tilde{h}_{pS_A}}\frac{\tilde{h}_{p\theta S_A}}{\tilde{h}_p} + \left(\frac{\tilde{h}_{p\theta}}{\tilde{h}_{pS_A}}\right)^2\frac{\tilde{h}_{pS_AS_A}}{\tilde{h}_p} \\
&= \frac{\tilde{v}_{\theta\theta}}{\tilde{v}} - 2\frac{\tilde{v}_{\theta}}{\tilde{v}_{S_A}}\frac{\tilde{v}_{\theta S_A}}{\tilde{v}} + \left(\frac{\tilde{v}_{\theta}}{\tilde{v}_{S_A}}\right)^2\frac{\tilde{v}_{S_AS_A}}{\tilde{v}} \\
&= -\frac{\tilde{\rho}_{\theta\theta}}{\tilde{\rho}} + 2\frac{\tilde{\rho}_{\theta}}{\tilde{\rho}_{S_A}}\frac{\tilde{\rho}_{\theta S_A}}{\tilde{\rho}} - \left(\frac{\tilde{\rho}_{\theta}}{\tilde{\rho}_{S_A}}\right)^2\frac{\tilde{\rho}_{S_AS_A}}{\tilde{\rho}},
\end{aligned} \tag{N.3}$$

$$\begin{aligned}
C_b^{\Theta} &= \frac{\hat{h}_{p\Theta\Theta}}{\hat{h}_p} - 2\frac{\hat{h}_{p\Theta}}{\hat{h}_{pS_A}}\frac{\hat{h}_{p\Theta S_A}}{\hat{h}_p} + \left(\frac{\hat{h}_{p\Theta}}{\hat{h}_{pS_A}}\right)^2\frac{\hat{h}_{pS_AS_A}}{\hat{h}_p} \\
&= \frac{\hat{v}_{\Theta\Theta}}{\hat{v}} - 2\frac{\hat{v}_{\Theta}}{\hat{v}_{S_A}}\frac{\hat{v}_{\Theta S_A}}{\hat{v}} + \left(\frac{\hat{v}_{\Theta}}{\hat{v}_{S_A}}\right)^2\frac{\hat{v}_{S_AS_A}}{\hat{v}} \\
&= -\frac{\hat{\rho}_{\Theta\Theta}}{\hat{\rho}} + 2\frac{\hat{\rho}_{\Theta}}{\hat{\rho}_{S_A}}\frac{\hat{\rho}_{\Theta S_A}}{\hat{\rho}} - \left(\frac{\hat{\rho}_{\Theta}}{\hat{\rho}_{S_A}}\right)^2\frac{\hat{\rho}_{S_AS_A}}{\hat{\rho}}.
\end{aligned} \tag{N.4}$$

Here are some interesting expressions that can be gleaned from Table N.1

$$c_p(0) = \tilde{h}_\theta(0) = -\frac{\hat{\eta}_\Theta^2}{\hat{\eta}_{\Theta\Theta}}, \tag{N.5}$$

$$\frac{(T_0+t)}{(T_0+\theta)} = \frac{\hat{h}_\Theta}{c_p^0}, \tag{N.6}$$

$$\left.\frac{\partial\theta}{\partial\Theta}\right|_{S_A,p} = \left.\frac{\partial\theta}{\partial\Theta}\right|_{S_A} = -\frac{c_p^0\,\hat{\eta}_{\Theta\Theta}}{\hat{\eta}_\Theta^2} = -\frac{(T_0+\theta)^2\,\hat{\eta}_{\Theta\Theta}}{c_p^0} = -\frac{c_p^0}{c_p(0)}, \tag{N.7}$$

$$\mu(0) = -\frac{c_p^0\,\hat{\eta}_{S_A}}{\hat{\eta}_\Theta} = -(T_0+\theta)\,\hat{\eta}_{S_A}, \tag{N.8}$$

and

$$\left.\frac{\partial\theta}{\partial S_A}\right|_{\Theta,p} = \left.\frac{\partial\theta}{\partial S_A}\right|_\Theta = -\frac{c_p^0\,\hat{\eta}_{S_A\Theta}}{\hat{\eta}_\Theta^2} = c_p^0\left.\frac{\partial\hat{\eta}_\Theta^{-1}}{\partial S_A}\right|_\Theta = -\frac{(T_0+\theta)^2\,\hat{\eta}_{S_A\Theta}}{c_p^0}, \tag{N.9}$$

or, equivalently,

$$\left.\frac{\partial(T_0+\theta)^{-1}}{\partial S_A}\right|_\Theta = \frac{\hat{\eta}_{S_A\Theta}}{c_p^0}. \tag{N.10}$$

In order to construct rather accurate polynomials for enthalpy and entropy in order to implement the expressions in Table N.1, the following remarks can be made. Passing over the form of the polynomial $\widehat{h}(S_A,\eta,p)$, we first discuss below the form of the polynomials for $\tilde{h}(S_A,\theta,p)$ and $\eta = \tilde{\eta}(S_A,\theta)$, and then go on to consider the pair of polynomials $\hat{h}(S_A,\Theta,p)$ and $\eta = \hat{\eta}(S_A,\Theta)$.

