Calculation of the Thermophysical Properties of Seawater

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Index

INTRODUCTION

BASIC THERMOPHYSICAL PROPERTIES

- ITS-90 Temperature
- Practical Salinity $S_P$
- Reference Composition and Reference-Composition Salinity $S_R$
- Absolute Salinity $S_A$
- The Gibbs Function of Seawater
- Specific Volume
- Density
- Chemical Potentials $\mu$, $\mu^W$ and $\mu^S$
- Entropy
- Internal Energy
- Enthalpy
- Helmholtz Energy
- Osmotic Coefficient
- Isothermal Compressibility
- Adiabatic Compressibility
- Sound Speed
- Thermal Expansion Coefficients
- Saline Contraction Coefficients
- Isobaric Heat Capacity
- Isochoric Heat Capacity
- The Adiabatic Lapse Rate
**DERIVED QUANTITIES**

Potential Temperature
Potential Enthalpy
Conservative Temperature
Potential Density
Density Anomaly
Potential Density Anomaly
Specific Volume Anomaly
The Cabling Coefficient
The Thermobaric Coefficient
Freezing Temperature
Boiling Temperature
Latent Heat of Melting
Latent Heat of Evaporation
Buoyancy Frequency
Neutral Tangent Plane
Neutral Helicity
Neutral Density
Stability Ratio $R_N$
Isopycnal Gradients compared with Epineutral Gradients
Slopes of Potential Density Surfaces and Neutral Tangent Planes Compared
Potential Vorticity
Freshwater Content and Freshwater Flux
The Vertical Velocity through the Sea Surface
Heat Fluxes
Dynamic Height Anomaly
Montgomery Potential
Geopotential
Total Energy
Bernoulli Function
Depth-Integrated Steric Height (DISH or PIDHA)
Pressure to Height Conversion
OTHER QUANTITIES

Coriolis Parameter
Gravitational Acceleration

CONCLUSIONS

APPENDIX A: Background Theoretical Constructs behind the use of the Gibbs Function of Seawater

A.1 ITS-90 Temperature
A.2 Reference Composition and the Reference-Composition Salinity Scale
A.3 Absolute Salinity
A.4 Spatial Variations in Seawater Composition: A First Algorithm for $S_A$
A.5 The Gibbs Function of Seawater
A.6 The Fundamental Thermodynamic Relation
A.7 The “conservative” and “isobaric conservative” properties
A.8 The “potential” property
A.9 Proof that $\theta = \Theta(S_A, \eta)$ and $\Theta = \Theta(S_A, S)$
A.10 The First Law of Thermodynamics
A.11 The Non-conservative Production of Entropy $\eta$
A.12 The Non-conservative Production of Potential Temperature $\theta$
A.13 The Non-conservative Production of Conservative Temperature $\Theta$
A.14 The Non-conservative Production of Density $\rho$ and of potential density $\rho_\Theta$
A.15 The Material Derivative of $S_A$ and $\Theta$ in a Turbulent Ocean
A.16 The Material Derivative of Density and of Locally-Referenced Potential Density
A.17 The Material Derivative of Potential Density
A.18 The Material Derivative of Orthobaric Density
A.19 The Material Derivative of Neutral Density
Appendix B: Derivation of the First Law of Thermodynamics

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

Appendix D: Fundamental Constants

Appendix E: Algorithm for calculating Practical Salinity $S_P$
E.1 Calculation of Practical Salinity $S_P$ in terms of $K_{15}$
E.2 Calculation of Practical Salinity $S_P$ at oceanographic temperature and pressure
E.3 Calculation of Conductivity ratio $R$ for a given Practical Salinity $S_P$
E.4 Evaluating Practical Salinity $S_P$ using ITS-90 temperatures


Appendix G: Coefficients of the Saline Gibbs Function of Seawater of Feistel (2008)

Appendix H: Recommended Nomenclature, Symbols and Units in Oceanography

Appendix I: Software in Library A; the Official Thermodynamic Description of Seawater

Appendix J: Software in Library B; the fast library in SI units

Appendix K: Software in Library C, the gsw Library; the fast library in oceanographic units

Appendix L: Checking $g(S_A,t,p)$ against the original thermodynamic data

Acknowledgements

References
1. INTRODUCTION

1.1 Existing Oceanographic standards

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 & 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 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 the present day.

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 have lent weight to the argument that it is timely to redefine the thermophysical 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 thermodynamic description of pure water has appeared (IAPWS-95). Also more and rather accurate measurements of the properties of seawater (such as for (i) heat capacity, (ii) sound speed and (iii) the temperature of maximum density) have been made and 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 enthalpy and internal energy of seawater so that heat fluxes can be more accurately determined in the ocean (enthalpy and internal energy were not available from EOS-80).
- The temperature scale has been revised from ITS-68 to ITS-90 and the atomic weights of the elements have been revised (IUPAC, 2005).
1.3 SCOR/IAPSO WG127 and the approach taken

In 2005 SCOR and IAPSO established Working Group 127 on the “Thermodynamics and Equation of State of Seawater” (henceforth referred to as WG127) and this group has been working through a series of issues in order to arrive at a series 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 thermophysical properties of seawater can be derived by purely mathematical manipulations (such as differentiation). This approach ensures that the various thermophysical 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 (rather than Practical Salinity), temperature and pressure. 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). The reason for preferring Absolute Salinity over Practical Salinity is because the thermodynamic properties of seawater are directly influenced by the mass of dissolved constituents (i.e. Absolute Salinity) whereas Practical Salinity depends on conductivity.

Consider for example exchanging a small amount of pure water with the same mass of silicate in an otherwise isolated seawater sample at constant temperature and pressure. Since silicate is non-ionic, the conductivity is almost unchanged but the Absolute Salinity is increased and Young’s rule indicates that the density, enthalpy etc are changed in proportion to the change in Absolute Salinity. Similarly, if a small mass of say NaCl is added and the same mass of silicate is taken out of the sample, Absolute Salinity will not have changed (and by Young’s rule the density, enthalpy etc will be almost unchanged) but the Practical Salinity will have increased. This issue is discussed a little more fully in Appendix A.3 below.

This Gibbs function of seawater has now been published (Feistel, 2008) and has also been issued by the International Association for the Properties of Water and Steam as the Release IAPWS-08. Appendix C summarizes the publications which lie behind the recommendations now being made to evaluate the thermophysical properties of seawater. This new approach to seawater thermodynamics should be referred to collectively as the “Thermodynamic Equation Of Seawater – 2010”, or “TEOS-10” for short.

A second notable difference from present practice that is being recommended by WG127 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 thermophysical 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 wrong 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. Second, it is imperative that confusion is not created in national data bases where a change in the reporting of salinity may be mis-handled 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 storage of Practical Salinity \( S_P \) in national data bases of oceanographic data. Thirdly, the algorithm for determining the "best" estimate of Absolute Salinity 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.2 to give the best estimate of Absolute Salinity of Standard Seawater) would also introduce the possibility of misuse of salinity data without providing any real advantage over storing Practical Salinity so we also avoid this possibility.

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 salinity 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.

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 \( ^\circ\text{C} \)) and 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).

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. These quantities were not available from the International Equation of State but are central to a proper accounting in the ocean of the heat that is transferred between the ocean, the ice cover and the atmosphere above.
- The thermophysical quantities available from the new approach are totally consistent with each other.
- The new salinity variable, Absolute Salinity, is part of the SI system of 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 so-called “thermal wind” relation).
- The Reference Composition of standard seawater supports marine physico-chemical studies such as the solubility of sea salt constituents, the alkalinity, the pH and the ocean acidification by rising concentrations of atmospheric CO2.

1.4 A guide to this Seawater Manual

The remainder of this manual begins by listing the definitions of various thermophysical quantities that follow directly from the Gibbs function of seawater by simple mathematical processes such as differentiation. This is then followed 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, 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 faster.

The third library, Library C (the so-called “gsw” library) is exactly the same as Library B except that its input parameters and its outputs 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 numerical computational efficiency compared with
Library A and because of the more familiar units compared with Library B. The library name “gsw” (GibbsSeaWater) has been chosen to be similar to, but different from the existing “sw” (SeaWater) library maintained by CSIRO in Hobart Australia. This “gsw” library, initially mainly in MATLAB, is available at [http://www.marine.csiro.au/~jackett/TEOS-10/](http://www.marine.csiro.au/~jackett/TEOS-10/).

After these descriptions of how to determine the thermophysical quantities and the derived quantities, we end with some conclusions and lists of symbols, nomenclature and succinct lists of thermodynamic formulae. 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 and the non-conservative nature of many oceanographic variables are given in the Appendices. Much of this work appears 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 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 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 gauge pressure in dbar and Absolute Salinity $S_A$ has 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 seem to demand that the variables are in SI units. As an example, the freshwater fraction of seawater is written correctly as $(1 - S_A)$, but it is clear that in this instance Absolute Salinity must be expressed in kg kg$^{-1}$ not in g kg$^{-1}$. 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.

Appendices I, J and K summarize three different libraries of computer software, Libraries A, B and C, the first two of which exclusively use basic SI units as inputs and deliver outputs in these same strict basic-SI units. Library C has input variables in units that are more familiar to oceanographers, and the outputs are (mostly) consistent with these oceanographic units.
**BASIC THERMOPHYSICAL PROPERTIES**

**ITS-90 Temperature**

In the year 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 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

\[
(t_{68}/^\circ C) = 1.00024 \times (t_{90}/^\circ C)
\]

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 (1).

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

**Practical Salinity \( S_p \)**

Practical salinity \( S_p \) is defined on the Practical Salinity Scale of 1978 in terms of the conductivity ratio \( K_{15} \) which is the electrical conductivity of the sample at temperature \( t_{68} = 15^\circ C \) and pressure equal to one standard atmosphere (\( p = 0 \) dbar and absolute pressure \( P \) equal to 101325 Pa), divided by the conductivity of a standard potassium chloride (KCl) solution at the same temperature and pressure. The mass fraction of KCl in the standard solution is \( 32.4356 \times 10^{-3} \) (mass of KCl per mass of solution). When \( K_{15} = 1 \), the Practical Salinity \( S_p \) is by definition 35. Note that Practical Salinity is a unit-less quantity. Though sometimes convenient, it is technically incorrect to quote Practical Salinity in “psu”; rather it should be quoted as a certain Practical Salinity “on the Practical Salinity Scale PSS-78”. 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.

Data stored in national and international data bases should, as a matter of principle, be measured values rather than derived quantities. In this way we continue to recommend the
storage of 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.

**Reference Composition and Reference-Composition Salinity**

The reference composition of seawater is defined by Millero et al. (2008) 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. (2008) show that

$$S_R \approx u_{PS} S_P \quad \text{where} \quad u_{PS} \equiv \left(35.165\ 04/35\right) \text{g kg}^{-1}. \quad (2)$$

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), 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. (2008) estimate that the absolute uncertainty in this value is $\pm 0.007$ g kg$^{-1}$.

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. (2008). For the user's convenience a brief summary of information from Millero et al. (2008), including the precise definition of Reference Salinity is given in the Appendix.
**Absolute Salinity**

Absolute Salinity is defined as the mass fraction of dissolved material in seawater. For seawater of Reference Composition, Absolute Salinity is the same as Reference Salinity. A practical procedure for estimating Absolute Salinity 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 assuming that the seawater sample has Reference Composition. The difference between the measured density and the Reference-Composition density is used to estimate the Absolute Salinity Anomaly $\delta S_A = S_A - S_R$ (Millero et al. (2008)). The procedure for estimating Absolute Salinity is sketched in Figure 1.

![Figure 1](image)

Figure 1. A sketch indicating how thermophysical 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 $\delta S_A$ to the Reference Salinity.

In a series of papers (Millero et al. (1976a, 1978, 2000, 2008)), this procedure has yielded estimates of $\delta S_A = S_A - S_R$ from most of the major basins of the world ocean. Since the density of seawater is rarely measured, we recommend the algorithm of McDougall et al. (2009a) for the evaluation of 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. In the McDougall et al. (2009a) algorithm the silicate is estimated by interpolation of a global atlas (Gouretski and Koltermann (2004)). The algorithm takes the form

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

(3)

where $\lambda$ is latitude (degrees North), $\phi$ 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 it affects the density of a seawater sample without significantly affecting its conductivity or its Practical Salinity. In practice this explains about 40% of the effect and the remainder is due to the correlation of other properties (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).

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 $\delta S_\lambda$ at $p = 2000$ dbar.

Figure 2 (b). A vertical section of Absolute Salinity Anomaly $\delta S_\lambda$ along 180°E 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 of $\delta S_A = S_A - S_R$ 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 $\phi$, latitude $\lambda$ and gauge pressure $p$ (in dbar) is available at http://www.marine.csiro.au/~jackett/TEOS-10/. 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.

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)

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p)$$  \hspace{1cm} (4)

The saline part of the Gibbs function of seawater is valid over the ranges $0 < S_A < 120 \text{ g kg}^{-1}$, $-6.0^\circ \text{C} < t < 80^\circ \text{C}$ and $0 < p < 10^4 \text{ dbar}$. 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 from the IAPWS-09 Gibbs function which is valid in the oceanographic ranges of temperature and pressure, from less than the freezing temperature of seawater (at any pressure), up to $40^\circ \text{C}$ (specifically from $-\left[2.65 + (p + P_0) \times 0.0743 \text{ MPa}^{-1}\right] ^\circ \text{C}$ to $40 ^\circ \text{C}$), and in the pressure range $0 < p < 10^4 \text{ dbar}$. For practical purposes in oceanography it is expected that IAPWS-09 will be used because it is a factor of approximately two orders of magnitude faster computationally than the IAPWS-95 code for pure water. However if one is concerned with temperatures between $40 ^\circ \text{C}$ and $80 ^\circ \text{C}$ then one must use the IAPWS-95 version of $g^W(t, p)$ rather than the IAPWS-09 version. The thermophysical properties derived from the IAPWS-95 and IAPWS-08 combination are available from Library A, while that derived from the IAPWS-09 and IAPWS-08 combination are available from the Libraries B and C. Libraries A and B are restricted to the oceanographic standard range in temperature and pressure, however it extends at $p = 0$ to Absolute Salinity up to mineral saturation concentrations (Marion et al. 2009). Models that use $S_A$ as input require 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, which will change the fixed ratios. Then models of seawater based on the Millero et al. (2008) Reference Composition will no longer be applicable. Figure 3 illustrates $S_A$-T boundaries ($p = 0$) for 2008 ($p_{CO_2} = 385 \mu \text{atm}$) and 2100 ($p_{CO_2} = 550 \mu \text{atm}$) (from Marion et al. (2009)).
The Gibbs function (4) contains four arbitrary constants that cannot be determined by any thermodynamic measurement. These arbitrary constants mean that the Gibbs function (4) is unknown and unknowable up to the arbitrary function of temperature and Absolute Salinity

\[(a_1 + a_2 t) + (a_3 + a_4 t) S_A\]  

(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 \(g^S(S_A, t, p)\). The first two coefficients are chosen to make the internal energy and the entropy of pure water zero at the triple point

\[\eta^W(t, p_t) = 0\]  

(6)

and

\[u^W(t, p_t) = 0\]  

(7)
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 (4) 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 (6) and (7).
The remaining two arbitrary constants $a_3$ and $a_4$ of (4) are determined by ensuring that the specific enthalpy $h$ and specific entropy $s$ of a sample of standard seawater with standard-ocean properties $(S_{SO}, t_{SO}, p_{SO}) = (35.16504\ \text{g kg}^{-1}, 0^\circ\text{C}, 0\ \text{dbar})$ are both zero, that is that
\[
h(S_{SO}, t_{SO}, p_{SO}) = 0
\]
and
\[
\eta(S_{SO}, t_{SO}, p_{SO}) = 0.
\]
In more detail, these conditions are actually officially written as (Feistel (2008), IAPWS-08)
\[
h^S(S_{SO}, t_{SO}, p_{SO}) = u^W(t_1, p_1) - h^W(t_{SO}, p_{SO})
\]
and
\[
\eta^S(S_{SO}, t_{SO}, p_{SO}) = \eta^W(t_1, p_1) - \eta^W(t_{SO}, p_{SO}).
\]
Written in this way, (11F) and (11G) 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 (6) and (7)), 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 substance. While the two slightly different thermodynamic definitions of pure water, namely IPAWS-95 and IAPWS-09, both achieve zero values of the internal energy and entropy at the triple point of pure water, the enthalpy and entropy of pure water at the temperature and pressure of standard seawater, $h^W(t_{SO}, p_{SO})$ and $\eta^W(t_{SO}, p_{SO})$ on the right-hand sides of (10) and (11), are slightly different in the two cases. For example $h^W(t_{SO}, p_{SO})$ is $3.3 \times 10^{-3}\ \text{J/kg}$ from IAPWS-09 (as described in the table of Appendix F) compared with the round-off error of $2 \times 10^{-8}\ \text{J/kg}$ 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 L. Further checking of these Gibbs functions has occurred in the process leading up to IAPWS (the International Association for the Properties of Water and Steam) approving these Gibbs functions as the Releases IAPWS-08 (the Release of the Feistel (2008) Gibbs function) and IPAWS-09 (the Release of the pure water part of Feistel (2003)).

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.
Specific Volume

The specific volume of seawater $v$ is the pressure derivative of the Gibbs function at constant Absolute Salinity $S_A$ and in situ temperature $t$, that is

$$v = v(S_A, t, p) = g_p = \frac{\partial g}{\partial p}|_{S_A, t}.$$  

(12)

Notice that specific volume is a function of Absolute Salinity $S_A$ rather than of Reference Salinity $S_R$ or Practical Salinity $S_P$.

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

$$\frac{\partial h}{\partial p}|_{S_A, \eta} = \frac{\partial h}{\partial p}|_{S_A, \Theta} = \frac{\partial h}{\partial p}|_{S_A, \theta} = v.$$  

(13)

Density

The density of seawater $\rho$ is the reciprocal of the pressure derivative of the Gibbs function at constant Absolute Salinity $S_A$ and in situ temperature $t$, that is

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

(14)

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 $\text{g kg}^{-1}$ is numerically greater than Practical Salinity by approximately $0.165 \text{ g kg}^{-1}$ so that if Practical Salinity were inadvertently used as the salinity argument for the density algorithm, a significant density error of approximately $0.12 \text{ kg m}^{-3}$ would result.

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

$$\rho = \rho(S_A, \theta, p) = \rho(S_A, \Theta, p),$$  

(14a)

where $\theta$ is potential temperature referenced to $p_r = 0 \text{ dbar}$. We will adopt the convention that when enthalpy $h$, specific volume $v$ or density $\rho$ are taken to be functions of potential temperature they attract an over-twiddle as in $\hat{h}, \hat{v}$ and $\hat{\rho}$, 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 (13) can be written more compactly as $\hat{h}_p = \hat{h}_p = v$ since the other variables are taken to be constant during the partial differentiation.
Chemical Potentials $\mu$, $\mu^W$ and $\mu^S$

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))

$$G(m_W, m_S, t, p) = m_W \mu^W + m_S \mu^S$$

(15a)

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

$$\mu^W = \left( \frac{\partial G}{\partial m_W} \right)_{m_S, t, p}, \quad \text{and} \quad \mu^S = \left( \frac{\partial G}{\partial m_S} \right)_{m_W, t, p}$$

(15b)

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

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

(15c)

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 (4). This Gibbs energy $g$ is used as the thermodynamic potential function (Gibbs function) for seawater. The above three equations can be used to write expressions for $\mu^W$ and $\mu^S$ in terms of the Gibbs function $g$ as

$$\mu^W = g + \left( m_W + m_S \right) \left( \frac{\partial g}{\partial S_A} \right)_{m_S, t, p} \left( \frac{\partial S_A}{\partial m_W} \right)_{m_S} = g - S_A \left( \frac{\partial g}{\partial S_A} \right)_{t, p}$$

(16)

and for the chemical potential of salt in seawater,

$$\mu^S = g + \left( m_W + m_S \right) \left( \frac{\partial g}{\partial S_A} \right)_{m_W, t, p} \left( \frac{\partial S_A}{\partial m_S} \right)_{m_W} = g + (1 - S_A) \left( \frac{\partial g}{\partial S_A} \right)_{t, p}$$

(17)

The relative chemical potential $\mu$ (commonly called the “chemical potential of seawater”) follows from (16) and (17) as

$$\mu = \mu^S - \mu^W = \left( \frac{\partial g}{\partial S_A} \right)_{t, p}$$

(18)

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. (A12) in Appendix A) it follows that the chemical potential of seawater $\mu$ describes the change of enthalpy $dh$ if at constant pressure and entropy, a small mass fraction of water is replaced by salt, $dS_A$. Equations (16) – (18) serve to define the three chemical potential 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 $\text{kg kg}^{-1}$ and $g$, $\mu$, $\mu^S$ and $\mu^W$ all have units of $\text{J kg}^{-1}$. In the “gsw” library of computer code (Library C, Appendix K) $S_A$ has units of $\text{g kg}^{-1}$ and $\mu$, $\mu^S$ and $\mu^W$ all have units of...
J g$^{-1}$. This adoption of oceanographic (i.e. non-basic-SI) units means that special care is needed in evaluating equations such as (15c) and (17) where it is clear that $S_A$ must have units of kg kg$^{-1}$ and $\mu$, $\mu^S$ and $\mu^W$ must have units of J kg$^{-1}$. The adoption of non-basic-SI units always causes some difficulties such as this.

**Specific Entropy**
The specific entropy of seawater $\eta$ is defined by

$$\eta = \eta(S_A, t, p) = -g_T = -\frac{\partial g}{\partial T}|_{S_A, p}.$$  \hfill (19)

**Specific Internal Energy**
The specific internal energy of seawater $u$ is defined by

$$u = u(S_A, t, p) = g + (T + T_0)\eta - (p + P_0)v = g - (T + T_0)\frac{\partial g}{\partial T}|_{S_A, p} - (p + P_0)\frac{\partial g}{\partial p}|_{S_A, T}.$$ \hfill (20)

**Specific Enthalpy**
The specific enthalpy of seawater $h$ is defined by

$$h = h(S_A, t, p) = g + (T_0 + t)\eta = g - (T_0 + t)\frac{\partial g}{\partial T}|_{S_A, p}.$$ \hfill (21)

**Specific Helmholtz Energy**
The specific Helmholtz energy of seawater $f$ is defined by

$$f = f(S_A, t, p) = g - (p + P_0)v = g - (p + P_0)\frac{\partial g}{\partial p}|_{S_A, t}.$$ \hfill (22)

**Osmotic Coefficient**
The osmotic coefficient of seawater $\phi$ is defined by

$$\phi = \phi(S_A, t, p) = -\left(g^S - S_A \frac{\partial g}{\partial S_A}|_{t, p}\right)(mR(T_0 + t))^{-1}.$$ \hfill (23)

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

$$\mu^W(0, t, p) = \mu^W(S_A, t, p) + mR(T_0 + t)\phi.$$ \hfill (24)

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. (2008), per mass of pure water. Note that the molality of seawater may take different values if neutral molecules of salt rather than ions are counted. The freezing-point lowering eqs. (57, 58) or the vapour-pressure lowering can be computed from the osmotic coefficient of seawater.
**Isothermal Compressibility**

The thermophysical quantities defined so far are all based on the Gibbs function itself and its first derivatives. The following quantities involve higher order derivatives.