The functional form $\tilde{\eta}(S_A,\theta)$ can be written in terms of the coefficients of the Gibbs function of seawater as the exact polynomial and logarithm terms given by

$$\tilde{\eta}(S_A,\theta) = -g_T(S_A,t=\theta,0). \tag{N.11}$$

Expressing $\tilde{h}(S_A,\theta,p)$ in powers of pressure, the coefficients of the polynomials of S_A and θ that multiply the two lowest order powers, namely p^0 and p^1, are found exactly from

$$\tilde{h}(S_A,\theta,0) = g(S_A,t=\theta,0) - (T_0+\theta)g_T(S_A,t=\theta,0) \tag{N.12}$$

and

$$\tilde{h}_p(S_A,\theta,0) = g_p(S_A,t=\theta,0). \tag{N.13}$$

The polynomials of S_A and θ that multiply the higher powers of pressure must be obtained by a least-squares fitting technique. In other words the entropy polynomial $\tilde{\eta}(S_A,\theta)$ is known exactly as is enthalpy at $p=0$ and potential density with reference pressure $p_r=0$. The only aspect that needs to be fitted by least squares is effectively in situ density at pressures other than

zero, that is, the fit is made to powers of pressure of p^1 and higher on the left-hand side of the following, knowing the right hand side at many data points

$$\tilde{h}_p\left(S_{\mathrm{A}},\theta,p\right) = g_p\left(S_{\mathrm{A}},t,p\right). \tag{N.14}$$

In the case of finding polynomial approximations for $\hat{h}\left(S_{\mathrm{A}},\Theta,p\right)$ and $\eta = \hat{\eta}\left(S_{\mathrm{A}},\Theta\right)$

there are fewer coefficients that follow directly from the Gibbs function of seawater; for example, none of the coefficients of $\eta = \hat{\eta}\left(S_{\mathrm{A}},\Theta\right)$ follow directly from g. That is, the polynomial $\hat{\eta}\left(S_{\mathrm{A}},\Theta\right)$ in S_{A} and Θ is determined by least squares fit to

$$\hat{\eta}\left(S_{\mathrm{A}},\Theta\right) = -g_T\left(S_{\mathrm{A}},t=\theta,0\right), \tag{N.15}$$

where the connection between Θ and θ is calculated offline by the exact polynomial

$$\Theta = \left(c_p^0\right)^{-1}\left[g\left(S_{\mathrm{A}},t=\theta,0\right) - \left(T_0+\theta\right)g_T\left(S_{\mathrm{A}},t=\theta,0\right)\right]. \tag{N.16}$$

The polynomial of S_{A} and Θ that multiplies the lowest power of p, p^0, in $\hat{h}\left(S_{\mathrm{A}},\Theta,p\right)$ is particularly simple, namely

$$\hat{h}\left(S_{\mathrm{A}},\Theta,0\right) = c_p^0\,\Theta. \tag{N.17}$$

The polynomials of S_{A} and Θ that multiply the other powers of p all need to be obtained by a least squares fitting procedure using

$$\hat{h}_p\left(S_{\mathrm{A}},\Theta,p\right) = g_p\left(S_{\mathrm{A}},t,p\right). \tag{N.18}$$

Table N.1. Expressions for various thermodynamic variables based on three different thermodynamic potentials