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

$$\kappa' = \kappa' \left( S_A, t, p \right) = \rho^{-1} \frac{\partial \rho}{\partial p} \bigg|_{S_A, T} = -v^{-1} \frac{\partial v}{\partial p} \bigg|_{S_A, T} = -\frac{g_{pp}}{g_p}$$

(25)

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 $\kappa'$ produced by the software Libraries A and B has units of $\text{Pa}^{-1}$ whereas in the “gsw” library (Library C, Appendix K) $\kappa'$ has units of $\text{dbar}^{-1}$.

**Isentropic and Isohaline Compressibility**

When the entropy and salinity are held constant while the pressure is changed, the isentropic and isohaline compressibility $\kappa$ is defined by

$$\kappa = \kappa \left( S_A, t, p \right) = \rho^{-1} \frac{\partial \rho}{\partial p} \bigg|_{S_A, \eta} = -v^{-1} \frac{\partial v}{\partial p} \bigg|_{S_A, \eta} = \rho^{-1} \frac{\partial \rho}{\partial p} \bigg|_{S_A, \theta} = \rho^{-1} \frac{\partial \rho}{\partial p} \bigg|_{S_A, \Theta}$$

$$= \frac{g_{ip}^2 - g_{nt} g_{pp}}{g_p g_{ut}}.$$  

(26)

The isentropic and isohaline compressibility $\kappa$ is sometimes called simply the isentropic compressibility (or sometimes the “adiabatic compressibility”), on the unstated understanding that the there is also no transfer of salt during the adiabatic change in pressure. The isentropic and isohaline compressibility of seawater $\kappa$ produced by the software Libraries A and B has units of $\text{Pa}^{-1}$ whereas in the “gsw” library (Library C, Appendix K) $\kappa$ has units of $\text{dbar}^{-1}$.

**Sound Speed**

The speed of sound in seawater $c$ is given by

$$c = c \left( S_A, t, p \right) = \sqrt{\frac{\partial p}{\partial \rho} \bigg|_{S_A, \eta}} = \sqrt{(\rho \kappa)^{-1}} = g_p \sqrt{\frac{g_{ip}^2 - g_{nt} g_{pp}}{g_p g_{ut}}}.$$  

(27)

The sound speed $c$ output of all the computer software libraries is in units of $\text{m s}^{-1}$. Note that in the third and fourth expressions in (27) the pressure of the partial derivative must be in Pa and the isentropic compressibility $\kappa$ in $\text{Pa}^{-1}$.

**Thermal Expansion Coefficients**

The thermal expansion coefficient $\alpha'$ with respect to in situ temperature $t$, is

$$\alpha' = \alpha' \left( S_A, t, p \right) = -\frac{1}{\rho} \frac{\partial \rho}{\partial t} \bigg|_{S_A, p} = v \frac{\partial v}{\partial t} \bigg|_{S_A, p} = \frac{g_{ip}}{g_p}.$$  

(28)

The thermal expansion coefficient $\alpha^\theta$ with respect to potential temperature $\theta$, is

$$\alpha^\theta = \alpha^\theta \left( S_A, t, p \right) = -\frac{1}{\rho} \frac{\partial \rho}{\partial \theta} \bigg|_{S_A, p} = \frac{1}{\rho} \frac{\partial \rho}{\partial \theta} \bigg|_{S_A, p} = \frac{g_{ip}}{g_p} \frac{g_{nt}}{g_{ut}} \left( S_A, \theta, p_r \right),$$  

(29)
where \( p_r \) is the reference pressure of the potential temperature. The \( g_{ht} \) derivative in the numerator is evaluated at \((S_A, \theta, p_r)\) whereas the other derivatives are all evaluated at \((S_A, t, p)\).

The thermal expansion coefficient \( \alpha^\Theta \) with respect to Conservative Temperature \( \Theta \), is

\[
\alpha^\Theta = \alpha^\Theta(S_A, t, p) = -\frac{1}{\rho} \left. \frac{\partial \rho}{\partial \Theta} \right|_{S_A, p} = -\frac{1}{\nu} \left. \frac{\partial \nu}{\partial \Theta} \right|_{S_A, p} = -\frac{g_{lp}}{g_p} \frac{c_p^0}{(T_0 + \Theta)g_{ht}}.
\]

(30)

Note that Conservative Temperature \( \Theta \) is defined only with respect to a reference pressure of 0 dbar so that the \( \theta \) in (30) is the potential temperature with \( p_r = 0 \) dbar. All the derivatives on the right-hand side of (30) are evaluated at \((S_A, t, p)\).

**Saline Contraction Coefficients**

The saline contraction coefficient \( \beta^t \) at constant in situ temperature \( t \), is

\[
\beta^t = \beta^t(S_A, t, p) = -\frac{1}{\rho} \left. \frac{\partial \rho}{\partial S_A} \right|_{t, p} = -\frac{1}{\nu} \left. \frac{\partial \nu}{\partial S_A} \right|_{t, p} = -\frac{g_{SAp}}{g_p}.
\]

(31)

The saline contraction coefficient \( \beta^\theta \) at constant potential temperature \( \theta \), is

\[
\beta^\theta = \beta^\theta(S_A, t, p) = \frac{g_{lp}}{g_p g_{ht}} \left[ g_{SA} - g_{SA}(S_A, \theta, p_r) \right] - g_{ht} g_{SAp},
\]

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

The saline contraction coefficient \( \beta^\Theta \) at constant Conservative Temperature \( \Theta \), is

\[
\beta^\Theta = \beta^\Theta(S_A, t, p) = \frac{g_{lp}}{g_p g_{ht}} \left[ g_{SA} - (T_0 + \Theta)^{-1} g_{SA}(S_A, \theta, 0) \right] - g_{ht} g_{SAp}.
\]

(33)

Note that Conservative Temperature \( \Theta \) is defined only with respect to a reference pressure of 0 dbar as indicated in this equation. The \( g_{SA} \) 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 K) 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\(^{-1}\).
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

$$c_p = c_p(S_A, t, p) = \frac{\partial h}{\partial t}_{S_A, p} = -(T_0 + t) g_{tt}.$$  \hfill (34)

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

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

$$c_v = c_v(S_A, t, p) = \frac{\partial u}{\partial t}_{S_A, v} = -(T_0 + t)(g_{tt} g_{pp} - g_{tp}^2) / g_{pp}.$$  \hfill (35)

Note that the isochoric and isobaric heat capacities are related by

$$c_v = c_p - \frac{(T_0 + t)(\alpha')^2}{(\rho \kappa')}, \quad \text{and by} \quad c_v = c_p \frac{\kappa}{\kappa'}. \hfill (36)$$
The Adiabatic Lapse Rate

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

$$
\Gamma = \Gamma(S_A, t, p) = \left. \frac{\partial t}{\partial p} \right|_{S_A, \eta} = \left. \frac{(T_0 + t)\alpha'}{\rho c_p} \frac{\partial v}{\partial \Theta} \right|_{S_A, p} = -\frac{g_H}{g_L}.
$$

(37)

Note that the adiabatic (and isohaline) lapse rate is not due to the compressibility of seawater. Indeed, the adiabatic lapse rate changes sign at the temperature of maximum density whereas the compressibility is always positive. The reference pressure of the potential temperature $\theta$ in (37) is $p_r = 0$ dbar.

The adiabatic lapse rate $\Gamma$ output of software Libraries A and B is in units of $1\text{K} \frac{\text{Pa}}{-}$ while it is $1\text{K} \frac{\text{d bar}}{-}$ in the “gsw” library (Library C, Appendix K). The middle expressions in the definition of $\Gamma$ in (37) naturally leads to $\Gamma$ being in $\text{K} \frac{\text{Pa}}{-}$. This inconsistency is an unavoidable consequence of adopting non-basic-SI (i.e. oceanographic) units for pressure. This is the price one pays for adopting the convenient oceanographic units; one has to be vigilant because many thermodynamic formulae expect variables to be in SI units.
**DERIVED QUANTITIES**

**Potential Temperature**

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

$$\theta = \theta(S_A, t, p, p_r) = t + \int_{p}^{p_r} \Gamma(S_A, \theta[S_A, t, p, p', p']) \, dp'. \quad (38)$$

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 $\theta$ is evaluated using a Newton-Raphson iterative solution technique to solve the following equation for $\theta$

$$s(S_A, \theta, p_r) = s(S_A, t, p), \quad \text{that is} \quad -g_l(S_A, \theta, p_r) = -g_l(S_A, t, p). \quad (39)$$

The potential temperature $\theta$ output of software Libraries A and B is in units of K while it is °C in the “gsw” library (Library C, Appendix K).

**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. Potential enthalpy can be expressed as the pressure integral of specific volume as (McDougall (2003) and see the discussion below eq. (14a))

$$h^0(S_A, t, p) = h(S_A, \theta, 0) = h^0(S_A, \theta) = h(S_A, t, p) - \int_{0}^{p} \nu(S_A, \theta[S_A, t, p, p'], p') \, dp'. \quad (40)$$

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

$$h^0(S_A, t, p) = h(S_A, \theta, 0) = g(S_A, \theta, 0) - (T_0 + \theta) g_l(S_A, \theta, 0). \quad (41)$$
**Conservative Temperature**

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

$$\Theta(S_A,t,p) = \tilde{\Theta}(S_A,\theta) = \frac{h^0(S_A,t,p)}{c_p^0} = \frac{\tilde{h}^0(S_A,\theta)}{c_p^0}$$  \hspace{1cm} (42)

where $c_p^0$ is motivated in terms of potential enthalpy evaluated at an Absolute Salinity of $S_{SO} = 35u_{ps} = 35.165 \ 04 \ \text{g kg}^{-1}$ and at $\theta = 25 \ ^\circ\text{C}$ by

$$c_p^0 \approx \frac{[h(S_{SO}, \ 25^\circ\text{C}, 0) - h(S_{SO}, 0^\circ\text{C}, 0)]}{(25 \ \text{K})} \approx 3991.867 \ 957 \ 119 \ 63 \ \text{J kg}^{-1} \ \text{K}^{-1}$$ \hspace{1cm} (43a)

noting that $h(S_{SO}, 0^\circ\text{C}, 0\text{dbar})$ is zero according to the way the Gibbs function is defined in (10). In fact we adopt the exact definition for $c_p^0$ to be the 15-digit value in (43a), so that

$$c_p^0 \equiv 3991.867 \ 957 \ 119 \ 63 \ \text{J kg}^{-1} \ \text{K}^{-1}.$$ \hspace{1cm} (43b)

When IAPWS-95 is used for the pure water part of the Gibbs function, $\Theta(S_{SO},0^\circ\text{C},0)$ and $\Theta(S_{SO},25^\circ\text{C},0)$ differ from 0 °C and 25 °C respectively by the round-off amount of $5 \times 10^{-12}$°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, $\Theta(S_{SO},0^\circ\text{C},0)$ differs from 0 °C by $-8.25 \times 10^{-8}$°C and $\Theta(S_{SO},25^\circ\text{C},0)$ differs from 25 °C by $9.3 \times 10^{-6}$°C. Over the temperature range from 0°C to 40°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.

Appendix A.13 outlines why Conservative Temperature gets its name as it is approximately two orders of magnitude more conservative compared with both potential temperature and entropy.

The software libraries A, B and C have an algorithm for determining potential temperature (referenced to 0 dbar) from Absolute Salinity $S_A$ and Conservative Temperature $\Theta$. This inverse algorithm, $\hat{\Theta}(S_A,\Theta)$, has an initial seed based on a polynomial 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)).

**Potential Density**

Potential density $\rho_\theta$ 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

$$\rho_\theta(S_A,t,p,p_r) = \rho(S_A,t,p) + \int_p^{p_r} \rho(S_A,\theta[S_A,t,p,p],p') \kappa(S_A,\theta[S_A,t,p,p'],p') \ dp'.$$  \hspace{1cm} (44)

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

$$\rho_\theta(S_A,t,p,p_r) = \rho(S_A,\theta[S_A,t,p,p_r],p_r) = g_p^{-1}(S_A,\theta[S_A,t,p,p_r],p_r).$$  \hspace{1cm} (45)
Using either of the functional forms (14a) for in situ density, that is, either \( \rho = \hat{\rho}(S_A, \theta, p) \) or \( \rho = \hat{\rho}(S_A, \Theta, p) \), potential density with respect to reference pressure \( p_r \) (e.g. 1000 dbar) can be easily evaluated as
\[
\rho_\theta(S_A, t, p, p_r) = \hat{\rho}(S_A, \theta, p_r) = \hat{\rho}(S_A, \Theta, p_r),
\]
where we note that the potential temperature \( \theta \) in the middle expression is the potential temperature with respect to 0 dbar.

### Density Anomaly
Density anomaly \( \sigma_t \) is simply the density minus 1000 kg m\(^{-3}\),
\[
\sigma_t(S_A, t, p) = \rho(S_A, t, p) - 1000 \text{ kg m}^{-3} = g_p^{-1}(S_A, t, p) - 1000 \text{ kg m}^{-3}. \tag{46}
\]

### Potential Density Anomaly
Potential density anomaly \( \sigma_\theta \) is simply potential density minus 1000 kg m\(^{-3}\),
\[
\begin{align*}
\sigma_\theta(S_A, t, p) &= \rho_\theta(S_A, t, p) - 1000 \text{ kg m}^{-3} \\
&= g_p^{-1}(S_A, \theta[S_A, t, p, p_r], p_r) - 1000 \text{ kg m}^{-3}. \tag{47}
\end{align*}
\]

### Specific Volume Anomaly
The specific volume anomaly \( \delta \) is defined as the difference between the specific volume and a given function of pressure. Traditionally \( \delta \) has been defined as
\[
\delta(S_A, t, p) = v(S_A, t, p) - v(S_{SO}, 0^\circ C, p)
\]
(where the traditional value of \( S_p = 35 \) has been updated to \( S_{SO} = 35 \mu_{PS} = 35.16504 \text{ g kg}^{-1} \) in the present formulation). Note that the second term, \( v(S_{SO}, 0^\circ C, p) \), is a function only of pressure. In order to have a specific volume anomaly surface better approximate neutral tangent planes along the surface, it is advisable to replace the arguments \( S_{SO} \) and \( 0^\circ C \) with more general values \( \tilde{S}_A \) and \( \tilde{t} \) that are carefully chosen (as say the median values of Absolute Salinity and temperature along the surface) so that the more general definition of specific volume anomaly is
\[
\delta(S_A, t, p) = v(S_A, t, p) - v(\tilde{S}_A, \tilde{t}, p) = g_p(S_A, t, p) - g_p(\tilde{S}_A, \tilde{t}, p). \tag{49}
\]

The last terms in (48) and (49) 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 \( \dot{v}(S_A, \Theta, p) \) and \( \dot{h}(S_A, \Theta, p) \) and write a slightly different definition of specific volume anomaly as
\[
\dot{\delta}(S_A, \Theta, p) = \dot{v}(S_A, \Theta, p) - \dot{v}(\tilde{S}_A, \tilde{\Theta}, p) = \dot{g}_p(S_A, \Theta, p) - \dot{g}_p(\tilde{S}_A, \tilde{\Theta}, p). \tag{50}
\]
The same can also be done with potential temperature so that in terms of the specific volume $\tilde{v}(S_A, \Theta, p)$ and enthalpy $\tilde{h}(S_A, \Theta, p)$ we can write another form of the specific volume anomaly as

$$\tilde{\delta}(S_A, \Theta, p) = \tilde{v}(S_A, \Theta, p) - \tilde{v}(S_A, \bar{\Theta}, p) = \tilde{h}(S_A, \Theta, p) - \tilde{h}(S_A, \bar{\Theta}, p).$$

(51)

These expression exploit the fact that

$$\frac{\partial h}{\partial p}|_{S_A, \eta} = \frac{\partial h}{\partial p}|_{S_A, \Theta} = \frac{\partial h}{\partial p}|_{S_A, \theta} = v.$$  

(52)

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 $\Theta$ the thermobaric coefficient is (McDougall, (1987b))

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

(53)

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

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

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

(54)

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

The thermobaric coefficient enters various quantities to do with the path-dependent nature of neutral trajectories and the ill-defined nature of neutral surfaces. The thermobaric dianeutral advection associated with the lateral mixing of heat and salt along neutral tangent planes is given by $e^{Tb} = -gN^{-2}K_{Tb} \nabla_n \Theta \cdot \nabla_n p$ or $e^{\tilde{T}b} = -gN^{-2}K_{\tilde{T}b} \nabla_n \tilde{\Theta} \cdot \nabla_n p$ where $\nabla_n \Theta$ and $\nabla_n \tilde{\Theta}$ 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.

In the software Libraries A and B both versions of the thermobaric parameter $T_b^\Theta$ and $T_b^\Theta$ are output in units of $K^{-1} \text{ Pa}^{-1}$ while in the “gsw” software library (Library C, Appendix K) they are output in units of $K^{-1} \text{ dbar}^{-1}$. 
**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 $\theta$ the cabbeling coefficient is (McDougall, (1987b))

$$C_b^\theta = C_b^\theta (S_A, t, p) = \frac{\partial \alpha^\theta}{\partial \theta} \bigg|_{S_A, p} + 2 \frac{\alpha^\theta}{\beta^\theta} \frac{\partial \alpha^\theta}{\partial S_A} - \left( \frac{\alpha^\theta}{\beta^\theta} \right)^2 \frac{\partial \beta^\theta}{\partial S_A} \bigg|_{\theta, p}. \quad (55)$$

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

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

$$C_b^{\Theta} = C_b^{\Theta} (S_A, t, p) = \frac{\partial \alpha^{\Theta}}{\partial \Theta} \bigg|_{S_A, p} + 2 \frac{\alpha^{\Theta}}{\beta^{\Theta}} \frac{\partial \alpha^{\Theta}}{\partial S_A} - \left( \frac{\alpha^{\Theta}}{\beta^{\Theta}} \right)^2 \frac{\partial \beta^{\Theta}}{\partial S_A} \bigg|_{\Theta, p}. \quad (56)$$

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

$$e^{Cab} = -gN^{-2} K C_b^{\Theta} \nabla n \Theta \cdot \nabla n \Theta$$

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.

**Freezing Temperature**

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

$$\mu^W (S_A, t_f, p) = \mu^{Ih} (t_f, p) \quad (57)$$

or equivalently, in terms of the two Gibbs functions,

$$g (S_A, t_f, p) - S_A g_{S_A} (S_A, t_f, p) = g^{Ih} (t_f, p). \quad (58)$$

The Gibbs function for ice Ih is defined by IAPWS-06.

**Boiling Temperature**

To come

**Isobaric Latent Heat of Melting**

To come
Isobaric Latent Heat of Evaporation

To come

Buoyancy Frequency

The square of the buoyancy frequency $N$ 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)

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

$$= \alpha^\theta \theta_z - \beta^\theta (S_\Lambda)_z,$$

$$= \alpha^\Theta \Theta_z - \beta^\Theta (S_\Lambda)_z. \quad (59)$$

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

$$g^{-1}N^2 = -\frac{1}{\rho} \frac{\Delta \rho \theta}{\Delta z}, \quad (60)$$

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.

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

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

$$= \alpha^\theta \nabla \theta - \beta^\theta \nabla S_\Lambda,$$

$$= \alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda. \quad (61)$$

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. Note that $\alpha^\theta \nabla \theta - \beta^\theta \nabla S_\Lambda$ is exactly equal to $\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_\Lambda$ (McDougall et al. (2009b)).

Expressing the two-dimensional gradient of properties in the neutral tangent plane by $\nabla_n$ (see McDougall (1995) for the definition of this operator) the property gradients in a neutral tangent plane obey
\[ \Theta = -\rho^{-1}\nabla_n\rho + \kappa \nabla_n p = -\rho^{-1}\left(\nabla_n\rho - \nabla_n p / c^2\right) \]
\[ = \alpha^\Theta \nabla_n \Theta - \beta^\Theta \nabla_n S_A \]
\[ = \alpha^\Theta \nabla_n \Theta - \beta^\Theta \nabla_n S_A. \]

Finite difference versions of (62) such as \[ \Theta \approx \alpha^\Theta \Delta \Theta - \beta^\Theta \Delta S_A \] are also very accurate. Here \( \alpha^\Theta \) and \( \beta^\Theta \) are the values of these coefficients evaluated at the average values of \( \Theta, S_A \) and \( p \) of two parcels \((S_A^1, \Theta_1, p_1)\) and \((S_A^2, \Theta_2, p_2)\) on a “neutral surface” and \(\Delta \Theta \) and \(\Delta S_A \) are the property differences between the two parcels. The error involved with this finite amplitude version of (62), namely

\[ - T_b^\Theta \int_1^2 (p - \bar{p}) \, d\Theta, \]  

is described in section 2 and Appendix A(c) of Jackett and McDougall (1997). An equally accurate finite amplitude version of (62) is to equate the potential densities of the two fluid parcels, each referenced to the average pressure \( \bar{p} = 0.5(p_1 + p_2) \).

**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,

\[ H^n \equiv \left(\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_A\right) \cdot \nabla \times \left(\alpha^\Theta \nabla \Theta - \beta^\Theta \nabla S_A\right) \]

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

\[ H^n = \beta^\Theta T_b^\Theta \nabla p \cdot \nabla S_A \times \nabla \Theta \]
\[ = \frac{g^{-1}}{N^2} T_b^\Theta \left(\nabla_n p \times \nabla_n \Theta\right) \cdot \mathbf{k} \]
\[ = p_z \beta^\Theta T_b^\Theta \left(\nabla_p S_A \times \nabla_p \Theta\right) \cdot \mathbf{k}. \]

where \( p_z \) is simply the vertical gradient of pressure and \( \nabla_n \Theta \) and \( \nabla_p \Theta \) are the two-dimension gradients of \( \Theta \) in the neural tangent plane and in the horizontal plane (actually the isobaric surface) respectively. 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. Neutral helicity has units of \( m^{-3} \).

In the evolution equation of potential vorticity defined with respect to potential density \( \rho_\Theta \) there is the baroclinic production term \( \rho^2 \nabla p_\rho \cdot \nabla \rho \times \nabla p \) 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))

\[ \rho^2 \nabla p_\rho \cdot \nabla \rho \times \nabla p \approx (p_r - p) H^n \]

where \( p_r \) is the reference pressure of the potential density.
Neutral Density

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

\[
\mathbf{s} = \nabla_n z - \nabla_a z = gN^{-2} \left( \beta^\Theta \nabla_a S_\Lambda - \alpha^\Theta \nabla_a \Theta \right) \tag{67}
\]

where \( \nabla_n z \) is the slope of the neutral tangent plane, \( \nabla_a z \) is the slope of the approximately neutral surface and \( \nabla_a \) is the two-dimensional gradient operator in the approximately neutral surface (of which a neutral density surface is one example). Since neutral density is not a thermodynamic variable, it will not be described more fully in this manual.

Stability Ratio \( R_\rho \)

The stability ratio \( R_\rho \) is the ratio of the vertical contribution from Conservative Temperature to that from Absolute Salinity to the static stability \( N^2 \) of the water column. From (59) above we find

\[
R_\rho = \frac{\alpha^\Theta \Theta_z}{\beta^\Theta (S_\Lambda)_z} \approx \frac{\alpha^\Theta \theta_z}{\beta^\Theta (S_\Lambda)_z} \tag{68}
\]

Isopycnal Gradients compared with Epineutral Gradients

The two-dimensional gradient of a scalar \( \varphi \) 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))

\[
\nabla_\sigma \varphi = \nabla_n \varphi + \frac{\Theta_z}{\Theta_z} \frac{R_\rho [A - 1]}{R_\rho - A} \nabla_n \Theta \tag{69}
\]

where \( A \) is defined by

\[
A = \frac{\alpha^\Theta (S_\Lambda, \Theta, p)}{\alpha^\Theta (S_\Lambda, \Theta, p_r) / \beta^\Theta (S_\Lambda, \Theta, p_r)}, \tag{70}
\]

being the ratio of the slope on the \( S_\Lambda - \Theta \) 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 (69) gives the following relation between the (parallel) isopycnal and epineutral gradients of \( \Theta \)

\[
\nabla_\sigma \Theta = \frac{A [R_\rho - 1]}{[R_\rho - A]} \nabla_n \Theta \tag{71}
\]
while substituting $\varphi = S_A$ into (69) gives the following relation between the (parallel) isopycnal and epineutral gradients of $S_A$

$$\nabla_\sigma S_A = \left[ \frac{R_\rho - 1}{R_\rho - A} \right] \nabla_n S_A. \quad (72)$$

**Slopes of Potential Density Surfaces and Neutral Tangent Planes Compared**

The two-dimensional slope of a surface is defined as the two-dimension gradient of height $z$ in that surface. The slope difference between a potential density surface with reference pressure $p_r$ and the neutral tangent plane $\nabla_\sigma z - \nabla_n z$ is given by (McDougall, 1988))

$$\nabla_\sigma z - \nabla_n z = \frac{R_\rho [A - 1]}{R_\rho - A} \nabla_n \Theta \frac{\Theta}{z}. \quad (73)$$

While potential density surfaces have been the most commonly used surfaces with which to separate “isopycnal” mixing processes from vertical mixing processes, many other types of density surface have been used. The list includes specific volume anomaly surfaces, patched potential density surfaces (Reid and Lynn (1971)), Neutral Density surfaces (Jackett and McDougall (1997)), orthobaric density surfaces (de Szoeke et al. (2000)) and some polynomial fits of Neutral Density as function of only salinity and either $\theta$ or $\Theta$ (Eden and Willebrand (1999), McDougall and Jackett (2005b)). The most recent method for forming approximately neutral surfaces is that of Klocker et al. (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).

**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 and diffusion because potential density surfaces are not a good approximation to neutral tangent planes and (ii) incurs the non-conservative baroclinic production term of equation (66). 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
NSPV = \(-g\rho^{-1} f\gamma^n \approx fN^2 \exp\left\{-\int_{\text{ams}} \rho g^2 N^{-2} T_b \left(\nabla_a \Theta - \Theta \nabla_a p\right) \cdot dl\right\}\).  

(74)

The exponential expression was derived by McDougall (1988) (his equation (47)) and is approximate because the variation of the saline contraction coefficient \(\beta^\Theta\) with pressure was neglected in comparison with the larger proportional change in the thermal expansion coefficient \(\alpha^\Theta\) with pressure. The integral in (74) is taken along an approximately neutral surface from a location where NSPV is equal to \(fN^2\). Interestingly the combination \(\nabla_a \Theta - \Theta \nabla_a p\) 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

\[
\text{NSPV} = -g\rho^{-1} f\gamma^n = fN^2 \exp\left\{-\int_{\text{ams}} g^2 N^{-2} \left(\left(\rho \alpha^\Theta\right)_p \nabla_p \Theta - \left(\rho \beta^\Theta\right)_p \nabla_p S_A\right) \cdot dl\right\}
\]

(75)

The exponential factor in (75) is the integrating factor \(b\) that allows spatial integrals of \(\rho b \left(\beta^\Theta \nabla S_A - \alpha^\Theta \nabla \Theta\right) \approx \nabla \gamma^n\) to be approximately independent of path for “vertical paths”, that is, for paths in surfaces whose normal has zero vertical component. Note also that \(b\) is non-constant even in a lake where neutral surfaces are well defined and neutral helicity is everywhere zero. NSPV has the units \(\text{s}^{-3}\).

**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 \((1 - S_A) = (1 - 0.001 S_A / (\text{g kg}^{-1}))\). 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 \(\rho u\) where \(u\) is the fluid velocity through the chosen area element while the advective flux of sea salt is \(\rho S_A u\). The advective flux of freshwater per unit area is the difference of these two mass fluxes, namely \(\rho (1 - S_A) u\).

**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 \(\rho^{\text{FW}} (E - P)\) 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 \(\rho^{\text{FW}}\), this density being the
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 \( w - \mathbf{V}_H \cdot \nabla \eta - \frac{\partial \eta}{\partial t} \) (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, \( \rho \). By equating the two mass fluxes on either side of the air-sea interface we arrive at the vertical ocean velocity through the air-sea interface as

\[
aw - \mathbf{V}_H \cdot \nabla \eta - \frac{\partial \eta}{\partial t} = \rho^{-1} \rho^{FW}(E-P). \tag{76}
\]

**Heat transports**

A flux of heat across the sea surface at a 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 \( \Theta \). By contrast, the same heat flux across the sea surface changes potential temperature \( \theta \) in inverse proportion to \( c_p(S_A,\theta,0) \) (see equation (6) above) and this heat capacity varies by 5% between fresh to saline water at the sea surface. McDougall (2003) has shown that the First Law of Thermodynamics, equation (A17) of Appendix A, can be approximated as

\[
\rho c_p^0 \frac{d\Theta}{dt} \approx -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \tag{77}
\]

with an error in \( \Theta \) that is less than one percent of the error incurred by treating either \( \theta \) or \( c_p(S_A,\theta,0) \) as the “heat content” of seawater. Equation (77) is exact at 0 dbar while at great depth in the ocean the error with the approximation (77) is similar to 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, (77), can be written as density times the material derivative of \( c_p^0 \Theta \) means that except for the small term \( \rho \varepsilon \) representing the dissipation of mechanical energy, \( \Theta \) 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 \( \rho v h^0 = \rho v c_p^0 \Theta \). 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 \( \rho vc_p^0 \theta \) or \( \rho vc_p(S_A,\theta,0) \theta \).

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 (5)), 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 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)).

**Dynamic Height Anomaly**

The dynamic height anomaly $\Phi'$ given by the vertical integral

$$
\Phi' = - \int_0^p \delta(S_A[p'], t[p'], p') \, dp'
$$

(78)

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 $\Phi'$ in the $p$ pressure surface is simply related to the difference between the horizontal geostrophic velocity $v$ at $p$ and at the sea surface $v_0$ according to

$$
\mathbf{k} \times \nabla_p \Phi' = f v - f v_0.
$$

(79)

This definition of dynamic height anomaly applies to all choices of the reference values $S_A$ and $t$, $\Theta$ or $\hat{\Theta}$ in the definition (48-51) of the specific volume anomaly $\delta$. The specific volume anomaly $\delta$ in (78) can be replaced with specific volume $v$ without affecting the isobaric gradient of the resulting streamfunction. That is, this substitution does not affect (79) 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 $\delta$ or $v$ can be used in the integrand of (78), so making it either the “dynamic height anomaly” or the dynamic height”.

The dynamic height anomaly $\Phi'$ should be quoted in units of m$^2$ s$^{-2}$. These are the units in which the “gsw” library (Library C, Appendix K) outputs dynamic height anomaly. Note that the integration (78) 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 (79) would not give the resultant horizontal gradient in units consistent with the product of the Coriolis parameter (units of s$^{-1}$) and the velocity (units of m s$^{-1}$). This is the reason why dynamic height anomaly is output in m$^2$ s$^{-2}$.

**Montgomery Potential**

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

$$
\pi = p \delta - \int_0^p \delta(S_A[p'], t[p'], p') \, dp'
$$

(80)

is the geostrophic streamfunction for the flow in the specific volume anomaly surface $\delta(S_A, t, p) = \delta_1$ relative to the flow at 0 dbar. Thus the two-dimensional gradient of $\pi$ in the
The definition (80) of the Montgomery potential applies to all choices of the reference values \( \hat{S}_A \) and \( \hat{\Theta} \) in the definition (49) of the specific volume anomaly \( \delta \). 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 (80) 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 (80) in a neutral tangent plane becomes (instead of (81) in the \( \delta = \delta_1 \) surface)

\[
\textbf{k} \times \nabla \delta \pi \approx f \mathbf{v} - f \mathbf{v}_0 \quad \text{(82)}
\]

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, \( \tilde{p} \), can be subtracted from \( p \) in the first term in (80) without changing the properties of the Montgomery streamfunction in the \( \delta_1 \) surface. That is, an alternative (and preferable) version of (80) is

\[
\tilde{\pi} = (p - \tilde{p}) \delta - \int_0^p \delta \left( \hat{S}_A \left[p', \hat{\Theta} \left[p', \mathcal{T} \right] \right], \mathcal{T} \left[p', \mathcal{T} \right] \right) dp' \quad \text{(83)}
\]

The gradient of the Montgomery potential (83) in a neutral tangent plane becomes

\[
\textbf{k} \times \nabla_n \tilde{\pi} = f \mathbf{v} - f \mathbf{v}_0 + (p - \tilde{p}) \textbf{k} \times \nabla_n \delta \quad \text{(84)}
\]

where the last term can be made significantly smaller than the corresponding term in (82) by choosing the constant pressure \( \tilde{p} \) 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 \( \hat{S}_A \) and \( \hat{\Theta} \) in the definition (50) of specific volume anomaly \( \delta \) so that this surface more closely approximates the neutral tangent plane. This improvement is available because it can be shown that

\[
\rho \nabla_n \delta = - \left[ \kappa(S_A, \Theta, p) - \kappa(\hat{S}_A, \hat{\Theta}, p) \right] \nabla_n p \approx T_b \Theta \left[ \Theta - \hat{\Theta} \right] \nabla_n p \quad \text{(85)}
\]

Hence suitable choices of \( \tilde{p}, \hat{S}_A \) and \( \hat{\Theta} \) can reduce the last term in (84) that represents the error in interpreting the Montgomery potential (83) as the geostrophic streamfunction in a surface other than a specific volume anomaly surface.

The Montgomery potential should be quoted in units of \( m^2 \text{ s}^{-2} \). These are the units in which the “gsw” library (Library C, Appendix K) outputs dynamic height anomaly. Note that the integration (80) or (83) of specific volume anomaly with pressure in dbar would yield dynamic height anomaly in units of \( m^3 \text{ kg}^{-1} \text{ dbar} \), however the use of these units in (81), (82) or (84) would not give the resultant horizontal gradient in units consistent with the product of the Coriolis parameter (units of \( \text{s}^{-1} \)) and the velocity (units of \( \text{m s}^{-1} \)). This is the reason why Montgomery potential is output in \( m^2 \text{ s}^{-2} \).
Geopotential
The geopotential $\Phi$ is the gravitational potential energy per unit mass with respect to the height $z = 0$. Allowing the gravitational acceleration to be a function of height, $\Phi$ is given by

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

(86)

If the gravitational acceleration is taken to be constant the gravitational potential energy per unit mass with respect to the height $z = 0$, $\Phi$ is simply $gz$. Note that height and $\Phi$ are negative quantities in the ocean since the sea surface (or the geoid) is taken as the reference height. In SI units $\Phi$ is measured in $\text{J kg}^{-1} \text{m}^2 \text{s}^{-2}$. If the ocean is assumed to be in hydrostatic balance so that $p_z = -g \rho$ (or $-g \, dz' = v \, dp'$) then the geopotential (86) may be expressed as the vertical pressure integral of the specific volume in the water column,

$$\Phi = \Phi^0 - \int_0^p v(p') \, dp',$$

(87)

where $\Phi^0$ is the value of the geopotential at zero sea pressure, that is, the gravitational acceleration times the height of the free surface above the geoid.

Total Energy
The total energy $\mathcal{E}$ is the sum of specific internal energy $u$ kinetic energy per unit mass $0.5q^2 = 0.5u \cdot u$ and the geopotential $\Phi$,

$$\mathcal{E} = u + \Phi + 0.5q^2.$$

(88)

Total energy $\mathcal{E}$ is not a function of only $(A, St, p)$ and so is not a thermophysical quantity.

Bernoulli Function
The Bernoulli function is the sum of specific enthalpy $h$, kinetic energy per unit mass $0.5q^2 = 0.5u \cdot u$, and the geopotential $\Phi$,

$$\mathcal{B} = h + \Phi + 0.5q^2.$$

(89)

Using the expression (40) that relates enthalpy and potential enthalpy, together with equation (87) for $\Phi$, the Bernoulli function (89) may be written as

$$\mathcal{B} = h^0 + \Phi^0 + 0.5q^2 - \int_0^p v(p') - \hat{\nu}(S_A, \Theta, p') \, dp'.$$

(90)

The pressure integral term here is a version of the dynamic height anomaly (78), 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 $p$.

The Bernoulli function $\mathcal{B}$ is not a function of only $(S_A, t, p)$ and so is not a thermophysical quantity.
The Bernoulli function is dominated by the contribution of enthalpy $h$ to (89) and by the contribution of potential enthalpy $h^0$ to (90). 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 (50) can be used to write (90) as (having used this same reference specific volume $\hat{v}(S_{SO},0^\circ C,p')$ in the specific volume anomaly of the definition of the dynamic height anomaly (78))

$$B = h^0 + \Phi^0 + \Phi' + \frac{q^2}{2} - \int_0^p \hat{v}(S_{SO},0^\circ C,p') - \hat{v}(S_A,\Theta,p') \, dp' \tag{91}$$

$$= h^0 + \Phi^0 + \Phi' + \frac{q^2}{2} - \hat{h}(S_{SO},0^\circ C,p) + \hat{h}(S_{SO},0^\circ C,0) + \hat{h}(S_A,\Theta,0) - \hat{h}(S_A,\Theta,0).$$

**Depth-Integrated Steric Height (DISH or PIDHA)**

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 $\int \rho v \, dz$ is given by $-g^{-1}\int v \, dp$ and this motivates taking the pressure integral of the Dynamic Height Anomaly $\Phi'$ (from equation (72)) to form the Pressure-Integrated-Dynamic-Height-Anomaly PIDHA or Depth-Integrated Steric Height DISH (Godfrey (1989)),

$$\text{PIDHA} = \Psi' = g^{-1} \int_0^p \Phi'(p') \, dp' = -g^{-1} \int_0^p \int_0^{p'} \delta(S_A[p'], t[p'], p') \, dp' \, dp'' \tag{92}$$

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

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

$$k \times \nabla_p \Psi' = f \int_{z(p)}^{z(p=0)} \rho[v'(z')-v_0] \, dz' = g^{-1} f \int_0^p [v'(p')-v_0] \, dp'. \tag{93}$$

The definition (86) of PIDHA applies to all choices of the reference values $\tilde{S}_A$ and $\tilde{t}$, $\tilde{\Theta}$ or $\tilde{\Theta}$ in the definition (48-51) of the specific volume anomaly $\delta$.

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 (72) becomes

$$\Phi' = \int_{p_1}^p \delta(S_A[p'], t[p'], p') \, dp' \tag{94}$$

and PIDHA is
The two-dimensional gradient of $\Psi'$ is now related to the depth-integrated mass flux of the velocity difference with respect to the velocity at $p_1$, $v_1$, according to

$$k \times \nabla_p \Psi' = \int_{z(p_1)}^{z(p=0)} \rho [v(z') - v_1] dz' = g^{-1} f \int_0^{p_1} \rho [v(p') - v_1] dp'.$$

(96)

The specific volume anomaly $\delta$ in (92), (94) and (95) can be replaced with specific volume $\nu$ without affecting the isobaric gradient of the resulting streamfunction. That is, this substitution in $\Psi'$ does not affect (93) or (96) as the additional term is a function only of pressure.

PIDHA (or DISH) should be quoted in units of kg s$^{-2}$ so that its two-dimensional gradient has the same units as the depth-integrated flux of $\rho [v(z') - v_1]$ times the Coriolis frequency. These are the units in which the “gsw” library (Library C, Appendix K) outputs PIDHA.

**Pressure to Height Conversion**

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

$$\Phi = \Phi^0 - \int_0^p v(p') dp',$$

(97)

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 (52), namely $h_p|_{S_A,\Theta} = v$) as a sum over $n$ layers of the differences in specific enthalpy so that

$$\Phi = \Phi^0 - \sum_{i=1}^{n-1} \left[ h\left(S_A^i,\Theta^i, p^{i+1}\right) - h\left(S_A^i,\Theta^i, p^i\right) \right].$$

(98)

This may be useful in the algorithm to convert between hydrostatic pressure and height.
OTHER QUANTITIES

Coriolis Parameter

The rotation rate of the earth $\Omega$ is (Griffies (2004))

$$\Omega = 7.2921 \times 10^{-5} \text{ s}^{-1}$$ (99)

and the Coriolis parameter $f$ is

$$f = 2\Omega \sin \phi = 1.45842 \times 10^{-4} \sin \phi \text{ s}^{-1}$$ (100)

where $\phi$ is latitude.

Gravitational Acceleration

The gravitational acceleration $g$ is (Moritz (2000))

$$g = 9.780327 \left[ 1 + 0.0053024 \sin^2 \phi - 0.0000058 \sin^2 2\phi \right] \text{ m s}^{-2}$$ (101)

where $\phi$ 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$^{-2}$ (Gill (1982)) but a more relevant average value of $g$ is that averaged over the surface of the ocean, namely 9.7963 m s$^{-2}$. 

CONCLUSIONS

The Thermodynamic Equation of Seawater – 2010 (TEOS-10) allows all the thermophysical properties of pure water, ice Ih and seawater to be evaluated in an internally self-consistent manner. The related properties of water vapour and of moist air are also accessible by using the IAPWS-95 Helmholtz function for water vapour. 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. This is done because Practical Salinity is virtually the measured variable (whereas Absolute Salinity is a calculated variable) and also so that the 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 thermophysical properties of seawater makes more sense simply because the thermophysical 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 an SI unit 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 \textit{in situ} temperature is used (i) in ocean models, (ii) to plot data and (iii) for theoretical studies, so too Practical Salinity should not be used as the prognostic variable in ocean models, as an axis on $S_A - \Theta$ diagrams or in theoretical studies.

Conceptually we can categorize \textit{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 $\Theta$ (or less accurately potential temperature $\theta$) 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 there variables that posses 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 McDougall et al. (2003)). In order to make ocean models totally consistent with TEOS-10 the models 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 $\Theta$. To complete the transition to $\Theta$ in ocean modeling, the models should be initialized with $\Theta$ rather than $\theta$, the output temperature must be compared with observed $\Theta$ data rather than to $\theta$ data, and during the model run, any air-sea fluxes that depends 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 now 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 $\rho(S_A, \Theta, p)$ equation of Jackett et al. (2006) is expected to be available during 2009].
APPENDIX A: Background Theoretical Constructs behind 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 VSMOW.) The Celsius temperature, symbol $t$, is defined by $t^\circ C = T/K - 273.15$, and $1^\circ C$ is the same size as $1 K$.

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 BIPM 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 $R(0^\circ C)$, while in ITS-90 $R_0$ is $R(0.01^\circ C)$. The details of these temperature scales and the differences between the two scales are therefore defined by the functions of $W$ used to calculate $T$. For ITS-90, and in the range $0^\circ C < t_90 < 968.71^\circ C$, $t_90$ is described by a polynomial with 10 coefficients given by Table 4 of Preston-Thomas (1990).

We note in passing that the conversions from $W$ to $T$ and from $T$ to $W$ are both defined by polynomials and these are not perfect inverses of one another. Preston-Thomas points out that the inverses are equivalent to within 0.13 mK. In fact the inverses have a difference of 0.13 mK at $861^\circ C$, and a maximum error in the range $0^\circ C < t_90 < 40^\circ C$ of 0.06 mK at $31^\circ C$. 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 $0.01^\circ\text{C} < t_{90} < 961.78^\circ\text{C}$. 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 ($t_{90} = 29.7646^\circ\text{C}$) and the triple point of Mercury ($t_{90} = -38.8344^\circ\text{C}$) 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 ($t_{90} = 29.7646^\circ\text{C}$). 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 8\textsuperscript{th} 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 8\textsuperscript{th} 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 thermophysical 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

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

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 \(-2 \text{°C} < t_{68} < 40 \text{°C}\), conversion could be achieved using

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

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) 8\textsuperscript{th} order fit are fully consistent with Saunders’ 1.00024 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 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 (A2) thus

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

(A3)

### A.2 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. (2008) 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 (IUPAC (2005)). 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, \( P = 101325 \) Pa is referred to as normalized seawater. Here, KCl refers to the normal isotopic abundances of potassium and chlorine as described by the International Union of Pure and Applied Chemistry (IUPAC (2005)).
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

$$S_{R12} = \frac{m_1 S_{R1} + m_2 S_{R2}}{m_1 + m_2}.$$  \hfill (A4)

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 $S_{R12} = 35.165 \, 04 \, \text{g kg}^{-1}$ and the original Reference-Composition Salinity of sample 1 is given by

$$S_{R1} = [1 + (m_2 / m_1)] \times 35.16504 \, \text{g kg}^{-1}. \hfill (A5)$$

The definitions and procedures above allow one to determine the Reference Salinity of any seawater sample at the ITS-90 temperature $t = 14.996 \, \text{°C}$ 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 $35.16504 \, \text{g kg}^{-1}$. This value was determined by Millero et al. (2008) using the reference composition model, the most recent atomic weights (IUPAC (2005)) and the relation $S = 1.80655 \, \text{Cl} / (\text{g kg}^{-1})$ 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

$$S_R \approx u_{PS} S_p \quad \text{where} \quad u_{PS} \equiv (35.165 \, 04/35) \, \text{g kg}^{-1}. \hfill (A6)$$

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 $35.165 \, 04 \, \text{g kg}^{-1}$. Millero et al. (2008) estimate that the absolute uncertainty in this value is $\pm 0.007 \, \text{g kg}^{-1}$. 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. (2008) and are briefly reviewed below.