variable	Expression based on $\hat{h}(S_A,\eta,p)$	Expression based on $\tilde{h}(S_A,\theta,p)$ and $\tilde{\eta}(S_A,\theta)$	Expression based on $\hat{h}(S_A,\Theta,p)$ and $\hat{\eta}(S_A,\Theta)$
t	$(T_0+t)=\hat{h}_\eta$	$(T_0+t)=\tilde{h}_\theta/\tilde{\eta}_\theta$	$(T_0+t)=\hat{h}_\Theta/\hat{\eta}_\Theta$
θ	$(T_0+\theta)=\hat{h}_\eta(0)$	$\theta;\quad (T_0+\theta)=\tilde{h}_\theta(0)/\tilde{\eta}_\theta$	$(T_0+\theta)=c_p^0/\hat{\eta}_\Theta$
Θ	$\Theta=\hat{h}(0)/c_p^0$	$\Theta=\tilde{h}(0)/c_p^0$	$\Theta;\quad \Theta=\hat{h}(0)/c_p^0$
g	$g=\hat{h}-\eta\,\hat{h}_\eta$	$g=\tilde{h}-\tilde{\eta}\,\tilde{h}_\theta/\tilde{\eta}_\theta$	$g=\hat{h}-\hat{\eta}\,\hat{h}_\Theta/\hat{\eta}_\Theta$
v	$v=\hat{h}_p$	$v=\tilde{h}_p$	$v=\hat{h}_p$
ρ	$\rho=\hat{h}_p^{-1}$	$\rho=\tilde{h}_p^{-1}$	$\rho=\hat{h}_p^{-1}$
μ	$\mu=\hat{h}_{S_A}$	$\mu=\tilde{h}_{S_A}-\tilde{\eta}_{S_A}\tilde{h}_\theta/\tilde{\eta}_\theta$	$\mu=\hat{h}_{S_A}-\hat{\eta}_{S_A}\hat{h}_\Theta/\hat{\eta}_\Theta$
u	$u=\hat{h}-(p+P_0)\hat{h}_p$	$u=\tilde{h}-(p+P_0)\tilde{h}_p$	$u=\hat{h}-(p+P_0)\hat{h}_p$
f	$f=\hat{h}-\eta\,\hat{h}_\eta-(p+P_0)\hat{h}_p$	$f=\tilde{h}-\tilde{\eta}\,\tilde{h}_\theta/\tilde{\eta}_\theta-(p+P_0)\tilde{h}_p$	$f=\hat{h}-\hat{\eta}\,\hat{h}_\Theta/\hat{\eta}_\Theta-(p+P_0)\hat{h}_p$
c_p	$c_p=\hat{h}_\eta/\hat{h}_{\eta\eta}$	$c_p=\tilde{h}_\theta\tilde{\eta}_\theta^2/(\tilde{\eta}_\theta\tilde{h}_{\theta\theta}-\tilde{h}_\theta\tilde{\eta}_{\theta\theta})$	$c_p=\hat{h}_\Theta\hat{\eta}_\Theta^2/(\hat{\eta}_\Theta\hat{h}_{\Theta\Theta}-\hat{h}_\Theta\hat{\eta}_{\Theta\Theta})$
h^0	$h^0=\hat{h}(0)$	$h^0=\tilde{h}(0)$	$h^0=\hat{h}(0)$
ρ^θ	$\rho^\theta=\hat{h}_p^{-1}(p_r)$	$\rho^\theta=\tilde{h}_p^{-1}(p_r)$	$\rho^\theta=\hat{h}_p^{-1}(p_r)$
κ^t	$\kappa^t=-\hat{h}_p^{-1}\hat{h}_{pp}+\hat{h}_p^{-1}\dfrac{\hat{h}_{\eta p}^2}{\hat{h}_{\eta\eta}}$	$\kappa^t=-\tilde{h}_p^{-1}\tilde{h}_{pp}-\tilde{h}_p^{-1}\dfrac{\tilde{h}_{\theta p}^2\tilde{\eta}_\theta}{(\tilde{h}_\theta\tilde{\eta}_{\theta\theta}-\tilde{h}_{\theta\theta}\tilde{\eta}_\theta)}$	$\kappa^t=-\hat{h}_p^{-1}\hat{h}_{pp}-\hat{h}_p^{-1}\dfrac{\hat{h}_{\Theta p}^2\hat{\eta}_\Theta}{(\hat{h}_\Theta\hat{\eta}_{\Theta\Theta}-\hat{h}_{\Theta\Theta}\hat{\eta}_\Theta)}$
κ	$\kappa=-\hat{h}_p^{-1}\hat{h}_{pp}$	$\kappa=-\tilde{h}_p^{-1}\tilde{h}_{pp}$	$\kappa=-\hat{h}_p^{-1}\hat{h}_{pp}$
c	$c=\hat{h}_p/\sqrt{-\hat{h}_{pp}}$	$c=\tilde{h}_p/\sqrt{-\tilde{h}_{pp}}$	$c=\hat{h}_p/\sqrt{-\hat{h}_{pp}}$
Γ	$\Gamma=\hat{h}_{p\eta}$	$\Gamma=\tilde{h}_{p\theta}/\tilde{\eta}_\theta$	$\Gamma=\hat{h}_{p\Theta}/\hat{\eta}_\Theta$

α^t	$\alpha^t = \hat{h}_p^{-1} \dfrac{\widehat{h}_{p\eta}}{\widehat{h}_{\eta\eta}}$	$\alpha^t = -\tilde{h}_p^{-1}\tilde{h}_{p\theta} \dfrac{\tilde{\eta}_\theta^2}{\left(\tilde{h}_\theta \tilde{\eta}_{\theta\theta} - \tilde{h}_{\theta\theta}\tilde{\eta}_\theta\right)}$	$\alpha^t = -\hat{h}_p^{-1}\hat{h}_{p\Theta} \dfrac{\hat{\eta}_\Theta^2}{\left(\hat{h}_\Theta \hat{\eta}_{\Theta\Theta} - \hat{h}_{\Theta\Theta}\hat{\eta}_\Theta\right)}$
α^θ	$\alpha^\theta = \hat{h}_p^{-1} \dfrac{\widehat{h}_{p\eta}}{\widehat{h}_{\eta\eta}(0)}$	$\alpha^\theta = \tilde{h}_p^{-1}\tilde{h}_{p\theta}$	$\alpha^\theta = -\hat{h}_p^{-1}\hat{h}_{p\Theta} \dfrac{\hat{\eta}_\Theta^2}{c_p^0 \hat{\eta}_{\Theta\Theta}}$
α^Θ	$\alpha^\Theta = \hat{h}_p^{-1}\hat{h}_{p\eta} \dfrac{c_p^0}{\hat{h}_\eta(0)}$	$\alpha^\Theta = \tilde{h}_p^{-1}\tilde{h}_{p\theta} \dfrac{c_p^0}{\tilde{h}_\theta(0)}$	$\alpha^\Theta = \hat{h}_p^{-1}\hat{h}_{p\Theta}$
β^t	$\beta^t = -\hat{h}_p^{-1}\hat{h}_{S_A p} + \hat{h}_p^{-1}\hat{h}_{\eta p} \dfrac{\hat{h}_{S_A\eta}}{\hat{h}_{\eta\eta}}$	$\beta^t = -\tilde{h}_p^{-1}\tilde{h}_{S_A p} + \tilde{h}_p^{-1}\tilde{h}_{\theta p} \dfrac{\left(\tilde{h}_\theta \tilde{\eta}_{S_A\theta} - \tilde{h}_{S_A\theta}\tilde{\eta}_\theta\right)}{\left(\tilde{h}_\theta \tilde{\eta}_{\theta\theta} - \tilde{h}_{\theta\theta}\tilde{\eta}_\theta\right)}$	$\beta^t = -\hat{h}_p^{-1}\hat{h}_{S_A p} + \hat{h}_p^{-1}\hat{h}_{\Theta p} \dfrac{\left(\hat{h}_\Theta \hat{\eta}_{S_A\Theta} - \hat{h}_{S_A\Theta}\hat{\eta}_\Theta\right)}{\left(\hat{h}_\Theta \hat{\eta}_{\Theta\Theta} - \hat{h}_{\Theta\Theta}\hat{\eta}_\Theta\right)}$
β^θ	$\beta^\theta = -\hat{h}_p^{-1}\hat{h}_{S_A p} + \hat{h}_p^{-1}\hat{h}_{\eta p} \dfrac{\hat{h}_{S_A\eta}(0)}{\hat{h}_{\eta\eta}(0)}$	$\beta^\theta = -\tilde{h}_p^{-1}\tilde{h}_{p S_A}$	$\beta^\theta = -\hat{h}_p^{-1}\hat{h}_{S_A p} + \hat{h}_p^{-1}\hat{h}_{\Theta p} \dfrac{\hat{\eta}_{S_A\Theta}}{\hat{\eta}_{\Theta\Theta}}$
β^Θ	$\beta^\Theta = -\hat{h}_p^{-1}\hat{h}_{S_A p} + \hat{h}_p^{-1}\hat{h}_{\eta p} \dfrac{\hat{h}_{S_A}(0)}{\hat{h}_\eta(0)}$	$\beta^\Theta = -\tilde{h}_p^{-1}\tilde{h}_{S_A p} + \tilde{h}_p^{-1}\tilde{h}_{\theta p} \dfrac{\tilde{h}_{S_A}(0)}{\tilde{h}_\theta(0)}$	$\beta^\Theta = -\hat{h}_p^{-1}\hat{h}_{p S_A}$