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

\[
S(\%o) = 0.03 + 1.805 \ Cl(\%o). \tag{A7}
\]

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

\[
S(\%o) = 1.80655 \ Cl(\%o) \tag{A8}
\]

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.3 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. (2008) 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 \( S_A / (g \text{ kg}^{-1}) \) and \( S \) 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. The next largest improvement in the equation of state of seawater will come from incorporating the variation in the composition of seawater. 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.

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)),

\[
34 \text{ g/kg} = 34 \text{ mg/g} = 0.034 \text{ kg/kg} = 0.034 = 3.4 \% = 34 000 \text{ ppm} = 34 000 \text{ mg/kg}.
\]  
(A9)

In particular, it is strictly correct to write the freshwater fraction of seawater as either \( (1 - 0.001 \frac{S_A}{\text{g kg}^{-1}}) \) 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 \( S \) we adopt the first option above, namely \( \text{g kg}^{-1} \) as the preferred unit for \( S_A \), (as in \( S_A = 35.165 \text{ 04 g kg}^{-1} \)). The Reference Salinity, \( S_R \), is defined to have the same units and follows the same conventions as \( S_A \). Salinity “\( S_{‰} \)” measured prior to PSS-78 available from the literature or from databases is usually reported in \( \%_{‰} \) or ppt (part per thousand) and is converted to the Reference Salinity, \( S_R = u_{PS} S_{‰} \), by the numerical factor \( u_{PS} \) from (A6).

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 \( C_l \) of Standard Seawater given in \( \%_{‰} \) is converted to the Reference Salinity, \( S_R = u_{C_l} C_l \), by the numerical factor \( u_{C_l} = 1.806 \text{ 55 } u_{PS} \).

Regarding point number 6, the composition of the dissolved material in seawater is not totally 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 thermophysical properties of seawater are better written as functions of Absolute Salinity (as well as of temperature and pressure) rather than as functions of Practical Salinity (Millero, 1974; Millero et al., 1976b). One can make reasonable estimates of the physicochemical properties of seawater from known properties of the components of the solution (this simple additivity is known as Young’s rule). All the physical properties of seawater as well as other multicomponent electrolyte solutions are directly related to the composition of the major components not the salinity determined by conductivity. Some of the variable nonelectrolytes (e.g., SiO₂, CO₂ 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 $g(A, t, p)$ rather than as a function of Practical Salinity $S_P$ or of Reference Salinity, $S_R$.

### A.4 Spatial Variations in Seawater Composition: A First Algorithm for $S_A$

In a series of papers Millero et al. (1976a, 1978, 2000, 2008) has 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 (A6), while the density measurement $\rho^\text{meas}$ implies an Absolute Salinity by using the equation of state and the equality $\rho^\text{meas} = \rho(A, 25^\circ\text{C}, 0\text{dbar})$. 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 $A_A - S_R$ 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 the other variables, (b) it accounts for a substantial fraction (about 0.4) 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 $\phi$, latitude $\lambda$ and gauge pressure $p$ (in dbar) is available at [http://www.marine.csiro.au/~jackett/TEOS-10/](http://www.marine.csiro.au/~jackett/TEOS-10/).
A.5 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

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p)$$

(A10)

In this way at zero Absolute Salinity, the thermophysical 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 thermophysical 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 (2). This $g^W(t, p)$ Gibbs function of liquid water is valid over extended ranges of temperature and pressure from the freezing point to the critical point ($-22 ^\circ C < t < 374 ^\circ C$ and $600 \text{ Pa} < p + P_0 < 1000 \text{ MPa}$) 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 $40 ^\circ C$ (specifically from $\left[-\left[2.65 + (p + P_0) \times 0.0743 \text{ MPa}^{-1}\right]\text{oC} \right.$ to $40 ^\circ C$), and in the pressure range $40 < 10 \text{ dbar}$ 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 thermophysical properties of seawater that are described in this Manual are available as both FORTRAN and MATLAB implementations. These implementations are available both 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. Beyond those former data, compared to EOS-80 the data basis of IAPWS-08 was significantly extended by various old and new measurements as well as theoretical relations, such as the ideal-solution law, the Debye-Hückel limiting law, measured temperatures of maximum density, vapour pressures or mixing heats, and implicitly in particular 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 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 at high pressures perfectly consistent with Chen and
Millero’s (1976) densities and Bradshaw and Schleicher’s (1970) thermal expansion data. The accuracy of high-pressure seawater densities has increased with the use of IAPWS-95, directly as the pure-water part, indirectly by correcting earlier seawater measurements, making them "new" seawater data. In this manner the sound-speed inconsistency of EOS-80 has been resolved in a natural way.

A.6 The Fundamental Thermodynamic Relation

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

\[
dh - vdP = (T_0 + t)d\eta + \mu dS_\lambda. \tag{A11}
\]

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 \( du + (p + P_0)dv \) where \( p + P_0 \) is the absolute pressure. Here \( h \) is the specific enthalpy (i.e. enthalpy per unit mass of seawater), \( u \) is the specific internal energy, \( v = \rho^{-1} \) is the specific volume, \( T_0 + t \) is the absolute temperature, \( \eta \) is the specific entropy and \( \mu \) is the relative chemical potential. In fluid dynamics we usually deal with material derivatives, \( d/dt \), that is, derivatives defined following the fluid motion, \( d/dt = \partial/\partial t + \mathbf{u} \cdot \nabla \) where \( \mathbf{u} \) is the fluid velocity. In terms of this type of derivative, the fundamental thermodynamic relation is

\[
\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} = (T_0 + t)\frac{d\eta}{dt} + \mu \frac{dS_\lambda}{dt}. \tag{A12}
\]

A.7 The “conservative” and “isobaric conservative” properties

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

\[
(\rho \varphi)_t + \nabla \cdot (\rho \varphi \mathbf{u}) = \rho \frac{d\varphi}{dt} = -\nabla \cdot \mathbf{F}^{\varphi}. \tag{A13}
\]

For such a “conservative” property, in the absence of fluxes \( \mathbf{F}^{\varphi} \) at the boundary of a control volume, the total amount of \( \varphi \)-stuff is constant inside the control volume. In the special case when the material derivative of a property is zero (that is, the left-hand side of (A13) is zero) the property is said to be “materially conserved”.

Quantities that are conservative in the ocean are (1) mass \( \varphi = 1 \) and \( \mathbf{F}^{1} = 0 \) as in equation (A14)], (2) Absolute Salinity \( S_\lambda \), (3) freshwater fraction \( 1 - S_\lambda \), and (4) Total Energy \( E = u + 0.5q^2 + \Phi \) (see equation (B15)). The middle part of (A13) has used the continuity equation (which is the equation for the conservation of mass)
\[ \rho_t + \nabla \cdot (\rho \mathbf{u}) = 0. \]  

(A14)

Other variables such as potential temperature \( \theta \), enthalpy \( h \), potential enthalpy \( h^0 \), Conservative Temperature \( \Theta \), internal energy \( u \), entropy \( \eta \), density \( \rho \), potential density \( \rho_\theta \), specific volume anomaly \( \delta \) and the Bernoulli function \( \mathcal{B} = h + 0.5q^2 + \Phi \) (see equation (B17)) are not conservative variables. Note that \( \Theta \) 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 \( \theta \), potential enthalpy \( h^0 \), Conservative Temperature \( \Theta \), internal energy \( u \), entropy \( \eta \), density \( \rho \), potential density \( \rho_\theta \), and specific volume anomaly \( \delta \). 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 \( \Theta \) 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 \( \Theta \), (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 \( \Theta \) is simply proportional to \( h^0 \), in essence we have mass and just three other variables, \( S_A \), \( \Theta \) and \( \mathcal{E} \) that are both “conservative” and “isobaric conservative”.

We note that for Absolute Salinity \( S_A \) the flux \( F^S \) in (A13) 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 particularly quantity usually applies to 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.8 The “potential” property

Any thermophysical 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 posses the “potential” property, or in other words, to be a “potential” variable. Prime examples of “potential” variables are Absolute Salinity $S_A$ and entropy $\eta$. The constancy of entropy $\eta$ 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 $\theta$, potential enthalpy $h^0$, Conservative Temperature $\Theta$ and potential density $\rho_\theta$ (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 $\rho$, specific volume anomaly $\delta$, total energy $E$ and the Bernoulli function $B$. From eq. (B17) we notice that in the absence of molecular fluxes, the Bernoulli function $B$ is constant following the fluid flow only if the pressure field is steady; in general this is not the case. The non-potential nature of $E$ is explained in the discussion following 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.7 above we concluded that only mass, and the three variables $S_A$, $\Theta$ and $E$ are both “conservative” and “isobaric conservative”. Since $E$ does not possess the “potential” property, we now conclude that only mass and the two variables $S_A$ and $\Theta$ possess all three highly desired properties, namely that they are “conservative”, “isobaric conservative” and “potential” variables. Also $S_A$ and $\Theta$ are thermophysical quantities, that is, they are function of only $(S_A, t, p)$ whereas $E$ is not a thermophysical quantity.

In Table A.8.1 various oceanographic variables are categorized according to whether or not they possess the “potential” property, whether or not they are “conservative” variables, whether or not they are “isobaric conservative” variables, and whether or not they are thermophysical quantities. Note that $S_A$ and $\Theta$ (and $h^0$) are the only variables that achieve four “ticks” in this table.

<table>
<thead>
<tr>
<th>Variable symbol</th>
<th>“Potential”?</th>
<th>“Conservative”?</th>
<th>“Isobaric Conservative”?</th>
<th>“Thermophysical Variable”?</th>
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<td>×</td>
<td>×</td>
</tr>
</tbody>
</table>

1 Taking $\varepsilon$ to be negligible.

2 Taking $\varepsilon$ and other terms of similar size to both be negligible (see the discussion following eq. (A64)).

3 Once the reference sound speed function $c_0(p,\rho)$ has been decided upon.
A.9 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 and the chemical potential to be functions of entropy $\eta$ in place of temperature $t$, that is, considering the functional form of $h$ and $\mu$ to be $h = h(S_A, \eta, p)$ and $\mu = \mu(S_A, \eta, p)$ it follows from (A10) that

$$h_\eta(S_A, \eta, 0) \, d\eta + h_{S_A}(S_A, \eta, 0) \, dS_A = (T_0 + \theta) \, d\eta + \mu(S_A, \eta, 0) \, dS_A,$$

which shows that specific entropy $\eta$ is simply a function of Absolute Salinity $S_A$ and potential temperature $\theta$, 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 (40) – (42), at $p = 0$ dbar it can be seen that (A11) implies

$$c_p^0 \, d\Theta = (T_0 + \theta) \, d\eta + \mu(S_A, \theta, 0) \, dS_A.$$

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 $\Theta$ is a function of only $S_A$ and $\eta$.

A.10 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 (3) by Gibbs (1873) and other early pioneers, and referred to as the First Law of Thermodynamics (Thomson (1851), Clausius (1876), Albery (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 Masur (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” (A17) (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 (A17a) (A18) and (A19) of this appendix; all of these equations are equally valid incarnations of the First Law of Thermodynamics)

$$\rho \left(\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt}\right) = -\nabla \cdot \mathbf{F}^{\text{R}} - \nabla \cdot \mathbf{F}^{\text{Q}} + \rho \varepsilon$$  \hspace{1cm} (A17)
where $\mathbf{F}^R$ is the radiative heat flux and $\mathbf{F}^Q$ is the sum of all manner of molecular diffusive fluxes of heat including the cross-diffusion of heat by the gradient of salinity (the Dufour Effect) as well as the “heat of transfer” $(\mu - T \mu_T) \mathbf{F}^S$ due to the flux of salt. Lastly, $\varepsilon$ is the rate of dissipation of mechanical energy per unit mass, transformed into internal energy. The derivation of (A17) 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 (A17) 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 (A17) with the continuity equation
$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$
and integrates over the volume that encompasses both fluid parcels while ignoring any radiative fluxes 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. The essential aspect here is the fact that the increase of entropy caused by the irreversible internal thermal equilibration is not accompanied by any related growth of enthalpy, i.e. of its “heat content”, in contrast to (A12) which holds only for reversible processes.

The First Law of Thermodynamics (A17) can be written as an evolution equation for entropy as follows
$$\rho \left( (T_0 + t) \frac{d \eta}{dt} + \mu \frac{d S_A}{dt} \right) = - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon .$$
(A17a)

The First Law of Thermodynamics (A17) can also be written in terms of potential temperature $\theta$ (with respect to reference pressure $p_r$) as (from Bacon and Fofonoff (1996) and McDougall (2003))
$$\rho \left( \frac{\eta}{\theta} \right) \frac{d \vartheta}{dt} \left[ \mu(p) - (T_0 + t) \mu_T(p_r) \right] \frac{d S_A}{dt} = - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon$$
(A18)
where $T_0$ is the Celsius zero point ($T_0$ is exactly 273.15 K), while in terms of Conservative Temperature $\Theta$, the First Law of Thermodynamics is (from McDougall (2003))
$$\rho \left( \frac{\Theta}{\Theta} \right) \frac{d \Theta}{dt} \left[ \mu(p) - \left( \frac{T_0 + t}{T_0 + \Theta} \right) \mu(0) \right] \frac{d S_A}{dt} = - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon$$
(A19)
where $c_p^0$ is the fixed constant defined by the exact 15-digit number in equation (43a).

In the following three sections of this Appendix 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 these variables, and also on the $S_\Lambda - \Theta$ diagram where variables are contoured which graphically illustrate the non-conservation of these variables.

A quick ranking of these three variables, $\eta$, $\theta$ and $\Theta$, from the viewpoint of the amount of their non-conservation, can be gleaned by examining the range of the terms (at fixed pressure) that multiply the material derivatives on the left-hand sides of the above equations (A17a), (A18) and (A19). The ocean circulation may be viewed as a series of adiabatic and isohaline movements of seawater parcels interrupted by a series of isolated turbulent mixing events. During any of the adiabatic and isohaline transport stages every “potential” property is constant, so each of the above variables, entropy, potential temperature and Conservative Temperature are 100% ideal during these adiabatic and isohaline advection stages. The turbulent mixing events occur at fixed pressure so the non-conservative production of say entropy depends on the extent to which the coefficients $(T_0 + t)$ and $\mu$ in (A17a) vary at fixed pressure. Similarly the non-conservative production of potential temperature depends on the extent to which the coefficients $c_p\left(p_r\right)/(T_0 + t)/(T_0 + \theta)$ and $\left[\mu(p) - (T_0 + t)\mu_T\left(p_r\right)\right]$ in (A18) vary at fixed pressure, while the non-conservative production of potential 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 (A19) vary at fixed pressure. In this way the material derivative of entropy appears in (A17a) multiplied by the absolute temperature $(T_0 + t)$ which varies by about 15% at the sea surface ($\left((273.15 + 40)/273.15 \approx 1.146\right)$, the term that multiplies $d\theta/dt$ in (A18) is dominated by the variations in the isobaric specific heat $c_p\left(S_\Lambda,t,p_r\right)$ which is mainly a function of $S_\Lambda$ and which varies by 5% at the sea surface, while the material derivative of Conservative Temperature $d\Theta/dt$ in (A19) 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 very small in the deep ocean because the range of temperature is very small there. The following three sections A.11, A.12 and A.13, 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 $\theta$ and Conservative Temperature $\Theta$ at the sea surface is shown in Figure A1 (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. (43a)), the neglect of the non-conservative source terms that should appear in the prognostic equation for $\theta$ means that
such an ocean model incurs errors in the model output. These errors will depend on the nature of the surface boundary condition; for flux boundary conditions the errors are as shown in Figure A1.

Figure A1. Contours (in °C) of the difference $\theta - \Theta$ between potential temperature $\theta$ and Conservative Temperature $\Theta$ at the sea surface of the annually-averaged atlas of Gouretski and Koltermann (2004).

A.11 The Non-conservative Production of Entropy $\eta$

Following Fofonoff (1962), consider mixing two fluid parcels (parcels 1 and 2) that have initially different temperatures and salinities. The mixing process occurs at pressure $p$. The mixing is assumed to happen to completion so that in the final state Absolute Salinity, entropy and all the other properties are uniform. Assuming that the mixing happens with a vanishingly small amount of dissipation of mechanical energy, the $\varepsilon$ term can be dropped from (A17), this equation becoming

$$\left(\rho h\right)_t + \nabla \cdot \left(\rho \mathbf{u} h\right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q. \quad \text{at constant pressure} \quad (A20)$$

Note that this equation has the form (A13) 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 or molecular heat fluxes coming through the outside boundary so the integral over space and time of the right-hand side of (A20) is zero. Similarly the integral of $\nabla \cdot \left(\rho \mathbf{u} h\right)$ 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

$$m_1 + m_2 = m, \quad (A21)$$
\[ m_1 S_{A1} + m_2 S_{A2} = m S_A, \]
\[ m_1 h_1 + m_2 h_2 = m h, \]
while the non-conservative nature of entropy means that it obeys the equation,
\[ m_1 \eta_1 + m_2 \eta_2 + m \delta \eta = m \eta. \]

Here \( S_A \), \( h \) and \( \eta \) are the values of Absolute Salinity, enthalpy and entropy of the final mixed fluid and \( \delta \eta \) is the production of entropy, that is, the amount by which entropy is not conserved during the mixing process. Entropy \( \eta \) is now regarded as the functional form
\[ \eta = \eta(S_A, h, p) \]
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 \( \eta_1 \) and \( \eta_2 \) are evaluated and (A23) and (A24) used to find
\[
\delta \eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\partial^2 \eta}{\partial h \partial h} (\Delta h)^2 + 2 \frac{\partial^2 \eta}{\partial h \partial S_A} \Delta h \Delta S_A + \frac{\partial^2 \eta}{\partial S_A \partial S_A} (\Delta S_A)^2 \right\}. \tag{A25}
\]

Towards the end of this section the implications of the production (A25) 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 (A25) this requirement implies the following three inequalities,
\[ \eta_{hh} < 0, \tag{A26} \]
\[ \eta_{S_A S_A} < 0, \tag{A27} \]
\[ \left( \eta_{hS_A} \right)^2 < \eta_{hh} \eta_{S_A S_A}, \tag{A28} \]
where the last requirement reflects the need for the discriminant of the quadratic in (A25) 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 (A11) we find that (where \( T \) is the absolute temperature, \( T = T_0 + t \))
\[ \eta_h = \left. \frac{\partial \eta}{\partial h} \right|_{S_A, p} = T^{-1}, \tag{A29} \]
\[ \eta_{S_A} = \left. \frac{\partial \eta}{\partial S_A} \right|_{h, p} = -\frac{\mu}{T}, \tag{A30} \]
and from these relations the following expressions for the second order derivatives of can be found,
\[ \eta_{hh} = \left. \frac{\partial^2 \eta}{\partial h^2} \right|_{S_A, p} = \left. \frac{\partial T^{-1}}{\partial h} \right|_{S_A, p} = \frac{-T^{-2}}{c_p}, \tag{A31} \]
\[ \tilde{\eta}_{S,h} = \frac{\partial^2 \eta}{\partial h \partial S_A} \bigg|_{p} = \frac{\partial (-\mu/T)}{\partial h} \bigg|_{S_A,p} = -\frac{1}{c_p} \left( \frac{\mu}{T} \right)_T, \quad (A32) \]

and

\[ \tilde{\eta}_{S_A S_A} = \frac{\partial^2 \eta}{\partial S_A^2} \bigg|_{h,p} = \frac{\partial (-\mu/T)}{\partial S_A} \bigg|_{T,p} - \frac{\partial (-\mu/T)}{\partial h} \bigg|_{S_A,p} \frac{\partial h}{\partial S_A}. \bigg|_{T,p} \]
\[ = -\frac{\mu_{S_A}}{T} - \frac{T^2}{c_p} \left[ \left( \frac{\mu}{T} \right)_T \right]^2. \quad (A33) \]

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

The constraint (A26) that \( \tilde{\eta}_{hh} < 0 \) simply requires (from (A31)) that the isobaric heat capacity \( c_p \) is positive, or that \( g_{TT} < 0 \). The constraint (A27) that \( \tilde{\eta}_{S_A S_A} < 0 \), requires (from (A33)) that

\[ g_{S_A S_A} > -\frac{T^3}{c_p} \left[ \left( \frac{\mu}{T} \right)_T \right]^2, \quad (A34) \]

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 (A28) that \( \left( \tilde{\eta}_{hS_A} \right)^2 < \tilde{\eta}_{hh} \tilde{\eta}_{S_A S_A} \) requires that (substituting from (A31), (A32) and (A33))

\[ \frac{g_{S_A S_A}}{T^3 c_p} > 0, \quad (A34) \]

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 (A34).

We conclude that while there are the three requirements (A26) to (A28) on the functional form of entropy \( \eta = \tilde{\eta}(S_A, h, p) \) 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 \( g(S_A, t, p) \),

\[ g_{TT} < 0 \quad (A35) \]

and

\[ g_{S_A S_A} > 0. \quad (A36) \]

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 (A36) 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 (A36) amounts to the requirement that the molecular diffusivity of salt is positive.
The two constraints (A35) and (A36) on the Gibbs function are well known in the thermodynamics literature. Landau & 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, Landau & Lifshitz (1980) in their §96 (this is §98 in editions before the 1976 extension made by Lifshitz and Pitayevski) infer these 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 (A35) and (A36) 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 (26))

\[ g_{pp} < 0 \] (A37)

and

\[ \left( g_{Tp} \right)^2 < g_{pp} g_{TT}, \] (A38)

recognizing that \( g_{TT} \) is negative (\( g_{Tp} \) may, and does, take either sign). Equation (A38) is more demanding of \( g_{pp} \) than is (A37), 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 \( \alpha' \), implying that its square must be less than \( g_{pp}^2 g_{pp} g_{TT} \) or otherwise the relevant compressibility \( (\kappa) \) would be negative and the sound speed complex.