References

Alberty, R.A., 2001: Use of Legendre transforms in chemical thermodynamics. *Pure Appl. Chem.*, **73**, 1349–1380.

Alderson, S. G. and P. D. Killworth, 2005: A preoperational scheme for calculating sea surface height by Bernoulli inverse of Agro float data in the North Atlantic. *J. Atmos. Oceanic Tech.*, **22**, 1416-1422.

Bacon, S., F. Culkin, N. Higgs and P. Ridout, 2007: IAPSO Standard Seawater: Definition of the uncertainty in the calibration procedure, and stability of recent batches. *J Atmos. Oceanic Technol.* **24**, 1785-1799.

Bacon, S. and N Fofonoff, 1996: Oceanic heat flux calculation. *J Atmos. Oceanic Technol.* **13**, 1327-1329.

Barber, C. R., 1969: The International Temperature Scale of 1968. *Metrologia*, **5**, 35-44.

Batchelor, G K, 1970: *An Introduction to Fluid Dynamics*, Cambridge University Press, 615pp.

Bezold, W.v., 1888: Zur Thermodynamik der Atmosphaere. Potentielle Temperatur. Verticaler Temperaturgradient. Zusammengesetzte Convection. *Sitzungsberichte der Koeniglich Preussischen Akademie der Wissenschaften zu Berlin*, **46**, 1189-1206. http://bibliothek.bbaw.de/bibliothek-digital/digitalequellen/schriften/anzeige/index_html?band=10-sitz/1888-2&seite:int=530

BIPM, 2005: Clarification of the definition of the kelvin, unit of thermodynamic temperature RECOMMENDATION 2 (CI-2005) The International Committee for Weights and Measures (CIPM), http://www.bipm.org/cc/CIPM/Allowed/94/CIPM-Recom2CI-2005-EN.pdf

BIPM, 2006: *The International System of Units (SI), 8th edition*. Bureau International des Poids et Mesures, Organisation Intergouvernementale de la Convention du Mètre, Sèvres, France. Internet: http://www.bipm.fr/utils/common/pdf/si_brochure_8_en.pdf

Bradshaw, A. and K. E. Schleicher, 1970: Direct measurements of thermal expansion of sea water under pressure. *Deep-Sea Res.*, **17**, 691-706.

Brewer, P.G., and A. Bradshaw, 1975. The effect of non-ideal composition of seawater on salinity and density, *J. Mar. Res*. **33**, 157-175.

Bromley, L.A., 1968: Relative enthalpies of sea salt solutions at 25 °C. *Journal of Chemical and Engineering Data*, **13**, 399-402.

Bromley, L.A., V. A. Desaussure, J. C. Clipp, and J. S. Wright, 1967: Heat capacities of sea water solutions at salinities of 1 to 12% and temperatures of 2° to 80°. *Journal of Chemical and Engineering Data,* **12**, 202-206.

Bromley, L.A., A. E. Diamond, E. Salami, and D. G. Wilkins, 1970: Heat capacities and enthalpies of sea salt solutions to 200 °C. *Journal of Chemical and Engineering Data*, **15,** 246-253.

Bromley, L.A., D. Singh, P. Ray, S. Sridhar, and S. M. Read, 1974: Thermodynamic properties of sea salt solutions. *AIChE Journal*, **20**, 326-335.

Bryden, H. L., 1973: New polynomials for thermal expansion, adiabatic temperature gradient and potential temperature of seawater. *Deep-Sea Res.*, **20**, 401-408.

Caldwell, D.R., 1978: The maximum density points of pure and saline water. *Deep-Sea Research*, **25**, 175-181.

Chen, C.-T. and F. J. Millero, 1976: The specific volume of seawater at high pressures. *Deep-Sea Res.* **23**, 595-612.

Chen, C.-T. and F. J. Millero, 1977: Sound speed of seawater at high pressures. *J. Acoust. Soc. Am.*, **62**, 1129-1135.

Clausius, R., 1876: Die Mechanische Wärmetheorie. Friedrich Vieweg und Sohn, Braunschweig.

Culkin, F. and P. S. Ridout, 1998: Stability of IAPSO Standard Seawater, *J. Atmos. Oceanic. Technol.*, **15**, 1072 – 1075.

De Groot, S. R. and P. Mazur, 1984: Non-equilibrium thermodynamics. Dover Publications, Inc., New York.

Del Grosso, V.A., 1974: New equation for the speed of sound in natural waters (with comparison to other equations). *J. Acoust. Soc. Am.*, **56**, 1084-1091.

de Szoeke, R. A., 2000: Equations of Motion Using Thermodynamic Coordinates. *Journal of Physical Oceanography*, **30**, 2814-2829.

de Szoeke, R. A., S. R. Springer and D. M. Oxilia, 2000: Orthobaric density: A thermodynamic variable for ocean circulation studies. *J. Phys. Oceanogr.*, **30**, 2830-2852.

Eden, C. and J. Willebrand, 1999: Neutral density revisited. *Deep-Sea Res. II*, **46**, 33-54.

Feistel, R.: Equilibrium thermodynamics of seawater revisited, 1993: *Progr. Oceanogr.*, **31**, 101-179.

Feistel, R., 2003: A new extended Gibbs thermodynamic potential of seawater, *Progr. Oceanogr.*, **58**, 43-114.

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.

Feistel, R and E. Hagen, 1995: On the GIBBS thermodynamic potential of seawater. *Prog. in Oceanogr.*, **36**, 249-327.

Feistel, R. and G. M. Marion, 2007: A Gibbs-Pitzer function of high-salinity seawater thermodynamics. *Progress in Oceanography*, **74**, 515-539.

Feistel, R. and W. Wagner, 2005. High-pressure thermodynamic Gibbs functions of ice and sea ice. *Journal of Marine Research*, **63**, 95-139.

Feistel, R. and W. Wagner, 2006: A New Equation of State for H_2O Ice Ih. *J. Phys. Chem. Ref. Data,* **35**, 2, 1021-1047.

Feistel, R., S. Weinreben, H. Wolf, S. Seitz, P. Spitzer, B. Adel, G. Nausch, B. Schneider and D. G. Wright, 2010: Density and Absolute Salinity of the Baltic Sea 2006 – 2009. *Ocean Science,* **xx**, yyy – yyy. submitted to Ocean Science Discussion.

Feistel, R., D. G. Wright, K. Miyagawa, A. H. Harvey, J. Hruby, D. R. Jackett, T. J. McDougall and W. Wagner, 2008: Mutually consistent thermodynamic potentials for fluid

water, ice and seawater: a new standard for oceanography. *Ocean Science*, **4**, 275-291.
http://www.ocean-sci.net/4/275/2008/os-4-275-2008.html

Feistel, R., D. G. Wright, D. R. Jackett, K. Miyagawa, W. Wagner, U. Overhoff, C. Guder, G. M. Marion, V. Tchijov, A. Feistel, J. H. Reissmann, 2009: Numerical implementation and oceanographic application of the thermodynamic potentials of water, vapour, ice, and seawater. Part I: Background and equations. *Ocean Science*, in preparation.

Fofonoff, N P, 1962: Physical properties of seawater. *The Sea*, Vol. 1, M N Hill, Ed., Wiley-Interscience, 3-30.

Fofonoff, N. P., 1985: Physical properties of seawater: A new salinity scale and equation of state for seawater. *J. Geophys. Res*., **90**, 3322–3342.

Gibbs, J. W., 1873: Graphical methods in the thermodynamics of fluids, Trans. Connecticut Acad. Arts and Sci., **2**, 309-342.

Gill, A E, 1982: *Atmosphere-Ocean Dynamics*. Academic Press, 662pp.

Godfrey, J. S., 1989: A Sverdrup model of the depth-integrated flow for the world ocean allowing for island circulations. *Geophysical and Astrophysical Fluid Dynamics*. **45**, 89-119.

Gouretski, V. V. and K. P. Koltermann, 2004: WOCE global hydrographic climatology. Berichte des Bundesamtes für Seeschifffahrt und Hydrographie Tech. Rep. 35/2004, 49 pp.

Griffies, S. M., 2004: *Fundamentals of Ocean Climate Models*. Princeton, NJ: Princeton University Press, 518 pp + xxxiv.

Greatbatch, R. J. and T. J. McDougall, 2003: The non-Boussinesq Temporal-Residual-Mean. *Journal of Physical Oceanography,* **33**, 1231-1239.