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

\[ g_p > 0, \ g_{S_A S_A} > 0, \ g_{pp} < 0, \ g_{TT} < 0, \text{ and } \left( g_{Tp} \right)^2 < g_{pp} g_{TT}. \] (A39)

We return now to quantify the non-conservative production of entropy in the ocean. When the mixing process occurs at \( p = 0 \), the expression (A25) for the production of entropy can be expressed in terms of Conservative Temperature \( \Theta \) (since \( \Theta \) is simply proportional to \( h \) at \( p = 0 \)) as follows (now entropy is taken to be the functional form \( \hat{\eta}(S_A, \Theta) \))

\[ \delta \eta = -\frac{1}{2} m_1 m_2 m^2 \left\{ \frac{\partial^2 \hat{\eta}}{\partial \Theta^2} (\Delta \Theta)^2 + 2 \frac{\partial^2 \hat{\eta}}{\partial \Theta \partial S_A} \Delta \Theta \Delta S_A + \frac{\partial^2 \hat{\eta}}{\partial S_A^2} (\Delta S_A)^2 \right\}. \] (A40)

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 \( (S_A, \Theta) = (S_{SO2}, 25^\circ C) \) and then \( \Theta \) is subtracted. The result is contoured in \( S_A - \Theta \) space in Figure A2. The fact that the variable in Figure A2 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 \((S_A, \Theta) = (0 \text{ kg}^{-1}, 0^\circ\text{C})\) and the other at the warmest and saltiest corner of the figure, the non-conservative production of \(\eta\) on mixing parcels of equal mass is approximately 0.9°C.

Figure A2. Contours (in °C) of a variable that illustrates the non-conservative production of entropy \(\eta\) in the ocean.

Since entropy can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature \(\eta = \tilde{\eta}(S_A, \Theta)\), and since at any pressure in the ocean both \(S_A\) and \(\Theta\) may be considered conservative variables (see section A.13 below), it is clear that the non-conservative production given by (A40) and illustrated in Figure A2 is equivalent to the slightly more accurate expression (A25). The only discrepancy between the production of entropy calculated from (A40) and that from (A25) is due to the very small non-conservative production of \(\Theta\) at pressures other than zero (as well as the fact that both expressions contain only the second order terms in an infinite Taylor series).
A.12 The Non-conservative Production of Potential Temperature $\theta$

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.11 two parcels are mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again equations (A21) – (A23). Potential temperature $\theta$ is not conserved during the mixing process and the production of potential temperature is given by

$$m_1 \theta_1 + m_2 \theta_2 + m \delta \theta = m \theta.$$  \hspace{1cm} (A41)

Enthalpy in the functional form $h = h(S_A, \theta, p)$ is expanded in a Taylor series of $S_A$ and $\theta$ about the values $S_A$ and $\theta$ of the mixed fluid, retaining terms to second order in $[S_{A2} - S_{A1}] = \Delta S_A$ and in $[\theta_2 - \theta_1] = \Delta \theta$. Then $h_1$ and $h_2$ are evaluated and (A23) and (A41) used to find

$$\delta \theta \ h_\theta = \frac{1}{2} \left( \frac{m_1 m_2}{m^2} \right) \left[ h_{\theta \theta} (\Delta \theta)^2 + 2 h_{\theta S_A} \Delta \theta \Delta S_A + h_{S_A S_A} \Delta S_A^2 \right].$$ \hspace{1cm} (A42)

The maximum production occurs when parcels of equal mass are mixed so that $\frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8}$. The “heat capacity” $h_\theta$ is not a strong function of $\theta$ but is a much stronger function of $S_A$ so the first term in the curly brackets in (A42) is generally small compared with the second term. Also, the third term in (A42), $h_{S_A S_A} (\Delta S_A)^2$, which causes the so-called “dilution heating”, is usually small compared with the second term. A typical value of $h_{\theta S_A}$ 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

$$\delta \theta \approx \frac{1}{4} h_{\theta S_A} \Delta \theta \Delta S_A / h_\theta \approx -3.4 \times 10^{-4} \Delta \theta \left( \Delta S_A / [\text{g kg}^{-1}] \right).$$ \hspace{1cm} (A43)

Since potential temperature $\theta = \hat{\theta}(S_A, \Theta)$ can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature, and since at any pressure in the ocean both $S_A$ and $\Theta$ may be considered conservative variables (see section A.13 below), it is clear that the non-conservative production given by (A42) can be approximated by the corresponding production of potential temperature that would occur if the mixing had occurred at $p = 0$, namely

$$\delta \theta = \frac{1}{2} \left( \frac{m_1 m_2}{m^2} \right) \left[ \frac{\Theta_{\theta \theta}}{\Theta_\theta} (\Delta \theta)^2 + 2 \frac{\Theta_{\theta S_A}}{\Theta_\theta} \Delta \theta \Delta S_A + \frac{\Theta_{S_A S_A}}{\Theta_\theta} (\Delta S_A)^2 \right].$$ \hspace{1cm} (A44)

where the exact proportionality between potential enthalpy and Conservative Temperature $h^0 = c_p^0 \Theta$ 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. To illustrate the magnitude of the non-conservation of potential temperature we take the difference between potential temperature and Conservative Temperature $\theta - \Theta$ and contour this temperature on the $S_A - \Theta$ diagram in Figure A3. 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 and then reading off the production (in °C) of θ from the figure.

Taking the most extreme situation with one parcel at \((S_A, \Theta) = (0 \text{ g kg}^{-1}, 0°C)\) and the other at the warmest and saltiest corner of Figure A3, the non-conservative production of \(\theta\) on mixing parcels of equal mass is approximately -0.55°C. This is to be compared with the corresponding maximum production of entropy, as discussed above in connection with Figure A2, of approximately 0.9°C. The values contoured in Figure A2 and A3 represent the error, expressed in °C, involved with assuming that \(\eta\) and \(\theta\) respectively are conservative variables. The maximum such error for entropy is approximately -1.0°C while for potential temperature the maximum error is approximately -1.8°C.

Figure A3. Contours (in °C) of the difference between potential temperature and Conservative Temperature \(\theta - \Theta\) which illustrates the non-conservative production of potential temperature \(\theta\) 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 A2 and A3 is that potential temperature and entropy are approximately as non-conserved in the ocean as each other. This implies that \(\theta\) is no better than \(\eta\) as an oceanographic variable with which to track water masses or as a variable to measure the “heat content” of seawater.

The material in sections A.12 and A.13 follows closely the paper of McDougall (2003).
A.13 The Non-conservative Production of Conservative Temperature $\Theta$

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved during the mixing process are mass, Absolute Salinity and enthalpy. As in sections A.11 and A.12 two parcels are mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again equations (A21) – (A23). Potential enthalpy $h^0$ and Conservative Temperature $\Theta$ are not conserved during the mixing process and the production of $\Theta$ is given by

$$m_1 \Theta_1 + m_2 \Theta_2 + m \partial \Theta = m \Theta.$$  \hspace{1cm} (A45)

Enthalpy in the functional form $h = \hat{h}(S_A, \Theta, p)$ is expanded in a Taylor series of $S_A$ and $\Theta$ about the values $S_A$ and $\Theta$ of the mixed fluid, retaining terms to second order in $[S_A - S_A] = \Delta S_A$ and in $[\Theta - \Theta] = \Delta \Theta$. Then $h_1$ and $h_2$ are evaluated and (A23) and (A45) are used to find

$$\Theta \hat{h}_\Theta = \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \hat{h}_\Theta \left( \Delta \Theta \right)^2 + 2 \hat{h}_\Theta S_A \Delta \Theta \Delta S_A + \hat{h}_S S_A \left( \Delta S_A \right)^2 \right\}. \hspace{1cm} (A46)$$

In order to evaluate these partial derivatives, the definition of potential enthalpy (40) is rewritten in terms of $v = \hat{v}(S_A, \Theta, p)$ as

$$h = \hat{h}(S_A, \Theta, p) = c^0_p \Theta + \int_0^p \hat{\nu}(S_A, \Theta, p') \, dp'.$$  \hspace{1cm} (A47)

This is differentiated with respect to $\Theta$ giving

$$\hat{h}_\Theta |_{S_A, p} = \hat{h}_\Theta = c^0_p + \int_0^p \alpha^\Theta / \rho \, dp'.$$  \hspace{1cm} (A48)

The right-hand side of (A48) scales as $c^0_p + \alpha^\Theta p / \rho$, which is more than $c^0_p$ by only about 0.0015 for $p$ of $10^7$ Pa (4,000 db). Hence, to a very good approximation, we may regard the left-hand side of (A46) as simply the production of Conservative Temperature $\partial \Theta$. 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 (40) and (A47), scales as $[p - p] / \rho$ which is as large as typical values of enthalpy itself. The reason is that the integral in (40) or (A47) 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 $h_\Theta$.

The second order derivatives of $\hat{h}$ are needed in (A46), and these can be estimated in terms of the strength of cabbeling as follows. Equation (A48) is differentiated with respect to Conservative Temperature, giving

$$\hat{h}_\Theta = \int_0^p \left( \alpha^\Theta / \rho \right)_\Theta \, dp' \approx \rho^{-1} \int_0^p \left( \alpha^\Theta \right)_\Theta \, dp'.$$  \hspace{1cm} (A49)

so that we may write (A46) approximately as (assuming $m_1 = m_2$)

$$\partial \Theta \approx \frac{P}{8 \rho c^0_p} \left\{ \alpha^\Theta_\Theta \left( \Delta \Theta \right)^2 + 2 \alpha^\Theta_{S_A} \Delta \Theta \Delta S_A - \beta^\Theta_{S_A} \left( \Delta S_A \right)^2 \right\}. \hspace{1cm} (A50)$$
Equation (A50) shows that the non-conservative production of Conservative Temperature is proportional to the non-conservative production of density (see equation (A56) below) often referred to loosely as “cabellaing” (McDougall, 1987b),

\[
\delta \rho_\Theta \approx \frac{p}{8} \left( \alpha^{\Theta}_\Theta (\Delta \Theta)^2 + 2 \alpha^{\Theta}_S \Delta \Theta \Delta S_S - \rho^{\Theta}_S \left( \Delta S_S \right)^2 \right) \\
= \frac{p}{8} \left( \alpha^{\Theta}_\Theta (\Delta \Theta)^2 + 2 \alpha^{\Theta}_S \Delta \Theta \Delta S - \rho^{\Theta}_S \left( \Delta S_S \right)^2 \right).
\]  

(A51)

The production of \( \Theta \) 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 to that caused by cabbeling 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 \( \Theta \). Nevertheless, from equation (A50) we see that the non-conservative production of \( \Theta \) is proportional to the product of pressure and the strength of cabbeling.

McDougall (1987b) has shown that the first term in the bracket in (A50) 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

\[
\frac{\delta \Theta}{\Delta \Theta} \approx \frac{p \alpha^{\Theta}_\Theta (\Delta \Theta)}{8 \rho c_p^0} \approx 3.3 \times 10^{-13} (p/\text{Pa})(\Delta \Theta/\text{C}^\circ).
\]  

(A52)

where \( \alpha^{\Theta}_\Theta \) has been taken to be 1.1x10\(^{-5}\) K\(^{-2}\) (McDougall, 1987b).

![Figure A4. Contours (in °C) of a variable that is used to illustrate the non-conservative production of Conservative Temperature \( \Theta \) at \( p = 600 \text{ dbar} \). The cloud of points show where most of the oceanic data reside at \( p = 600 \text{ dbar} (6 \text{ Mpa}) \).](image)

At the sea surface Conservative Temperature \( \Theta \) is totally conserved (\( \delta \Theta = 0 \)). The non-conservative production of Conservative Temperature, \( \delta \Theta \), increases linearly with pressure (see...
equation (A50)) 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 A4 for data at this pressure. The quantity contoured on this figure is the difference between $\Theta$ and the following totally conservative quantity at $p = 600$ dbar. This conservative quantity was constructed by taking the conservative property enthalpy $h$ at this pressure and adding the linear function of $S_A$ which makes the result equal to zero at $(S_A = 0, \Theta = 0^\circ C)$ and at $(S_A = 35.165 \text{ g kg}^{-1}, \Theta = 0^\circ C)$. This quantity is then scaled so that it becomes $25^\circ C$ at $(S_A = 35.165 \text{ g kg}^{-1}, \Theta = 25^\circ C)$. In this manner the quantity that is contoured in Figure A4 represents the amount by which Conservative Temperature 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 A4 is about $4 \times 10^{-3}$ $^\circ C$ and the range of values encountered in the real ocean at this pressure is actually quite small, as indicated in Figure A4. McDougall (2003) concludes that the maximum non-conservation of $\Theta$ in the real ocean is a factor of more than one hundred less than the maximum non-conservative production of potential temperature $\theta$.

A.14 The Non-conservative Production of Density $\rho$ and of potential density $\rho_\Theta$

For the purpose of calculating the non-conservative production of density we take Conservative Temperature $\Theta$ to be 100% conservative (see Appendix A.13 above). Density is written in the functional form

$$\rho = \hat{\rho}(S_A, \Theta, p)$$  \hspace{1cm} (A53)

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 (A21) and (A22)) as is Conservative Temperature, that is

$$m_1 \Theta_1 + m_2 \Theta_2 = m \Theta,$$  \hspace{1cm} (A54)

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

$$m_1 \rho_1 + m_2 \rho_2 + m \delta \rho = m \rho.$$  \hspace{1cm} (A55)

Density is expanded in a Taylor series of $S_A$ and $\Theta$ about the values of $S_A$ and $\Theta$ of the mixed fluid, retaining terms to second order in $[S_A - S_{A1}] = \Delta S_A$ and in $[\Theta_2 - \Theta_1] = \Delta \Theta$. Then $\rho_1$ and $\rho_2$ are evaluated and (A55) is used to find

$$\delta \rho = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \hat{\rho}_{\Theta \Theta} (\Delta \Theta)^2 + 2 \hat{\rho}_{S_A \Theta} \Delta \Theta \Delta S_A + \hat{\rho}_{S_A S_A} (\Delta S_A)^2 \right\}.$$  \hspace{1cm} (A56)

This non-conservative production of density $\delta \rho$ is illustrated in Figure A5 for mixing at $p = 0$ dbar. That is, this figure shows the production $\delta \rho_\Theta$ of potential density $\rho_\Theta$. The quantity contoured on this figure is formed as follows. First the linear function of $S_A$ is found that is equal
to \( \rho_\Theta \) at \((S_A=0, \Theta=0^\circ \text{C})\) and at \((S_A=35.165 \text{ g kg}^{-1}, \Theta=0^\circ \text{C})\). This linear function of \( S_A \) is subtracted from \( \rho_\Theta \) and the result is scaled to equal 25°C at \((S_A=35.165 \text{ g kg}^{-1}, \Theta=25^\circ \text{C})\).

The variable that is contoured in Figure A5 is the difference between this scaled linear combination of \( \rho_\Theta \) and \( S_A \), and Conservative Temperature. This figure allows the non-conservative nature of density to be understood in temperature units. The mixing of extreme fluid parcels on Figure A5 causes the same increase in density as a cooling of approximately 10°C. From Figure A4 it is seen that the (tiny) non-conservative nature of \( \Theta \) is a factor of approximately 4000 smaller than this.

Figure A5. Contours (in \(^\circ \text{C}\)) of a variable that is used to illustrate the non-conservative production of potential density \( \rho_\Theta \). The three dots that are forced to be zero are shown with black dots.

A.15 The Material Derivative of \( S_A \) and \( \Theta \) in a Turbulent Ocean

Absolute Salinity obeys the instantaneous conservation equation (eq. (A13), see the discussion in Appendix A.7)

\[
(\rho S_A)_t + \nabla \cdot (\rho S_A \mathbf{u}) = \rho \frac{dS_A}{dt} = -\nabla \cdot \mathbf{F}^S, \tag{A57}
\]

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 (A14) here as

\[
\rho_t + \nabla \cdot (\rho \mathbf{u}) = 0. \tag{A58}
\]

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

\[
\bar{\rho}_t + \nabla \cdot (\bar{\rho} \mathbf{u}) = 0, \tag{A59}
\]
which we choose to write in the following form, after division by a constant density \( \rho_0 \) (usually taken to be 1035 kg m\(^{-3}\), see Griffies, 2004)

\[
(\overline{\rho}/\rho_0)_t + \nabla \cdot \mathbf{u} = 0 \quad \text{where} \quad \mathbf{u} = \overline{\rho \mathbf{u}}/\rho_0. \tag{A60}
\]

This velocity \( \mathbf{u} \) is actually proportional to the average mass flux per unit area.

The conservation equation for Absolute Salinity (A57) is now averaged in the corresponding manner obtaining (McDougall et al, 2002)

\[
\left( \frac{\overline{\rho}}{\rho_0} \frac{\overline{S_A}}{\rho} \right)_t + \nabla \cdot \left( \frac{\overline{\rho}}{\rho_0} \frac{\overline{S_A}}{\rho} \mathbf{u} \right) = -\frac{1}{\rho_0} \nabla \cdot \mathbf{F}_S - \frac{1}{\rho_0} \nabla \cdot \left( \frac{\rho \overline{S_A} \mathbf{u}^2}{\rho} \right). \tag{A61}
\]

Here the Absolute Salinity has been density-weighted averaged, that is, \( \overline{S_A}/\rho \equiv \overline{\rho S_A}/\rho \), 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 (A61) 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 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

\[
\left( \frac{\hat{\rho}}{\rho_0} \hat{S}_A \right)_t + \nabla \cdot \left( \frac{\hat{\rho}}{\rho_0} \hat{S}_A \hat{\mathbf{v}} \right) + \left( \hat{e} \frac{\hat{\rho}}{\rho_0} \frac{\partial \hat{S}_A}{\partial z} \right)_z = \frac{\hat{\rho}}{\rho_0} \frac{\partial \hat{S}_A}{\partial t} + \frac{\hat{\rho}}{\rho_0} \hat{\mathbf{v}} \cdot \nabla \hat{S}_A + \frac{\hat{\rho}}{\rho_0} \hat{e} \frac{\partial \hat{S}_A}{\partial z} \tag{A62}
\]

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

Having derived this evolution equation (A62) for Absolute Salinity without invoking the Boussinesq approximation, we now follow common practice and invoke this approximation, finding the simpler expression

\[
\frac{\partial \hat{S}_A}{\partial t} + \hat{\mathbf{v}} \cdot \nabla \hat{S}_A + \hat{e} \frac{\partial \hat{S}_A}{\partial z} = \frac{1}{h} \nabla \cdot \left( h K \nabla \hat{S}_A \right) + \left( D \frac{\partial \hat{S}_A}{\partial z} \right)_z. \tag{A63}
\]

The left-hand side is the material derivate 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 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 (A19) the instantaneous material derivative of \( \Theta \) is, without approximation,

\[
\rho c_p^0 \frac{d \Theta}{dt} = \frac{(T_0 + \theta)}{(T_0 + t)} \left( -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \right) + \left[ \frac{(T_0 + \theta)}{(T_0 + t)} \mu(p) - \mu(0) \right] \nabla \cdot \mathbf{F}^S. \tag{A64}
\]

The fact that the right-hand side of (A64) is not the divergence of a flux means that \( \Theta \) is not a 100% conservative variable. However, the finite amplitude analysis of mixing pairs of seawater parcels in Appendix A.13 has shown that the non-ideal nature of the molecular fluxes of heat and salt appearing on the right-hand side of (A64) are of no practical consequence. These non-ideal terms on the right-hand side of (A64) 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 (A64) 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 \( \theta \) and in situ temperature \( t \) are equal so that this term is simply \( -\nabla \cdot \mathbf{F}^R \) so that there are no approximations with treating the air-sea sensible, latent and radiative heat fluxes as being fluxes of \( c_p^0 \Theta \). 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 a certain amount of geothermal heat will cause a local change in \( \Theta \) as though the seawater had the specific heat capacity \( (T_0 + t) c_p^0/(T_0 + \theta) \) rather than being \( c_p^0 \).

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 be allowed for in an ocean model by an artificial proportional boosting of 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

\[
\rho c_p^0 \left( \rho \Theta \right)_t + \rho c_p^0 \nabla \cdot \left( \rho \Theta \mathbf{u} \right) = \rho c_p^0 \frac{d \Theta}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q. \tag{A65}
\]

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 (A63))

\[
\frac{\partial \Theta}{\partial t} + \mathbf{v} \cdot \nabla_n \Theta + \mathbf{e} \frac{\partial \Theta}{\partial z} = \frac{1}{h} \nabla_n \cdot \left( \nu K \nabla_n \Theta \right) + \left( D \frac{\partial \Theta}{\partial z} - F_{\text{bound}} \right). \tag{A66}
\]

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 (A66) in the vertical heat flux \( F_{\text{bound}} \) which is these boundary heat fluxes divided by \( c_p^0 \).

The material derivatives of Absolute Salinity (A63) and Conservative Temperature (A66) 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 \( \mathbf{v} \) to the Eulerian-mean horizontal velocity \( \mathbf{v} \). This area of research involves the so-called residual-mean theory. We will not discuss this topic here.

### A.16 The Material Derivative of Density and of Locally-Referenced Potential Density

Regarding density to be a function of Conservative Temperature (i.e. \( \rho\left(S_A, \Theta, p \right) \)) and taking the material derivative of the natural logarithm of density following the mesoscale-thickness-weighted-averaged mean flow, we have

\[
\rho^{-1} \frac{d\rho}{dt} = \beta \Theta \frac{d\hat{S}_\Lambda}{dt} - \alpha \Theta \frac{d\hat{\Theta}}{dt} + \kappa \frac{d\hat{p}}{dt}.
\]  

(A67)

One can continue to consider the material derivative of in situ density, and in so doing, one carries along the last term in (A67), namely the isentropic compressibility \( \kappa \) 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, \( \rho' \), since this variable is locally constant in the neutral tangent plane. The material derivative of \( \rho' \) is given by

\[
\rho^{-1} \frac{d\rho'}{dt} = \rho^{-1} \frac{d\rho}{dt} - \kappa \frac{d\hat{p}}{dt} = \beta \Theta \frac{d\hat{S}_\Lambda}{dt} - \alpha \Theta \frac{d\hat{\Theta}}{dt}.
\]  

(A68)

Substituting from equations (A63) and (A66) above, and noting that both the temporal and the lateral gradients of \( \rho' \) vanish along the neutral tangent plane (\( \alpha \Theta \mathbf{n} \cdot \nabla \hat{\Theta} - \beta \Theta \mathbf{n} \cdot \hat{S}_\Lambda = 0 \) and \( \alpha \Theta \mathbf{n} \cdot \hat{\Theta} - \beta \Theta \hat{S}_\Lambda\big|_n = 0 \)), the material derivative of \( \rho' \) amounts to the following equation for the dianeutral velocity \( \mathbf{e} \) (note that the boundary heat flux \( F_{\text{bound}} \) also needs to be included for fluid volumes that abut the sea surface)

\[
\mathbf{e} \left( \alpha \Theta \hat{\Theta}_z - \beta \Theta \hat{S}_\Lambda z \right) = \alpha \Theta h^{-1} \mathbf{n} \cdot \left( hK \nabla \hat{\Theta} \right) - \beta \Theta h^{-1} \mathbf{n} \cdot \left( hK \nabla \hat{S}_\Lambda \right) + \alpha \Theta \left( D\hat{\Theta}_z \right)_z - \beta \Theta \left( D\hat{S}_\Lambda z \right)_z.
\]  

(A69)

The left-hand side is equal to \( \mathbf{e} g^{-1} N^2 \) 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 (from McDougall, 1987b, and see equations (56) and (54) for the definitions of \( C_b^\Theta \) and \( T_b^\Theta \))

\[
\mathbf{e} g^{-1} N^2 = - K \left( C_b^\Theta \nabla \hat{\Theta} \cdot \nabla \hat{\Theta} + T_b^\Theta \nabla \hat{\Theta} \cdot \nabla \hat{\rho} \right) + \alpha \Theta \left( D\hat{\Theta}_z \right)_z - \beta \Theta \left( D\hat{S}_\Lambda z \right)_z.
\]  

(A70)
The cabbeling nonlinearity (the $C_b^\Theta$ term) always causes “densification”, that is, a negative dianeutral velocity $\tilde{e}$, while the thermobaric nonlinearity (the $T_b^\Theta$ term) can cause either diapycnal upwelling or downwelling.