Helland-Hansen, B., 1912: The Ocean Waters. *Intern. Rev. Hydrobiol. Hydrog.*, Hydrog. Supp. Ser. 1 No. 2, Leipzig.

Helmholtz, H.v., 1888: Ueber atmosphaerische Bewegungen. *Sitzungsberichte der Koeniglich Preussischen Akademie der Wissenschaften zu Berlin,* **46**, 647–663.
http://bibliothek.bbaw.de/bibliothek-digital/digitalequellen/schriften/anzeige/index_html?band=10-sitz/1888-1&seite:int=665

Hill, K.D., T. M. Dauphinee and D. J. Woods, 1986: The extension of the Practical Salinity Scale 1978 to low salinities, *IEEE J. Oceanic Eng.,* **11**, 109–112.

IAPWS, 1995: 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. Fredericia, Denmark, September 1996, available at
http://www.iapws.org/relguide/IAPWS95.pdf

IAPWS, 2001: Guideline on the Use of Fundamental Physical Constants and Basic Constants of Water, The International Association for the Properties of Water and Steam, Gaithersburg, Maryland, USA, September 2001, revised July 2005, available at
http://www.iapws.org/relguide/fundam.pdf

IAPWS, 2006: Release on an Equation of State for H₂O Ice Ih, The International Association for the Properties of Water and Steam, Witney, UK, September 2006, available at http://www.iapws.org/relguide/Ice.pdf

IAPWS, 2008: 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 at http://www.iapws.org

IAPWS, 2009: Supplementary Release on a Computationally Efficient Thermodynamic Formulation for Liquid Water for Oceanographic Use, The International Association for the Properties of Water and Steam, Arnhem, Netherlands, September 2009, proposed Release.

IOC, 1987: GF3 - A General Formatting System for Geo-Referenced Data. Vol. 2, Technical Description of the GF3 Format and Code Tables. Intergovernmental Oceanographic Commission, Manuals and Guides 17, Unesco.

ISO, 1993: *ISO Standards Handbook: Quantities and Units*. International Organization for Standardization, Geneva, Switzerland.

Jackett, D. R. and T. J. McDougall, 1997: A neutral density variable for the world's oceans. *Journal of Physical Oceanography*, **27**, 237-263.

Jackett, D. R., T. J. McDougall, R. Feistel, D. G. Wright and S. M. Griffies, 2006: Algorithms for density, potential temperature, conservative temperature and freezing temperature of seawater. *Journal of Atmospheric and Oceanic Technology,* **23**, 1709-1728.

Killworth, P. D., 1986: A Bernoulli inverse method for determining the ocean circulation. *Journal of Physical Oceanography*, **16**, 2031-2051.

Klocker, A. and T. J. McDougall, 2010a: Quantifying the consequences of the ill-defined nature of neutral surfaces. in press, *Journal of Physical Oceanography*.

Klocker, A. and T. J. McDougall, 2010b: Water-mass transformation and ocean energetics in a nonlinear ocean. Submitted to *Journal of Physical Oceanography*

Klocker, A., T. J. McDougall and D. R. Jackett, 2009: A new method for forming approximately neutral surfaces. *Ocean Sci.*, **5**, 155-172. http://www.ocean-sci.net/5/155/2009/os-5-155-2009.html

Klocker, A., T. J. McDougall and D. R. Jackett, 2009b: Corrigendum to "A new method for forming approximately neutral surfaces", published in Ocean Science, 5, 155–172, 2009, *Ocean Sci.*, **5**, 191-191. http://www.ocean-sci.net/5/191/2009/os-5-191-2009.html

Kremling, K., 1971: New Method for measuring density of seawater, *Nature,* **229**, 109 – 110.

Landau, L. D. and E. M. Lifshitz, 1959: *Fluid Mechanics*. Pergamon, 536 pp.

Landau, L.D. and E. M. Lifshitz, 1980: *Statistical Physics*. Reed Educational and Professional Publishing Ltd. 544 pp.

Marion, G.M., F. J. Millero, and R. Feistel, 2009: Precipitation of solid phase calcium carbonates and their effect on application of seawater $S_A - T - P$ models, *Ocean Sci.*, 5, 285-291. www.ocean-sci.net/5/285/2009/

McDougall, T. J., 1984: The relative roles of diapycnal and isopycnal mixing on subsurface water mass conversion. *Journal of Physical Oceanography,* **14**, 1577-1589.

McDougall, T. J., 1987a: Neutral surfaces. *Journal of Physical Oceanography,* **17**, 1950-1964.

McDougall, T. J., 1987b: Thermobaricity, cabbeling, and water-mass conversion. *J. Geophys. Res.,* **92**, 5448-5464.

McDougall, T. J., 1988: Neutral-surface potential vorticity. *Progress in Oceanography,* **20**, 185-221.

McDougall, T. J., 1989: Streamfunctions for the lateral velocity vector in a compressible ocean. *J. Marine Research*, **47,** 267-284.

McDougall, T. J., 1991: Parameterizing mixing in inverse models in *Dynamics of Oceanic Internal Gravity Waves,* edited by P. Müller and D. Henderson, Proceedings of the sixth 'Aha Huliko'a Hawaiian Winter Workshop, University of Hawaii at Manoa, 355-386.

McDougall, T. J., 1995: The influence of ocean mixing on the absolute velocity vector. *Journal of Physical Oceanography,* **25**, 705-725.

McDougall, T.J., 2003: Potential enthalpy: A conservative oceanic variable for evaluating heat content and heat fluxes. *Journal of Physical Oceanography*, **33**, 945-963.

McDougall, T. J., J. A. Church and D. R. Jackett, 2003: Does the nonlinearity of the equation of state impose an upper bound on the buoyancy frequency? *Journal of Marine Research*, **61**, 745-764.

McDougall, T. J. and R. Feistel, 2003: What causes the adiabatic lapse rate? *Deep-Sea Research,* **50**, 1523-1535.

McDougall, T. J., R. J. Greatbatch and Y. Lu, 2002: On conservation equations in oceanography: How accurate are Boussinesq ocean models? *Journal of Physical Oceanography,* **32**, 1574-1584.

McDougall, T. J. and D. R. Jackett, 1988: On the helical nature of neutral trajectories in the ocean. *Progress in Oceanography,* **20**, 153-183.

McDougall, T. J. and D. R. Jackett, 2005a: An assessment of orthobaric density in the global ocean. *Journal of Physical Oceanography*, **35**, 2054–2075.

McDougall, T. J. and D. R. Jackett, 2005b: The material derivative of neutral density. *Journal of Marine Research*, **63**, 159-185.

McDougall, T. J. and D. R. Jackett, 2007: The thinness of the ocean in $S - \Theta - p$ space and the implications for mean diapycnal advection. *Journal of Physical Oceanography*, **37**, 1714-1732.

McDougall, T. J., D. R. Jackett, D. G. Wright and R. Feistel 2003: Accurate and computationally efficient algorithms for potential temperature and density of seawater. *J. Atm. Ocean. Technol.*, **20**, 730-741.

McDougall, T. J., D. R. Jackett and F. J. Millero, 2009a: An algorithm for estimating Absolute Salinity in the global ocean. *Ocean Sci. Discuss.*, **6**, 215-242. http://www.ocean-sci-discuss.net/6/215/2009/osd-6-215-2009.html

McDougall, T.J., R. Feistel, D. R. Jackett, D. G. Wright, F. J. Millero, B. A. King, G. M. Marion, P. Spitzer and C-T. A. Chen, 2009b: Oceanographic application of the Gibbs function 2008 of seawater. *Deep-Sea Res I.*, in preparation.

McDougall, T. J. and A. Klocker, 2010: An approximate geostrophic streamfunction for use in density surfaces. submitted to *Ocean Modelling*.

McDougall, T. J., S. A. Thorpe and C. H. Gibson, 1988: Small-scale turbulence and mixing in the ocean: A glossary, in *Small-scale turbulence and mixing in the ocean*, edited by J. C. J. Nihoul and B. M. Jamart, Elsevier, Amsterdam. 3-9.

Millero, F.J., 1974: Seawater as a multicomponent electrolyte solution. *The Sea*, Vol. 5, E. D. Goldberg, Ed., Wiley-Interscience, 3-80.

Millero, F.J., 2000. Effect of changes in the composition of seawater on the density-salinity relationship. *Deep-Sea Res. I* **47**, 1583-1590.

Millero, F.J., 2008: A review of the definitions of Salinity in oceanography. in preparation.

Millero, F.J., Feistel, R., Wright, D.G., and McDougall, T.J., 2008a: The composition of Standard Seawater and the definition of the Reference-Composition Salinity Scale, *Deep-Sea Res. I*, **55**, 50-72.

Millero, F.J., Forsht, D., Means, D., Giekes, J., Kenyon, K., 1978: The density of North Pacific Ocean waters. *J. Geophys. Res*. **83**, 2359-2364.

Millero, F.J., A. Gonzalez, A. and G. K. Ward, 1976c: The density of seawater solutions at one atmosphere as a function of temperature and salinity. *J. Mar. Res*., **34**, 61-93.

Millero, F.J., Gonzalez, A., Brewer, P.G., Bradshaw, A., 1976a: The density of North Atlantic and North Pacific deep waters. *Earth and Planetary Sci.Letters* **32**, 468-472.

Millero, F. J., F. Huang, N. Williams, J. Waters and R. Woosley, 2009: The effect of composition on the density of South Pacific Ocean waters, *Mar. Chem*., **114**, 56-62.

Millero, F.J., Lawson, D., Gonzalez, A., 1976b: The density of artificial river and estuarine waters. *J. Geophys. Res*. **81**, 1177-1179.

Millero, F.J. and W. H. Leung, 1976: The thermodynamics of seawater at one atmosphere, *Am. J. Sci*., **276**, 1035– 1077.

Millero, F.J. and X. Li, 1994: Comments on "On equations for the speed of sound in seawater" [*J. Acoust. Soc. Am*. 94, 255-275 (1993)]. *J. Acoust. Soc. Am*. **95**, 2757-2759.

Millero, F. J. and K. Kremling, 1976: The densities of Baltic Sea waters. *Deep-Sea Research*, **23**, 1129-1138.

Millero, F. J., G. Perron and J. F. Desnoyers, 1973: Heat capacity of seawater solutions from 5 to 35 °C and .05 to 22 ‰ chlorinity. *J. Geophys. Res*., **78**, 4499-4506.

Millero, F.J., J. Waters, R. Woosley, F. Huang, and M. Chanson, 2008b: The effect of composition on the density of Indian Ocean waters, *Deep-Sea Res. I*, **55**, 460-470.