To summarize this appendix so far, one finds that the material derivative of in situ density (A67), when adjusted for the dynamically passive compressibility term, becomes the material derivative for locally-referenced potential density (A68), which can be interpreted as an expression (A70) 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 $D$, (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, and (iii) double-diffusive convection (which we have ignored in the above development).

It is instructive to substitute equation (A70) for $\tilde{e}$ into the expression (A66) for the material derivative of $\Theta$, thus eliminating $\tilde{e}$ and obtaining the following equation for the temporal and spatial evolution of $\Theta$ along the neutral tangent plane

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

(A71)

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 $D\beta^\Theta gN^{-2} \left( \frac{\partial}{\partial z} \hat{S}_A - \frac{\partial}{\partial z} \hat{\Theta} \right)$. The form of equation (A71) 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.
A.17 The Material Derivative of Potential Density

The temporal and lateral gradients of Absolute Salinity and Conservative Temperature in a potential density surface are related by (McDougall, 1991)

\[
\left. \alpha^\Theta \right|_\sigma \left( p_r \right) \hat{\Theta} + \beta^\Theta \left( p_r \right) \hat{S}_\Lambda = 0 \quad \text{and} \quad \alpha^\Theta \left( p_r \right) \nabla_\sigma \hat{\Theta} - \beta^\Theta \left( p_r \right) \nabla_\sigma \hat{S}_\Lambda = \mathbf{0},
\]

(A72)

where \( \alpha^\Theta \left( p_r \right) \) and \( \beta^\Theta \left( p_r \right) \) are shorthand notations for \( \alpha^\Theta \left( S_\Lambda, \Theta, p_r \right) \) and \( \beta^\Theta \left( S_\Lambda, \Theta, p_r \right) \) respectively, and \( p_r \) is the reference pressure of the potential density. 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

\[
\frac{\partial \hat{C}}{\partial t} + \hat{\mathbf{v}} \cdot \nabla_\sigma \hat{C} + \hat{\mathbf{e}} \frac{\partial \hat{C}}{\partial z} = \frac{\partial \hat{C}}{\partial t} + \hat{\mathbf{v}} \cdot \nabla_\sigma \hat{C} + \tilde{w}^d \frac{\partial \hat{C}}{\partial z} = \left( \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \hat{C} \right) \right)_z + \left( D \hat{C}_z \right)_z,
\]

(A73)

where \( \tilde{w}^d \) is the component of the total transport velocity through the potential density surface. We will find that potential density does not satisfy an equation of this form because it is not a conservative variable; we will find more terms than those in (A73) on the right-hand side of the evolution equation (A75) for potential density.

The material derivative of the natural logarithm of potential density is \( \beta^\Theta \left( p_r \right) \) times the material derivative (A63) of Absolute salinity minus \( \alpha^\Theta \left( p_r \right) \) times the material derivative (A66) 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 \( \tilde{w}^d \) as follows

\[
\tilde{w}^d \frac{1}{\rho^\Theta} \frac{\partial \hat{\rho}^\Theta}{\partial z} = \beta^\Theta \left( p_r \right) \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \hat{S}_\Lambda \right) - \alpha^\Theta \left( p_r \right) \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \hat{\Theta} \right)
\]

\[
+ \beta^\Theta \left( p_r \right) \left( D \hat{S}_\Lambda_z \right)_z - \alpha^\Theta \left( p_r \right) \left( D \hat{\Theta}_z \right)_z,
\]

(A74)

which can be written more informatively as (McDougall, 1991)

\[
\tilde{w}^d \frac{1}{\rho^\Theta} \frac{\partial \hat{\rho}^\Theta}{\partial z} = \left( \frac{\hat{D} \hat{\rho}^\Theta}{\hat{\rho}^\Theta} \frac{\partial \hat{\rho}^\Theta}{\partial z} \right)_z
\]

\[
+ D \left\{ \alpha^\Theta \left( p_r \right) \hat{\Theta}_z^2 + 2 \alpha^\Theta \left( p_r \right) \hat{\Theta}_z \hat{S}_\Lambda_z - \beta^\Theta \left( p_r \right) \hat{S}_\Lambda_z^2 \right\}
\]

\[
+ \alpha^\Theta \left( p_r \right) \left[ A - 1 \right] \frac{1}{h} \nabla_n \cdot \left( hK \nabla_n \hat{\Theta} \right)
\]

\[
+ \frac{\beta^\Theta \left( p_r \right)}{\beta^\Theta \left( p \right)} \left( C^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + T^\Theta \nabla_n \hat{\Theta} \cdot \nabla_n \hat{p} \right),
\]

(A75)

where \( A \) is defined in equation (70) as the ratio of \( \alpha^\Theta / \rho^\Theta \) 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 (A75).
A.18 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 and 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 $\rho_v$ can be expressed with respect to orthobaric density surfaces as

$$\frac{\partial \rho_v}{\partial t} + \mathbf{v} \cdot \nabla \rho_v \rho_v + \mathbf{v} \rho_v \frac{\partial \rho_v}{\partial z} = \varepsilon \rho_v \frac{\partial \rho_v}{\partial z},$$

(A76)

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

$$\varepsilon \rho_v = gN^{-2} \left( \alpha^\Theta \hat{\Theta} - \beta^\Theta \hat{S} \right) + (\psi - 1) \left( \hat{p}_v \rho_v + \mathbf{v} \cdot \nabla \rho_v \hat{p} \right) / \hat{p}_v,$$

(A77)

where

$$(\psi - 1) \approx 2g^2N^{-2}c_0^3 \Delta c \approx -\rho g^2T_0^\Theta N^{-2} \left[ \hat{\Theta} - \Theta_0(p, \rho) \right],$$

(A78)

and $\Delta c$ is the difference between the reference sound speed function $c_0(p, \rho)$ and the sound speed of seawater which can be expressed in the functional form $c(p, \rho, \Theta)$. This approximation to the sound speed is equivalent to difference between the actual Conservative Temperature of a water parcel and the reference value $\Theta_0(p, \rho)$. Here $\hat{S}_\lambda$ is shorthand for the material derivative of $\hat{S}_\lambda$ and is expressed in terms of mixing processes by the right-hand side of (A63), $\hat{\Theta}$ is similarly shorthand for the material derivate of $\hat{\Theta}$ and is given by the right-hand side of equation (A66).

The first term on the right of (A77) represents the effects of irreversible mixing processes on the flow through orthobaric density surfaces, and this contribution to $\varepsilon \rho_v$ is exactly the same as the flow through neutral tangent planes, $\varepsilon$ (equation (A69)). The second term in (A77) 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 form the vertical heaving of these surfaces.

A.19 The Material Derivative of Neutral Density

Neutral Density $\gamma^n$ is not a thermodynamic function since it depends on latitude and longitude. The Neutral Density algorithm finds the data point in a pre-labeled reference data set that has the same potential density as the data point that is being labeled; the reference pressure of this potential density is the average of the pressures of these two seawater parcels. The material derivative of $\gamma^n$ can be expressed with respect to Neutral Density surfaces as
\[
\frac{\partial \gamma^n}{\partial t} \bigg|_\gamma + \mathbf{\hat{v}} \cdot \nabla \gamma^n + \bar{\varepsilon}^\gamma \gamma_z^n = \bar{\varepsilon}^\gamma \gamma_z^n,
\]
(A79)
where the temporally averaged vertical velocity through the \(\gamma^n\) surface is given by (from McDougall and Jackett, 2005b)

\[
\bar{\varepsilon}^\gamma \approx \frac{\left( \alpha^\theta(\bar{p}) \hat{\Theta} - \beta^\theta(\bar{p}) \hat{S}_\lambda \right)}{\left( \alpha^\theta(\bar{p}) \Theta - \beta^\theta(\bar{p}) S'_z \right)} + \mathbf{\hat{v}} \cdot \mathbf{s} \\
+ \left( \psi^{\gamma} - 1 \right) \left( \hat{p}_1 \mathbf{\hat{v}} \cdot \nabla \hat{p} \right) \left( \hat{p}_z \right)^{-1} \\
+ \left( \psi^{\gamma} - 1 \right) \left( \mathbf{\hat{v}} \cdot \nabla \psi \mathbf{p}^r - \frac{(\hat{p} - p^r)}{(\hat{\Theta} - \Theta^r)} \mathbf{\hat{v}} \cdot \nabla \hat{\Theta} \right) \left( p_z \right)^{-1} \\
+ 2(\psi^{\gamma} - 1) \frac{\left( \alpha^\theta(\bar{p}) \hat{\Theta} - \beta^\theta(\bar{p}) \hat{S}_\lambda \right)}{\left( \alpha^\theta(\bar{p}) \Theta - \beta^\theta(\bar{p}) S'_z \right)} \\
+ \left( \psi^{\gamma} - 1 \right) \bar{\mathbf{v}} \cdot \bar{\mathbf{s}} .
\]
(A80)

Here \(\hat{S}_\lambda\) is shorthand for the material derivative of \(\hat{S}_\lambda\) and is expressed in terms of mixing processes by the right-hand side of (A63), \(\hat{\Theta}\) is similarly shorthand for the material derivate of \(\hat{\Theta}\) and is given by the right-hand side of equation (A66), and \(\left( \psi^{\gamma} - 1 \right)\) is defined by

\[
\left( \psi^{\gamma} - 1 \right) = \frac{-\frac{1}{2} \rho g^2 T_b^\Theta (\hat{\Theta} - \Theta^r)}{N^2 + \rho g^2 T_b^\Theta (\hat{\Theta} - \Theta^r) - \frac{1}{2} \rho g^2 T_b^\Theta (\hat{p} - p^r) \Theta^r_p} .
\]
(A81)

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 (A81) is close to \(N^2\) and \(\left( \psi^{\gamma} - 1 \right)\) is small.

The first term in (A80) is expected in the sense that when there are irreversible mixing processes so that \(\hat{\Theta}\) and \(\hat{S}\) are non-zero, one expects that neutral density would change. The next term in (A80), \(\mathbf{V} \cdot \mathbf{s},\) is the mean vertical motion through the \(\gamma^n\) surface due to the helical motion of neutral trajectories, caused in turn by the non-zero neutral helicity. The remaining four terms in (A80) arise because of the non-quasi-material (non-potential) nature of Neutral Density. This vertical advection arises 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 \(\bar{\varepsilon}^\gamma\) 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 (A80) is well-behaved and becomes proportional to \((\hat{p} - p^r)\mathbf{\hat{v}} \cdot \nabla \hat{\Theta} \mathbf{r} .\)
## Appendix B: Derivation of the First Law of Thermodynamics

### Motivation

For a pure fluid in which there are no gradients of Absolute Salinity the derivation of the First Law of Thermodynamics usually starts with a discussion of how the internal energy $U$ of a fixed mass of fluid is changed under the influence of it being heated by the amount $\delta q$ and its volume $V$ being changed. The infinitesimal change in the internal energy of the parcel is written as $dU = \delta Q - (p + P_0) dV$ where $-(p + P_0) dV$ is the mechanical work done on the fluid by the pressure at the moving boundaries of the fluid parcel. This can be written in terms of the specific (i.e. per unit mass) internal energy $u$, the specific volume $v$, and $\delta Q$ per unit volume, $\delta q$, as

$$
\rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \frac{\delta q}{dt}.
$$

for pure water (B1)

It is recognized that the right-hand side of (B1) 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 (B1). Apart from this familiar dissipation term, the right-hand side is the divergence of the radiative $F^R$ and molecular $F^q$ fluxes of heat, so that the First Law of Thermodynamics for pure water is

$$
\rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = -\nabla \cdot F^R - \nabla \cdot F^q + \rho \varepsilon.
$$

for pure water (B2)

Now consider seawater in which the Absolute Salinity is 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 has (B1) becoming (see equation 6b) of Warren (2006))

$$
\rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \frac{\delta q}{dt} + \rho \left( \mu - [T_0 + t] \mu_T \right) \frac{dS_\Delta}{dt}.
$$

(B3)

How do we now construct an expression for the right-hand side of (B3) in terms of the dissipation of mechanical energy and the molecular and radiative fluxes of heat and salt? If we were to assume that the “heating” term $\delta q/dt$ is the same as in the pure water case (B2) then the forcing terms on the right-hand side of (B3) would have two terms that are not the divergence of a flux, namely $\rho \varepsilon$ and $-(\mu - [T_0 + t] \mu_T) \nabla \cdot F^S$ (since $\rho dS_\Lambda/dt = -\nabla \cdot F^S$). If this were the case the very important property of the First Law of Thermodynamics that enthalpy is conserved when fluid parcels are mixed (with vanishingly small amount of dissipation of mechanical energy) would be lost. That is, a term such as $-(\mu - [T_0 + t] \mu_T) \nabla \cdot F^S$ on the right-hand side would upset this important property of the conservation of enthalpy for mixing at constant pressure because $h_{\Lambda_\Lambda} = (\mu - [T_0 + t] \mu_T)$ is not constant.

Based on the First Law of Thermodynamics which we derive below (equation (B19)) we deduce that the “heating term” is actually
\[
\frac{\delta q}{dt} = (\mu - [T_0 + t] \mu_r) \nabla \cdot \mathbf{F}^S - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon, \tag{B4}
\]

where \( \mathbf{F}^Q \) is a different molecular flux of heat than appears in the pure water version of the First Law, (B2). The relationship between \( \mathbf{F}^q \) and \( \mathbf{F}^Q \) can be found at equations (58.9) to (58.12) of Landau and Lifshitz (1959). Importantly we see from (B4) that the “heating term” \( \delta q/dt \) deviates significantly from being the divergence of molecular and radiative heat fluxes plus the dissipation of mechanical energy. Since there appears to be no way of guessing the form (B4) of the “heating term” \( \delta q/dt \) from a direct derivation of the First Law, we follow Landau and Lifshitz (1959) and Griffies (2004) and derive it 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 flux 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 local balance 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 heat flux. 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 and radiative 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 (A10) repeated here in terms of material derivatives following the instantaneous motion of a fluid parcel \( d/dt = \partial / \partial t \big|_{x,y,z} + \mathbf{u} \cdot \nabla \),

\[
\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} = \frac{du}{dt} + (p + P_0) \frac{dv}{dt} = (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt}. \tag{B5}
\]

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 (B5) 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 \( \Phi \) with respect to some fixed height \( z_0 \) is defined by

\[
\Phi = \int_{z_0}^{z} g(z') \, dz'.
\]

At a fixed location in space \( \Phi \) is independent of time while its spatial gradient is given by \( \nabla \Phi = g \mathbf{k} \) where \( \mathbf{k} \) is the unit vector pointing upwards in the vertical direction. The evolution equation for \( \Phi \) is then readily constructed as

\[
\left( \rho \Phi \right)_t + \nabla \cdot (\rho \Phi \mathbf{u}) = \rho \frac{d\Phi}{dt} = \rho g w,
\]

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 (A13) required of a conservative variable since the right-hand side of (B7) 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 \( \nu^{\text{visc}} \) and the velocity divergence \( \nabla \cdot \mathbf{u} \) (following Gill (1982)), so arriving at

\[
\rho \frac{d\mathbf{u}}{dt} + f \mathbf{k} \times \rho \mathbf{u} = -\nabla p - \rho g \mathbf{k} + \nabla \cdot \left( \rho \nu^{\text{visc}} \nabla \mathbf{u} \right),
\]

where \( f \) is the Coriolis frequency and \( \nu^{\text{visc}} \) is the viscosity. 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 (B8) (Griffies (2004)). When the material derivative term \( \rho \frac{d\mathbf{u}}{dt} \) in (B8) is expressed in divergence form, an extra advective metric frequency \( \mathcal{M} = \left( \mathbf{u} \cdot \mathbf{i} / r \right) \tan \lambda \) arises (where \( \mathbf{u} \cdot \mathbf{i} \) is simply the eastward velocity component, \( r \) is the radius of the earth and \( \lambda \) is latitude, see Griffies (2004)) so that (B8) can also be written as

\[
\left( \rho \mathbf{u} \right)_t + \nabla \cdot (\rho \mathbf{u} \mathbf{u}) + \left( f + \mathcal{M} \right) \mathbf{k} \times \rho \mathbf{u} = -\nabla p - \rho g \mathbf{k} + \nabla \cdot \left( \rho \nu^{\text{visc}} \nabla \mathbf{u} \right).
\]
The kinetic energy evolution equation

The kinetic energy evolution equation is found by taking the scalar product of equation (B9) with \( \mathbf{u} \) giving (we use the shorthand \( q^2 = \mathbf{u} \cdot \mathbf{u} \) for the square of the fluid speed)

\[
\left( \frac{\rho}{2} q^2 \right)_t + \nabla \cdot \left( \rho \mathbf{u} \frac{1}{2} q^2 \right) = \frac{\rho}{2} d \left( \frac{1}{2} q^2 \right) / dt = - \mathbf{u} \cdot \nabla p - \rho g w + \nabla \cdot \left( \rho v^{\text{visc}} \nabla \frac{1}{2} q^2 \right) - \rho \varepsilon, \tag{B10}
\]

where the dissipation of mechanical energy \( \varepsilon \) is the positive definite quantity

\[
\varepsilon \equiv v^{\text{visc}} (\nabla \mathbf{u} \cdot \nabla \mathbf{u}) \quad \text{where} \quad \nabla \mathbf{u} = (\partial \mathbf{u} / \partial x, \partial \mathbf{u} / \partial y, \partial \mathbf{u} / \partial z). \tag{B11}
\]

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

The evolution equation for total mechanical energy \( 0.5 q^2 + \Phi \) is found by adding equations (B7) and (B10) giving

\[
\left( \frac{\rho}{2} q^2 + \Phi \right)_t + \nabla \cdot \left( \rho \mathbf{u} \left( \frac{1}{2} q^2 + \Phi \right) \right) = \frac{\rho}{2} d \left( \frac{1}{2} q^2 + \Phi \right) / dt = - \mathbf{u} \cdot \nabla p + \nabla \cdot \left( \rho v^{\text{visc}} \nabla \frac{1}{2} q^2 \right) - \rho \varepsilon. \tag{B12}
\]

Notice that the term \( \rho g w \) 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 \( E \) 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 \( S \) of each fluid parcel is constant following the fluid motion so that the right-hand side of (B5) is zero and the material derivative of internal energy satisfies \( du / dt = -(p + P_0) dv / dt \) so that the internal energy changes only as a result of the work done in compressing the fluid parcel. Realizing that \( v = \rho^{-1} \) and using the continuity equation (4b) in the form \( d \rho / dt + \rho \nabla \cdot \mathbf{u} = 0 \), \( du / dt \) can be expressed in this situation of no molecular and radiative fluxes as \( du / dt = - \rho^{-1} (p + P_0) \nabla \cdot \mathbf{u} \). Adding this equation to the non-viscous, non-dissipative version of (B12) gives

\[
\left( \rho E \right)_t + \nabla \cdot \left( \rho \mathbf{u} E \right) = \rho d E / dt = - \nabla \cdot \left[ (p + P_0) \mathbf{u} \right], \quad \text{no molecular fluxes} \tag{B13}
\]

where the total energy

\[
E = u + \frac{1}{2} q^2 + \Phi \tag{B14}
\]

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 (B14). The molecular viscosity gives rise to a stress in the fluid represented by the tensor \( \sigma \), and the interior flux of energy due to this stress tensor is \( \mathbf{u} \cdot \sigma \) so that there needs to
be the additional term $-\nabla \cdot (u \cdot \sigma)$ added to the right-hand side of the total energy conservation equation. Consistently with equation (B9) above we take the stress tensor to be $\sigma = -\rho v^{\text{visc}} \nabla u$ so that the extra term $-\nabla \cdot (u \cdot \sigma) = \nabla \cdot \left( \rho v^{\text{visc}} \nabla \frac{1}{2} q^2 \right)$. Also heat fluxes by radiation $F^R$ and molecular diffusion $F^Q$ necessitate the additional terms $-\nabla \cdot F^R - \nabla \cdot F^Q$. The total energy conservation equation in the presence of molecular and radiative fluxes is then

$$
(\rho E)_t + \nabla \cdot (\rho u E) = \rho dE/dt = -\nabla \cdot \left( [p + P_0] u \right) - \nabla \cdot F^R - \nabla \cdot F^Q + \nabla \cdot \left( \rho v^{\text{visc}} \nabla \frac{1}{2} q^2 \right)
$$

(B15)

The right-hand side of the $E$ 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 $E$ is both a “conservative” variable and an “isobaric conservative” variable.

Two alternative forms of the conservation equation for total energy

Another way of expressing the total energy equation (B15) is to write it in a quasi-divergence form, with the temporal derivative being of $\rho E = \rho \left( u + \frac{1}{2} q^2 + \Phi \right)$ while the divergence part of the left-hand side based on a different quantity, namely the Bernoulli function $B = h + \frac{1}{2} q^2 + \Phi$. This form of the total energy equation is

$$
(\rho E)_t + \nabla \cdot (\rho u B) = -\nabla \cdot F^R - \nabla \cdot F^Q + \nabla \cdot \left( \rho v^{\text{visc}} \nabla \frac{1}{2} q^2 \right).
$$

(B16)

In an ocean modeling context, it is rather strange to contemplate the energy variable that is advected through the face of a model grid, $B$, to be different to the energy variable that is changed in the grid cell, $E$. Hence this form of the total energy equation has not proved popular.

A third way of expressing the total energy equation (B15) is to write the left-hand side in terms of only the Bernoulli function $B = h + \frac{1}{2} q^2 + \Phi$ so that the prognostic equation for the Bernoulli function is

$$
(\rho B)_t + \nabla \cdot (\rho u B) = \rho dB/dt = p_t - \nabla \cdot F^R - \nabla \cdot F^Q + \nabla \cdot \left( \rho v^{\text{visc}} \nabla \frac{1}{2} q^2 \right).
$$

(B17)

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 $B$ is conserved following the fluid motion in the absence of radiative and molecular fluxes. Subject to this steady-state assumption, the Bernoulli function $B$ possesses the “potential” property. The negative aspect of this $B$ evolution equation (B17) 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 (B17) is not the divergence of a flux. In this general non-steady situation $B$ is “isobaric conservative” but is not a “conservative” variable nor does it posses the “potential” property.

Noting that the total energy $E$ is related to the Bernoulli function by $E = B - (p + P_0)/\rho$ and continuing to consider the situation where the whole ocean is in a steady state so that $B$ has the “potential” property, it is clear that $E$ 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 \( p_r = 0 \) everywhere, then \( \mathcal{E} \) 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 (B12) for the sum of kinetic and gravitational potential energies is now subtracted from the total energy conservation equation (B15) giving

\[
\frac{\rho u}{t} + \nabla \cdot (\rho u u) = \rho \frac{du}{dt} = -(p + P_0)\nabla \cdot u - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon. \tag{B18}
\]

Using the continuity equation in the form \( d\rho/dt + \rho \nabla \cdot \mathbf{u} = 0 \) this equation can be written as

\[
\rho \left( \frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} \right) = \rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left( T_0 + t \right) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon, \tag{B19}
\]

which is the First Law of Thermodynamics. At first sight this equation 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 \( \rho \) times the material derivative of any quantity as is required of a conservation equation of a conservative variable. Equation (B19) is repeated at equation (6) in the Introduction section 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 and radiative 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 and radiative fluxes do enter the total energy conservation equation (B15) as the divergence of fluxes so that the total energy is ensured 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. This comment applies particularly to the molecular flux of salinity.
Appendix C: Papers Describing the TEOS-10 Thermodynamic Properties of Seawater

Primary Standard Documents


Background papers to the declared standards


McDougall, T. J., D. R. Jackett and F. J. Millero, 2009a: An algorithm for estimating Absolute Salinity in the global ocean. accepted by *Ocean Science Discussions* and is available form the OSD website.


Papers describing computer software

Jackett et al. (2010) 25-term fast EOS for ocean models, including fast code for freezing temperatures. (This exists for FH95, F03 (using both the pure and saline parts in each case), but not yet for F03(pure water)+F08(saline)) *J. Atmos. Ocean. Techn.*
Appendix D: Fundamental Constants

Following the recommendation of IAPWS (2005), the values of the fundamental constants were taken from CODATA 2002 (Mohr and Taylor 2005), 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. (2008) is given in Table D3. Selected seawater constants derived from the Reference Composition are listed in Table D4. The exact value of $c_p^0$ is given in Table D5.

Table D1. Fundamental constants from CODATA 2002 (Mohr and Taylor, 2005) and ISO (1993).

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<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
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<td>0.000 015</td>
<td>J mol$^{-1}$ K$^{-1}$</td>
<td>molar gas constant</td>
</tr>
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<td>$P_0$</td>
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<td>exact</td>
<td>K</td>
<td>Celsius zero point</td>
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<table>
<thead>
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<th>Symbol</th>
<th>Value</th>
<th>Uncertainty</th>
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<td>18.015 268</td>
<td>0.000 002</td>
<td>g mol$^{-1}$</td>
<td>molar mass</td>
</tr>
<tr>
<td>$T_{MD}$</td>
<td>3.978 121</td>
<td>0.04</td>
<td>°C</td>
<td>maximum density, temperature</td>
</tr>
<tr>
<td>$\rho_{MD}$</td>
<td>999.974 95</td>
<td>0.000 84</td>
<td>kg m$^{-3}$</td>
<td>maximum density at $P_0$</td>
</tr>
<tr>
<td>$\rho^0$</td>
<td>999.8431</td>
<td>0.001</td>
<td>kg m$^{-3}$</td>
<td>density at $T_0$ and $P_0$, $\rho^0 = 1/\nu^0$</td>
</tr>
<tr>
<td>$(\partial \rho^0 / \partial T)_P$</td>
<td>6.774 876 $\times$ 10$^{-2}$</td>
<td>0.06 $\times$ 10$^{-2}$</td>
<td>kg m$^{-3}$ K$^{-1}$</td>
<td>$(\partial \rho / \partial T)_P$ at $T_0$ and $P_0$</td>
</tr>
<tr>
<td>$T_t$</td>
<td>273.16</td>
<td>exact</td>
<td>K</td>
<td>triple point temperature</td>
</tr>
<tr>
<td>$P_t$</td>
<td>611.657</td>
<td>0.01</td>
<td>Pa</td>
<td>triple point pressure</td>
</tr>
<tr>
<td>$\rho_t$</td>
<td>999.793</td>
<td>0.01</td>
<td>kg m$^{-3}$</td>
<td>triple point density</td>
</tr>
<tr>
<td>$\eta_t$</td>
<td>0</td>
<td>exact</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>triple point entropy</td>
</tr>
<tr>
<td>$u_t$</td>
<td>0</td>
<td>exact</td>
<td>J kg$^{-1}$</td>
<td>triple point internal energy</td>
</tr>
<tr>
<td>$T_t^0$</td>
<td>273.152 519</td>
<td>0.000 002</td>
<td>K</td>
<td>freezing point at $P_0$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Solute $j$</th>
<th>$Z_j$</th>
<th>$M_j$ g mol$^{-1}$</th>
<th>$X_j \times 10^{-7}$</th>
<th>$X_j \times Z_j$</th>
<th>$W_j$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>+1</td>
<td>22.98976928(2)</td>
<td>4188071</td>
<td>4188071</td>
<td>0.3065958</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>+2</td>
<td>24.3050(6)</td>
<td>471678</td>
<td>943356</td>
<td>0.0365055</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>+2</td>
<td>40.078(4)</td>
<td>91823</td>
<td>183646</td>
<td>0.0117186</td>
</tr>
<tr>
<td>K$^+$</td>
<td>+1</td>
<td>39.0983(1)</td>
<td>91159</td>
<td>91159</td>
<td>0.0113495</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>+2</td>
<td>87.62(1)</td>
<td>810</td>
<td>1620</td>
<td>0.0002260</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>−1</td>
<td>35.453(2)</td>
<td>4874839</td>
<td>−4874839</td>
<td>0.5503396</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>−2</td>
<td>96.0626(50)</td>
<td>252152</td>
<td>−504304</td>
<td>0.0771319</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>−1</td>
<td>61.0168496</td>
<td>15340</td>
<td>−15340</td>
<td>0.0029805</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>−1</td>
<td>79.904(1)</td>
<td>7520</td>
<td>−7520</td>
<td>0.0019134</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>−2</td>
<td>60.0089(10)</td>
<td>2134</td>
<td>−4268</td>
<td>0.0004078</td>
</tr>
<tr>
<td>B(OH)$_4^-$</td>
<td>−1</td>
<td>78.840470</td>
<td>900</td>
<td>−900</td>
<td>0.0002259</td>
</tr>
<tr>
<td>F$^-$</td>
<td>−1</td>
<td>18.9984032(5)</td>
<td>610</td>
<td>−610</td>
<td>0.0000369</td>
</tr>
<tr>
<td>OH$^-$</td>
<td>−1</td>
<td>17.007337</td>
<td>71</td>
<td>−71</td>
<td>0.0000386</td>
</tr>
<tr>
<td>B(OH)$_3^-$</td>
<td>0</td>
<td>61.8339970</td>
<td>0</td>
<td>0</td>
<td>0.0005527</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>0</td>
<td>44.0095(9)</td>
<td>0</td>
<td>0</td>
<td>0.0000121</td>
</tr>
</tbody>
</table>

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).

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_S$</td>
<td>31.403 8218</td>
<td>0.001</td>
<td>g mol$^{-1}$</td>
<td>reference salinity molar mass $M_S = \sum_j X_j M_j$</td>
</tr>
<tr>
<td>$Z^2$</td>
<td>1.245 2898</td>
<td>exact$^a$</td>
<td>-</td>
<td>reference salinity valence factor $Z^2 = \sum_j X_j Z_j^2$</td>
</tr>
<tr>
<td>$N_S$</td>
<td>1.917 6461 $\times$ 10$^{22}$</td>
<td>6 $\times$ 10$^{17}$</td>
<td>g$^{-1}$</td>
<td>reference salinity particle number $N_S = N_A / M_S$</td>
</tr>
<tr>
<td>$u_{ps}$</td>
<td>1.004 715…</td>
<td>exact$^a$</td>
<td>g kg$^{-1}$</td>
<td>unit conversion factor, 35.165 04 g kg$^{-1}$ / 35</td>
</tr>
<tr>
<td>$S_{SO}$</td>
<td>35.165 04</td>
<td>exact$^a$</td>
<td>g kg$^{-1}$</td>
<td>standard ocean reference salinity, 35 $u_{ps}$</td>
</tr>
<tr>
<td>$T_{SO}$</td>
<td>273.15</td>
<td>exact</td>
<td>K</td>
<td>standard ocean temperature $T_{SO} = T_0$</td>
</tr>
<tr>
<td>$t_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>°C</td>
<td>standard ocean temperature $t_{SO} = T_{SO} - T_0$</td>
</tr>
<tr>
<td>$P_{SO}$</td>
<td>101 325</td>
<td>exact</td>
<td>Pa</td>
<td>standard ocean surface pressure $P_{SO} = P_0$</td>
</tr>
<tr>
<td>$p_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>Pa</td>
<td>standard ocean surface sea pressure $p_{SO} = P_{SO} - P_0$</td>
</tr>
<tr>
<td>$h_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>J kg$^{-1}$</td>
<td>standard ocean surface enthalpy $h_{SO} = u_t$</td>
</tr>
<tr>
<td>$\eta_{SO}$</td>
<td>0</td>
<td>exact</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>standard ocean surface entropy $\eta_{SO} = \eta_t$</td>
</tr>
<tr>
<td>$S_u$</td>
<td>40.188 617…</td>
<td>exact$^a$</td>
<td>g kg$^{-1}$</td>
<td>unit-related scaling constant, 40 $u_{ps}$</td>
</tr>
<tr>
<td>$t_u$</td>
<td>40</td>
<td>exact</td>
<td>°C</td>
<td>unit-related scaling constant</td>
</tr>
<tr>
<td>$p_u$</td>
<td>10$^8$</td>
<td>exact</td>
<td>Pa</td>
<td>unit-related scaling constant</td>
</tr>
<tr>
<td>$g_u$</td>
<td>1</td>
<td>exact</td>
<td>J kg$^{-1}$</td>
<td>unit-related scaling constant</td>
</tr>
</tbody>
</table>

$^a$ by definition of Reference Salinity and reference composition

Table D5. The exact definition of the “heat capacity” that relates potential enthalpy to Conservative Temperature $\Theta$.

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Value</th>
<th>Uncertainty</th>
<th>Unit</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p^0$</td>
<td>3991.867 957 119 63</td>
<td>exact</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>See eq. (43b)</td>
</tr>
</tbody>
</table>
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 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 $32.4356 \times 10^{-3}$ (mass of KCl per mass of solution). When $K_{15} = 1$, the Practical Salinity $S_P$ is by definition 35. Note that Practical Salinity is a unit-less quantity. Though sometimes convenient, it is technically incorrect to quote Practical Salinity in “psu”; rather it should be quoted as a certain Practical Salinity “on the Practical Salinity Scale PSS-78”. When $K_{15}$ is not unity, $S_P$ and $K_{15}$ are related by (Unesco, 1981, 1983) the PSS-78 equation

$$S_P = \sum_{i=0}^{5} a_i (K_{15})^{i/2} \quad \text{where} \quad K_{15} = \frac{C(S_P, t_{68} = 15°C, 0)}{C(35, t_{68} = 15°C, 0)},$$

(E1)

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 (E1) is valid in the range $2 < S_P < 42$.

<table>
<thead>
<tr>
<th>$i$</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>$c_i$</th>
<th>$d_i$</th>
<th>$e_i$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0080</td>
<td>0.0005</td>
<td>6.766097 x 10^{-1}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>-0.1692</td>
<td>-0.0056</td>
<td>2.00564 x 10^{-2}</td>
<td>3.426 x 10^{-2}</td>
<td>2.070 x 10^{-5}</td>
</tr>
<tr>
<td>2</td>
<td>25.3851</td>
<td>-0.0066</td>
<td>1.104259 x 10^{-4}</td>
<td>4.464 x 10^{-4}</td>
<td>-6.370 x 10^{-10}</td>
</tr>
<tr>
<td>3</td>
<td>14.0941</td>
<td>-0.0375</td>
<td>-6.9698 x 10^{-7}</td>
<td>4.215 x 10^{-1}</td>
<td>3.989 x 10^{15}</td>
</tr>
<tr>
<td>4</td>
<td>-7.0261</td>
<td>0.0636</td>
<td>1.0031 x 10^{-9}</td>
<td>-3.107 x 10^{-3}</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.7081</td>
<td>-0.0144</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

E.2 Calculation of Practical Salinity $S_P$ at oceanographic temperature and pressure

The following formulae from Unesco (1983) are valid over the range $-2°C \leq t \leq 35°C$ and $0 \leq p \leq 10 000$ dbar. Measurements of salinity in the field generally measure the conductivity ratio $R$

$$R = \frac{C(S_P, t_{68}, p)}{C(35, t_{68} = 15°C, 0)} = \frac{C(S_P, t_{68}, p)}{C(S_P, t_{68}, 0)} \frac{C(S_P, t_{68}, 0)}{C(35, t_{68}, 0)} \frac{C(35, t_{68}, 0)}{C(35, t_{68} = 15°C, 0)},$$

(E2)

which has been expressed in (E2) as the product of three factors, which are labeled $R_p$, $R_t$ and $r_t$ as follows

$$R = \frac{C(S_P, t_{68}, p)}{C(35, t_{68} = 15°C, 0)} = R_p R_t r_t.$$

(E3)

The last factor $r_t$ has been fitted to experimental data as the polynomial in temperature ($t_{68}$).
\[ r_i = \sum_{i=0}^{4} c_i \left( t_{68}/\degree C \right)^i \]  
\text{(E4)}

and the factor \( R_p \) has been fitted to experimental data as a function of \( p \), \( t_{68} \) and \( R \) as

\[ R_p = 1 + \sum_{i=1}^{3} e_i p^i \left( t_{68}/\degree C \right) + d_1 \left( t_{68}/\degree C \right) + d_2 \left( t_{68}/\degree C \right)^2 + R \left[ d_3 + d_4 \left( t_{68}/\degree C \right) \right]. \]  
\text{(E5)}

Thus for any sample measurement of \( R \) it is possible to evaluate \( r_i \) and \( R_p \) and hence calculate

\[ R_i = \frac{R}{R_p r_i}. \]  
\text{(E6)}

At a temperature of \( t_{68} = 15 \degree C \), \( R_i \) is simply \( K_{15} \) and Practical Salinity \( S_p \) can be determined form (E1). For temperatures other than \( t_{68} = 15 \degree C \), Practical Salinity \( S_p \) is given by the following function of \( R_i \) with \( k = 0.0162 \),

\[ S_p = \sum_{i=0}^{4} a_i \left( R_i \right)^{i/2} + \left( t_{68}/\degree C - 15 \right) \sum_{i=0}^{5} b_i \left( R_i \right)^{i/2}. \]  
\text{(E7)}

Equations (E1) and (E7) 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), namely \( S_R \approx u_{ps} S_p \) to estimate Reference Salinity \( S_R \).

The temperatures in equations (E2) to (E7) 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 (A3) of appendix A. This is done as the first line of the computer code described in the “gsw” software library (Library C, Appendix K). 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 (E7) is first performed to evaluate \( R_i \). Because \( r_i \) is a function only of temperature, at this stage both \( R_i \) and \( r_i \) are known so that equation (E5) 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 K). 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 (E1) but using $K_{15-90}$ instead of $K_{15}$, where $K_{15-90}$ is defined

$$K_{15-90} = \frac{C(S_p, t_{90} = 15^\circ C, 0)}{C(35, t_{90} = 15^\circ C, 0)}.$$  \hfill (E8)

The magnitude of the difference $K_{15-90} - K_{15}$ can be calculated and is found to be less than $6.8 \times 10^{-7}$ everywhere in the range $2 < S_p < 42$. Further calculation shows that $\partial S_p / \partial K_{15} < 41$ everywhere in the valid range of Practical Salinity, so that the consequence of using $K_{15-90}$ in (E1) instead of $K_{15}$ incurs a change in Practical Salinity of less than $3 \times 10^{-5}$. This is nearly two orders of magnitude below the measurement accuracy of a sample, and an order of magnitude smaller than the error caused by the uncertainty in the definition of the mass fraction of KCl. If all the original measurements that form the basis of the Practical Salinity Scale were converted to ITS-90, and the analysis repeated to determine the appropriate mass fraction to give the required conductivity at $t_{90} = 15^\circ C$, the same mass fraction $32.4356 \times 10^{-3}$ would be derived.

Notwithstanding the insensitivity of this conductivity ratio to such a small temperature difference, following Millero et al. (2008) the definition of Practical Salinity can be restated with reference to the ITS-90 scale by noting that the $K_{15}$ ratio in equation (E1) can equivalently refer to a ratio of conductivities at $t_{90} = 14.996^\circ C$.

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 (E7) 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) into 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 (E2) – (E7).

Non-zero coefficients $g_{jk}$ 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, $p = p_u \times z$.

$$g^W (t, p) = g_u \sum_{j=0}^{7} \sum_{k=0}^{6} g_{jk} y^j z^k,$$

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,

$$s(T_t, p_t) = 0, \quad (F2)$$
$$u(T_t, p_t) = 0. \quad (F3)$$

Note that the values of $g_{00}$ and $g_{10}$ are not identical to the values in Feistel (2003). The values in the present table have been chosen to most accurately achieve the triple-point conditions (F2) and (F3).

<table>
<thead>
<tr>
<th>$j$</th>
<th>$k$</th>
<th>$g_{jk}$</th>
<th>$j$</th>
<th>$k$</th>
<th>$g_{jk}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.101 342 743 139 674 × 10$^3$</td>
<td>3</td>
<td>2</td>
<td>0.499 360 390 819 152 × 10$^3$</td>
</tr>
<tr>
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<td>1</td>
<td>0.100 015 695 367 145 × 10$^6$</td>
<td>3</td>
<td>3</td>
<td>−0.239 545 330 654 412 × 10$^3$</td>
</tr>
<tr>
<td>0</td>
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<td>−0.254 457 654 203 630 × 10$^4$</td>
<td>3</td>
<td>4</td>
<td>0.488 012 518 593 872 × 10$^2$</td>
</tr>
<tr>
<td>0</td>
<td>3</td>
<td>0.284 517 778 446 287 × 10$^3$</td>
<td>3</td>
<td>5</td>
<td>−0.166 307 106 208 905 × 10$^2$</td>
</tr>
<tr>
<td>0</td>
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<td>−0.333 146 754 253 611 × 10$^2$</td>
<td>4</td>
<td>0</td>
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<tr>
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<td>0.420 263 108 803 084 × 10$^1$</td>
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<td>1</td>
<td>0.397 968 445 406 972 × 10$^3$</td>
</tr>
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<td>4</td>
<td>2</td>
<td>−0.301 815 380 621 876 × 10$^3$</td>
</tr>
<tr>
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<td>0</td>
<td>0.590 578 347 909 402 × 10$^1$</td>
<td>4</td>
<td>3</td>
<td>0.152 196 371 733 841 × 10$^3$</td>
</tr>
<tr>
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<td>1</td>
<td>−0.270 983 805 184 062 × 10$^3$</td>
<td>4</td>
<td>4</td>
<td>−0.263 748 377 232 802 × 10$^2$</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>0.776 153 611 613 101 × 10$^3$</td>
<td>5</td>
<td>0</td>
<td>0.580 259 125 842 571 × 10$^3$</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>−0.196 512 550 881 220 × 10$^2$</td>
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</table>
Appendix G: Coefficients of the Saline Gibbs Function of Seawater of Feistel (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, $S_A = S_u x^2$, ITS-90 Celsius temperature, $t = t_u x y$, and sea pressure, $p = p_u x z$:

$$g^S(S_A, t, p) = g_u \sum_{i,j,k} \left\{ g_{1,ik} x^2 \ln x + \sum_{i>1} g_{ijk} x^i \right\} y^j/z^k.$$  \hfill (G1)

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 (10) and (11) when the pure water Gibbs function was that of IAPWS-95.

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<th>$g_{ijk}$</th>
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Appendix H: Recommended Nomenclature, Symbols and Units in Oceanography

The strict SI units of Absolute Salinity, temperature and pressure are \( \text{kg kg}^{-1} \), 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 K) 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 \( \text{g kg}^{-1} \), temperature in \( ^\circ C \) 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 K).