Mohr, P.J., B. N. Taylor and D. B. Newell, 2008: CODATA recommended values of the fundamental physical constants: 2006. *Rev. Mod. Phys.*, **80**, 633-730; also published in *J. Phys. Chem. Ref. Data*, **37**, 1187-1284 (2008).

Mohr, P.J. and B. N. Taylor, 2005: CODATA recommended values of the fundamental physical constants: 2002. *Rev. Mod. Phys.,* **77**, 1-107.

Moritz, H., 2000: Geodetic reference system 1980. *Journal of Geodesy*, **74**, 128-133.

Planck, M. 1935: Bemerkungen über Quantitätsparameter, Intensitätsparameter und stabiles Gleichgewicht. *Physica II*, 1029-1032. Reprinted in Ebeling, W., Hoffmann, D. (Eds.), 2008, *Über Thermodynamische Gleichgewichte, von Max Planck*. Verlag Harry Deutsch, Frankfurt am Main, 236 pp.

Poisson, A., and M. H. Gadhoumi, 1993: An extension of the Practical Salinity Scale 1978 and the Equation of State 1980 to high salinities. *Deep-Sea Res. I*, **40**, 1689-1698.

Preston-Thomas, H., 1990: The international temperature scale of 1990 (ITS-90), *Metrologia* **27**, 3-10.

Reid, J. L. and R. J. Lynn, 1971: On the influence of the Norwegian-Greenland and Weddell seas upon the bottom waters of the Indian and Pacific oceans. *Deep-Sea Res.*, **18**, 1063-1088.

Robinson, R.A., 1954: The vapour pressure and osmotic equivalence of sea water. *Journal of the Marine Biological Association of the U.K.* **33**, 449-455.

Ruddick, B., 1983: A practical indicator of the stability of the water column to double-diffusive activity. *Deep-Sea Res.,* **30,** 1105–1107.

Rusby, R. L., 1991: The conversion of thermal reference values to the ITS-90. *J. Chem. Thermodynamics*, **23**, 1153-1161.

Saunders, P. 1990: The International Temperature Scale of 1990, ITS-90. *WOCE Newsletter* **10**, IOS, Wormley, UK.

Saunders, P. M., 1995: The Bernoulli function and flux of energy in the ocean. *J. Geophys. Res.*, **100**, 22,647-22,648.

Seitz, S., P. Spitzer and R. J. C. Brown, 2008: Consistency of practical salinity measurements traceable to primary conductivity standards: Euromet project 918, *Accred. Qual. Assur*. **13**, 601–605.

Straub, D. N., 1999: On thermobaric production of potential vorticity in the ocean. *Tellus A*, **51**, 314-325.

Thomson, W., 1851: On the dynamical theory of heat; with numerical results deduced from Mr. Joule's equivalent of a thermal unit and M. Regnault's observations on steam. Trans. Roy. Soc. Edinburgh, **3**, 48-52.

Unesco, 1981: The Practical Salinity Scale 1978 and the International Equation of State of Seawater 1980. Unesco technical papers in marine science **36**, 25pp.

Unesco, 1983: Algorithms for computation of fundamental properties of seawater. Unesco technical papers in marine science **44**, 53pp.

Veronis, G., 1975: The role of models in tracer studies, in: *Numerical Models of Ocean Circulation,* pp. 133–146, National Academy of Science.

VIM, 2008: International Vocabulary of Metrology (VIM), ISO/IEC Guide 99-2007.

Wagner, W. and A. Pruß, 2002: The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data,* **31**, 387-535.

Warren, B. A., 2006: The first law of thermodynamics in a salty ocean. *Progress in Oceanography*, **70**, 149-167.

Weiser, M. E., 2006: Atomic weights of the elements 2005 (IUPAC Technical Report). *Pure Appl. Chem*. **78**, 2051-2066.

Wolf, H., 2008: Determination of water density: limitations at the uncertainty level of 1 x 10^{-6}, *Accred. Qual. Assur.* **13**, 587–591.

Wright, D. G., R. Feistel, D. R. Jackett, K. Miyagawa, A. Feistel, C. Guder, G. M. Marion, U. Overhoff, J. H. Reissmann, V. Tchijov, and W. Wagner, 2009a: Numerical implementation and oceanographic application of the thermodynamic potentials of water, vapour, ice, and seawater. Part II: The library routines. *Ocean Science*, in preparation.

Wright, D. G., D. R. Jackett, R. Feistel and T. J. McDougall, 2009b: Consistent modular implementation of the thermodynamic potentials of water, ice and seawater. *Ocean Science*, in preparation.

You, Y. and T. J. McDougall, 1990: Neutral surfaces and potential vorticity in the World's Oceans. *Journal of Geophysical Research,* **95**, 13235-13261.

Zhang, H-M and N. G. Hogg 1992: Circulation and water mass balance in the Brazil Basin. *J. Marine Research*, **50**, 385-420.

Zika, J. D., T. J. McDougall and B. M. Sloyan, 2009: A Tracer Contour Inverse Method for estimating ocean circulation and mixing. *J. Physical Oceanography*, in press.

Zika, J. D., T. J. McDougall and B. M. Sloyan, 2010: Weak mixing in the North East Atlantic: An application of the Tracer-Contour Inverse Method. submitted to *J. Physical Oceanography*.