<table>
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<th>Quantity</th>
<th>Symbol</th>
<th>Units</th>
<th>Comments</th>
</tr>
</thead>
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<tr>
<td>Chlorinity</td>
<td>( Cl )</td>
<td>( g \text{ kg}^{-1} )</td>
<td>WG127 is recommending that Chlorinity be defined in terms of a mass fraction as 0.328 523 4 times the ratio of the mass of pure silver required to precipitate all dissolved chloride, bromide and iodide in seawater to the mass of seawater. Hence WG127 recommends that we use mass fraction units for Chlorinity.</td>
</tr>
<tr>
<td>Standard Ocean Reference Salinity</td>
<td>( S_{SO} )</td>
<td>( g \text{ kg}^{-1} )</td>
<td>35.165 04 ( g \text{ kg}^{-1} ) being exactly ( 35 u_{PS} ), corresponding to the standard ocean Practical Salinity of 35.</td>
</tr>
<tr>
<td>Freezing temperatures</td>
<td>( t^f, \theta^f )</td>
<td>( ^\circ C )</td>
<td>In situ, potential and conservative values, each as a function of ( S_A ) and ( p ).</td>
</tr>
<tr>
<td>Absolute pressure</td>
<td>( P )</td>
<td>Pa</td>
<td>When absolute pressure is used it should always be in Pa, not in Mpa nor in dbar.</td>
</tr>
<tr>
<td>Gauge pressure (also called sea pressure or applied pressure) is the pressure argument to all software in the “gsw” library.</td>
<td>( p )</td>
<td>dbar</td>
<td>Equal to ( P - P^0 ) but expressed in dbar not Pa.</td>
</tr>
<tr>
<td>One standard atmosphere</td>
<td>( P^0 )</td>
<td>Pa</td>
<td>101 325 Pa</td>
</tr>
<tr>
<td>Practical Salinity</td>
<td>( S_p )</td>
<td>( l )</td>
<td>Defined in the range ( 2&lt;S_p&lt;42 ) by PSS-78 based on measured conductivity ratios.</td>
</tr>
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</table>
### Calculation of the Thermophysical Properties of Seawater

<table>
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<tr>
<th>Property</th>
<th>Symbol</th>
<th>Unit</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference Salinity</td>
<td>$S_R$</td>
<td>g kg$^{-1}$</td>
<td>Reference-Composition Salinity (or Reference Salinity for short) is the Absolute Salinity of seawater samples that have Reference Composition. At $S_p = 35$, $S_R$ is exactly $u_{ps}S_p$, while in the range $2 &lt; S_p &lt; 42$ $S_R \approx u_{ps}S_p$.</td>
</tr>
<tr>
<td>Absolute Salinity</td>
<td>$S_A$</td>
<td>g kg$^{-1}$</td>
<td>(This is the salinity argument to all the “gsw” library functions.)</td>
</tr>
<tr>
<td>Absolute Salinity Anomaly</td>
<td>$\delta S_A$</td>
<td>g kg$^{-1}$</td>
<td>$\delta S_A = S_A - S_R$, the difference between Absolute Salinity and Reference-Composition Salinity.</td>
</tr>
<tr>
<td>Temperature</td>
<td>$t$</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Absolute Temperature</td>
<td>$T$</td>
<td>K</td>
<td>$T / K = T_0 / K + t / (°C) = 273.15 + t / (°C)$</td>
</tr>
<tr>
<td>Potential temperature</td>
<td>$\Theta$</td>
<td>°C</td>
<td>Defined implicitly by equation (39)</td>
</tr>
<tr>
<td>Conservative Temperature</td>
<td>$\Theta$</td>
<td>°C</td>
<td>Defined in equation (42) as exactly potential enthalpy divided by $c_p^0$.</td>
</tr>
<tr>
<td>A constant “specific heat”, for use with Conservative Temperature</td>
<td>$c_p^0$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>$c_p^0 \equiv 3991.867 \ 957 \ 119 \ 63 \ J \ kg^{-1} K^{-1}$. This 15-digit number is defined to be the exact value of $c_p^0$.</td>
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<tr>
<td>Combined standard uncertainty</td>
<td>$u_c$</td>
<td>Varies</td>
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<td>Enthalpy</td>
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<td>Specific enthalpy</td>
<td>$h$</td>
<td>J kg$^{-1}$</td>
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<td>Specific potential enthalpy</td>
<td>$h^0$</td>
<td>J kg$^{-1}$</td>
<td>Specific enthalpy referenced to zero gauge pressure. $h^0 = h(S_A, \theta(S_A,t,p,p_r = 0),p_r = 0)$</td>
</tr>
<tr>
<td>Specific isobaric heat capacity</td>
<td>$c_p$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>$c_p = \partial h / \partial T</td>
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<td>Specific internal energy</td>
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<td>J kg$^{-1}$</td>
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<td>Specific isochoric heat capacity</td>
<td>$c_v$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>$c_v = \partial u / \partial T</td>
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<td>$G$</td>
<td>J</td>
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<td>Specific Gibbs function (Gibbs energy)</td>
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<td>J kg$^{-1}$</td>
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<tr>
<td>Specific Helmholtz Energy</td>
<td>$f$</td>
<td>J kg$^{-1}$</td>
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<tr>
<td>Unit conversion factor for salinities</td>
<td>$u_{ps}$</td>
<td>g kg$^{-1}$</td>
<td>$u_{ps} = (35.16504/35) \ g \ kg^{-1} \approx 1.004 \ 715... \ g \ kg^{-1}$ The first part of this expression is exact.</td>
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<tr>
<td>Entropy</td>
<td>$\Sigma$</td>
<td>J K$^{-1}$</td>
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</tr>
<tr>
<td>Specific entropy</td>
<td>$\eta$</td>
<td>J kg$^{-1}$ K$^{-1}$</td>
<td>In other publications the symbol $s$ is used for specific entropy.</td>
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<td>Density anomaly</td>
<td>$\sigma_t$</td>
<td>kg m$^{-3}$</td>
<td>$\rho - 1000$ kg m$^{-3}$</td>
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<td>Potential density anomaly referenced to a gauge pressure of 10 MPa</td>
<td>$\sigma_1$</td>
<td>kg m$^{-3}$</td>
<td>$\rho(S_A, \theta(S_A,t,p,p_r),p_r) - 1000 \ kg \ m^{-3}$ where $p_r = 10$ MPa</td>
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</table>
Calculation of the Thermophysical Properties of Seawater

Potential density anomaly referenced to a gauge pressure of 40 MPa

\[ \sigma_A \quad \text{kg m}^{-3} \]

\[ \rho \left( S_A, \theta \left[ S_A, t, \rho_r, \rho_t \right], \rho_t \right) - 1000 \text{ kg m}^{-3} \text{ where } \rho_r = 40 \text{ MPa} \]

Thermal expansion coefficient with respect to \textit{in situ} temperature

\[ \alpha^t \quad \text{K}^{-1} \]

\[ v^{-1} \frac{\partial \rho}{\partial t} \bigg|_{S_A, \rho} = - \rho^{-1} \frac{\partial \rho}{\partial t} \bigg|_{S_A, \rho} \]

Thermal expansion coefficient with respect to potential temperature \( \theta \)

\[ \alpha^\theta \quad \text{K}^{-1} \]

\[ v^{-1} \frac{\partial \rho}{\partial \theta} \bigg|_{S_A, \rho} = - \rho^{-1} \frac{\partial \rho}{\partial \theta} \bigg|_{S_A, \rho} \]

Thermal expansion coefficient with respect to Conservative Temperature \( \Theta \)

\[ \alpha^{\Theta} \quad \text{K}^{-1} \]

\[ v^{-1} \frac{\partial \rho}{\partial \Theta} \bigg|_{S_A, \rho} = - \rho^{-1} \frac{\partial \rho}{\partial \Theta} \bigg|_{S_A, \rho} \]

Haline contraction coefficient at constant \textit{in situ} temperature

\[ \beta^t \quad \text{kg g}^{-1} \]

\[ -v^{-1} \frac{\partial \rho}{\partial \rho} \bigg|_{S_A, \rho} = - \rho^{-1} \frac{\partial \rho}{\partial \rho} \bigg|_{S_A, \rho} \]

Note that the units for \( \beta^t \) are consistent with \( S_A \) being in g kg\(^{-1}\).

Haline contraction coefficient at constant potential temperature \( \beta^\theta \quad \text{kg g}^{-1} \)

\[ -v^{-1} \frac{\partial \rho}{\partial \rho} \bigg|_{S_A, \rho} = \rho^{-1} \frac{\partial \rho}{\partial \rho} \bigg|_{S_A, \rho} \]

Note that the units for \( \beta^\theta \) are consistent with \( S_A \) being in g kg\(^{-1}\).

Haline contraction coefficient at constant Conservative Temperature \( \beta^{\Theta} \quad \text{kg g}^{-1} \)

\[ -v^{-1} \frac{\partial \rho}{\partial \rho} \bigg|_{S_A, \rho} = \rho^{-1} \frac{\partial \rho}{\partial \rho} \bigg|_{S_A, \rho} \]

Note that the units for \( \beta^{\Theta} \) are consistent with \( S_A \) being in g kg\(^{-1}\).

Isothermal compressibility \( \kappa^t \quad \text{dbar}^{-1} \)

Isentropic and isohaline compressibility \( \kappa \quad \text{dbar}^{-1} \)

Chemical potential of water in seawater \( \mu^w \quad \text{J g}^{-1} \)

Chemical potential of sea salt in seawater \( \mu^S \quad \text{J g}^{-1} \)

Relative chemical potential of (sea salt and water in) seawater \( \mu \quad \text{J g}^{-1} \)

\[ (\frac{\partial g}{\partial S_A})_{t, \rho} = \mu^S - \mu^w \]

Dissipation rate of kinetic energy per unit mass \( \varepsilon \quad \text{J kg}^{-1} \text{s}^{-1} = \text{m}^2 \text{s}^{-3} \)

Adiabatic lapse rate \( \Gamma \quad \text{K dbar}^{-1} \)

\[ \Gamma = \frac{\partial t}{\partial \rho} \bigg|_{S_A, \Theta} = \frac{\partial t}{\partial \rho} \bigg|_{S_A, \Theta} = \frac{\partial t}{\partial \rho} \bigg|_{S_A, \eta} \]

Sound speed \( c \quad \text{m s}^{-1} \)

Specific volume anomaly \( \delta \quad \text{m}^3 \text{kg}^{-1} \)

Thermobaric coefficient based on \( \Theta \)

\[ T_b^\theta \quad \text{K}^{-1} \text{dbar}^{-1} \]

Thermobaric coefficient based on \( \Theta \)

\[ T_b^{\Theta} \quad \text{K}^{-1} \text{dbar}^{-1} \]

Cabbeling coefficient based on \( \Theta \)

\[ C_b^\theta \quad \text{K}^{-2} \]

Cabbeling coefficient based on \( \Theta \)

\[ C_b^{\Theta} \quad \text{K}^{-2} \]

Buoyancy frequency \( N \quad \text{s}^{-1} \)

Neutral helicity \( H^n \quad \text{m}^3 \)

Neutral density \( \gamma^n \quad \text{kg m}^{-3} \)

Defined by (64) and (65)

Neutral-Surface-Potential-Vorticity \( \text{NSPV} \quad \text{s}^{-3} \)

\[ \text{NSPV} = -g \rho^{-1} f \gamma^n \] where \( f \) is the Coriolis parameter.

Dynamic height anomaly \( \Phi' \quad \text{m}^2 \text{s}^{-2} \)

\[ \text{Pa m}^3 \text{kg}^{-1} = \text{m}^2 \text{s}^{-2} \]
Montgomery potential \( \pi \) \( \text{m}^2 \text{s}^{-2} \) \( \text{Pa m}^3 \text{kg}^{-1} = \text{m}^2 \text{s}^{-2} \)

Montgomery potential \( \bar{\pi} \) \( \text{m}^2 \text{s}^{-2} \) \( \text{Pa m}^3 \text{kg}^{-1} = \text{m}^2 \text{s}^{-2} \)

**PIDHA (Pressure-Integrated Dynamic Height Anomaly) or DISH (Depth-Integrated Steric Height)**

\( \Psi' \) \( \text{kg s}^{-2} \)

Streamfunction for \( f \) times the depth-integrated relative mass flux, see eq. (92) – (96).

**Coriolis parameter**

\( f \) \( \text{s}^{-1} \)

\( 1.45842 \times 10^{-4} \sin \phi \text{ s}^{-1} \)

**Molality**

\( m \) \( \text{mol kg}^{-1} \)

\[ m = \sum m_i = \frac{1}{\langle A \rangle} \frac{S_A}{(1 - S_A)} \]

where \( \langle A \rangle \) is the mole-weighted average atomic weight of the elements of sea salt,

\( \langle A \rangle = 31.4038218\ldots \text{g mol}^{-1} \)

**Ionic strength**

\( I \) \( \text{mol kg}^{-1} \)

\[ I = \frac{1}{2} m \langle Z^2 \rangle = \frac{1}{2} \sum_m m_i z_i^2 \]

\[ = 0.6226449 \times m \]

\[ \approx \frac{622.6449}{31.4038218} \text{mol kg}^{-1} \times \frac{S_A}{(1 - S_A)} \]

**Osmotic coefficient**

\( \phi \) \( 1 \)

\[ \phi(S_A, T, p) = \frac{g(0, t, p) - \mu^w(S_A, t, p)}{mR(T_0 + t)} \]

where the molar gas constant,

\[ R = 8.314472 \text{ J mol}^{-1} \text{ K}^{-1} \]

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 \( \mu \text{mol/kg} \) and not \( \text{cm}^3\text{dm}^{-3}, \text{ml/l} \) or \( \mu \text{mol/l} \) (this reflects a desire for consistency with reporting of other quantities and will avoid problems associated with conversion between moles and ml using the gas equations).
Appendix I: 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 $\phi$ (°E) latitude $\lambda$ (°N) and Absolute Pressure $P$ (Pa),
- the inverse function $S_p = S_p(S_A, \phi, \lambda, P)$,
- the function that calculates Conservative Temperature (in K) which has potential temperature $\theta$ (in K, with reference pressure $P_r = 0$) as its temperature variable, that is $\Theta = \Theta(S_A, \theta)$, and does not have a pressure input variable,
- the inverse function $\Theta = \Theta(S_A, \Theta)$, and
- the code for potential temperature and potential density which have an additional input parameter, namely the reference pressure $P_r$ (the reference value of Absolute Pressure in Pa).

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 submitted, accepted and published by that journal. In the meantime, Library A can be found at http://www.marine.csiro.au/~jackett/TEOS-10/
Appendix J: 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 IAPWS-09), 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\(^{-1}\)]), \textit{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 \( \phi \) (°E) latitude \( \lambda \) (°N) and Absolute Pressure \( P \) (Pa),
- the inverse function \( S_p = S_p(S_A, \phi, \lambda, P) \),
- the function that calculates Conservative Temperature (in K) which has potential temperature \( \theta \) (in K, with reference pressure \( P_r = 0 \)) as its temperature variable, that is \( \Theta = \Theta(S_A, \theta) \), and does not have a pressure input variable,
- the inverse function \( \Theta = \Theta(S_A, \Theta) \), and
- the code for potential temperature and potential density which have an additional input parameter, namely the reference pressure \( P_r \) (the reference value of Absolute Pressure in Pa).

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 \( g(T, P) \) 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 L). 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 submitted, accepted and published by that journal. In the meantime, Library B can be found at http://www.marine.csiro.au/~jackett/TEOS-10/
Appendix K: Software in Library C, the gsw Library; the fast library in oceanographic units

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 oceangraphers 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\(^{-1}\)], \textit{in situ} temperature \(t\) in \(^\circ\)C and pressure as sea pressure \(p\) (or gauge pressure) in dbar. Hence the salinity is Absolute Salinity 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\(^{-1}\)), temperature is Absolute Temperature in K and pressure is Absolute Pressure in Pa. Use of these basic-SI units greatly simplifies all the theoretical expressions in thermodynamics.

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 \(\phi\) (°E) latitude \(\lambda\) (°N) and pressure \(p\) (dbar),
- the inverse function \(S_p = S_p(S_A,\phi,\lambda, p)\),
- the function that calculates Conservative Temperature which has potential temperature \(\theta\) (with reference pressure \(p_r = 0\)) as its temperature variable, that is \(\Theta = \Theta(S_A, \theta)\), and does not have a pressure input variable,
- the inverse function \(\theta = \theta(S_A, \Theta)\), and
- the code for potential temperature and potential density which have an additional input parameter, namely the reference pressure \(p_r\) (the reference value of sea pressure in dbar).

Library C, the “gsw” library is available from the web site
Table K1. A Selection of Function Names in the gsw Library

<table>
<thead>
<tr>
<th>Thermodynamic Property</th>
<th>Function name</th>
<th>Units of the output</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Practical Salinity $S_p$</td>
<td>gsw_PSal</td>
<td>unitless</td>
<td>PSal from PSS-78</td>
</tr>
<tr>
<td>Absolute Salinity $S_A$</td>
<td>gsw_ASal</td>
<td>g kg⁻¹</td>
<td>The McDougall, Jackett and Millero (2009a) algorithm</td>
</tr>
<tr>
<td>Practical Salinity $S_p$</td>
<td>gsw_PSal_from_ASal</td>
<td>Unitless $2 &lt; S_p &lt; 42$</td>
<td>Inverse function of gsw_ASal</td>
</tr>
<tr>
<td>Gibbs function $g$ and its 1st and 2nd derivatives</td>
<td>gsw_g</td>
<td>various units</td>
<td></td>
</tr>
<tr>
<td>specific volume $v$</td>
<td>gsw_specvol</td>
<td>m³ kg⁻¹</td>
<td></td>
</tr>
<tr>
<td>density $\rho$</td>
<td>gsw_dens</td>
<td>kg m⁻³</td>
<td></td>
</tr>
<tr>
<td>entropy $\eta$</td>
<td>gsw_entropy</td>
<td>J kg⁻¹ K⁻¹</td>
<td></td>
</tr>
<tr>
<td>enthalpy $h$</td>
<td>gsw_enthalpy</td>
<td>J kg⁻¹</td>
<td></td>
</tr>
<tr>
<td>isothermal compressibility $\kappa_t$</td>
<td>gsw_kappa_t</td>
<td>dbar⁻¹</td>
<td></td>
</tr>
<tr>
<td>isentropic compressibility $\kappa$</td>
<td>gsw_kappa</td>
<td>dbar⁻¹</td>
<td></td>
</tr>
<tr>
<td>sound speed</td>
<td>gsw_svel</td>
<td>m s⁻¹</td>
<td></td>
</tr>
<tr>
<td>thermal expansion coefficient with respect to in situ temperature $t$</td>
<td>gsw_alpha_t</td>
<td>K⁻¹</td>
<td></td>
</tr>
<tr>
<td>thermal expansion coefficient with respect to potential temperature $\theta$</td>
<td>gsw_alpha_ptmp</td>
<td>K⁻¹</td>
<td></td>
</tr>
<tr>
<td>thermal expansion coefficient with respect to Conservative Temperature $\Theta$</td>
<td>gsw_alpha_ctmp</td>
<td>K⁻¹</td>
<td></td>
</tr>
<tr>
<td>saline contraction coefficient at constant in situ temperature $t$</td>
<td>gsw_beta_t</td>
<td>kg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>saline contraction coefficient at constant potential temperature $\theta$</td>
<td>gsw_beta_ptmp</td>
<td>kg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>saline contraction coefficient at constant Conservative Temperature $\Theta$</td>
<td>gsw_beta_ctmp</td>
<td>kg g⁻¹</td>
<td></td>
</tr>
<tr>
<td>isobaric heat capacity $c_p$</td>
<td>gsw_cp</td>
<td>J kg⁻¹ K⁻¹</td>
<td></td>
</tr>
<tr>
<td>potential temperature $\theta$</td>
<td>gsw_ptmp</td>
<td>°C</td>
<td>$\theta(S_A, t, p, p_r)$</td>
</tr>
<tr>
<td>Conservative Temperature $\Theta$</td>
<td>gsw_ctmp</td>
<td>°C</td>
<td>$\Theta(S_A, \theta)$ where $\theta$ is potential temperature with $p_r = 0.$</td>
</tr>
<tr>
<td>potential temperature $\theta$</td>
<td>gsw_ptmp0_from_ctmp</td>
<td>°C</td>
<td>Inverse function of gsw_ctmp</td>
</tr>
<tr>
<td>potential density $\rho_\theta$</td>
<td>gsw_pden</td>
<td>kg m⁻³</td>
<td>$\rho_\theta(S_A, t, p, p_r)$</td>
</tr>
</tbody>
</table>
Appendix L: 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 L1 here, this estimate is the column labeled “Resulting r.m.s.”. All the data in Table L1 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 L1) included density $\rho$, isobaric specific heat capacity $c_p$, thermal expansion coefficient $\alpha$, sound speed $c$, specific volume $v$, freezing temperature $t_f$, mixing heat $\Delta h$. This dataset included 1834 observations. Column 2 of Table L1 are the data sources that are listed in the references. The r.m.s. values were calculated with the equation:

$$\text{r.m.s} = \left[ \frac{1}{n} \sum_{n} (\text{F03 - expt.datum})^2 \right]^{0.5} \quad (L1)$$

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 L1 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 $S_p = 20.062$, $t = 25^\circ C$, 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 L1 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 L2). 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 L2) included isobaric specific heat capacity \(c_p\), mixing heat \(\Delta h\), freezing point depression \(t_f\), water vapor pressure \(p_{\text{vap}}\), and the Debye-Hückel limiting law \(g^{LL}\). This salinity dataset included 602 observations. Column 2 of Table L2 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 L2), 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 L1. Summary of data used in the regression to determine the coefficients of the Feistel (2003) Gibbs potential.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Source</th>
<th>$S_A$ (g kg$^{-1}$)</th>
<th>$T$/°C</th>
<th>$p$/MPa</th>
<th>Points</th>
<th>Required r.m.s.</th>
<th>Resulting r.m.s.</th>
<th>Verifying r.m.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho$</td>
<td>MGW76c</td>
<td>0.5-40</td>
<td>0-40</td>
<td>0</td>
<td>122</td>
<td>4 ppm</td>
<td>4.1 ppm</td>
<td>4.2 ppm</td>
</tr>
<tr>
<td>$\rho$</td>
<td>PB80</td>
<td>5-42</td>
<td>0-30</td>
<td>0</td>
<td>345</td>
<td>4 ppm</td>
<td>4.0 ppm</td>
<td>4.2 ppm</td>
</tr>
<tr>
<td>$\rho$</td>
<td>PG93</td>
<td>34-50</td>
<td>15-30</td>
<td>0</td>
<td>81</td>
<td>10 ppm</td>
<td>12.0 ppm</td>
<td>11.9 ppm</td>
</tr>
<tr>
<td>$c_p$</td>
<td>BDSW70</td>
<td>10-50</td>
<td>0-40</td>
<td>0</td>
<td>25</td>
<td>2 J/(kg K)</td>
<td>1.45 J/(kg K)</td>
<td>1.43 J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>MPD73</td>
<td>1-40</td>
<td>5-35</td>
<td>0</td>
<td>48</td>
<td>0.5 J/(kg K)</td>
<td>0.52 J/(kg K)</td>
<td>0.45 J/(kg K)</td>
</tr>
<tr>
<td>$\alpha'$</td>
<td>C78</td>
<td>10-30</td>
<td>-6-1</td>
<td>0.7-33</td>
<td>31</td>
<td>0.6 ppm/K</td>
<td>0.73 ppm/K</td>
<td>0.74 ppm/K</td>
</tr>
<tr>
<td>$c$</td>
<td>D74(I-III)</td>
<td>29-43</td>
<td>0-35</td>
<td>0-2</td>
<td>92</td>
<td>5 cm/s</td>
<td>1.7 cm/s</td>
<td>1.6 cm/s</td>
</tr>
<tr>
<td>$c$</td>
<td>D74(Va-d)</td>
<td>29-43</td>
<td>0-30</td>
<td>0.1-5</td>
<td>32</td>
<td>5 cm/s</td>
<td>1.2 cm/s</td>
<td>1.2 cm/s</td>
</tr>
<tr>
<td>$c$</td>
<td>D74(V-VI)</td>
<td>33-37</td>
<td>0-5</td>
<td>0-100</td>
<td>128</td>
<td>5 cm/s</td>
<td>3.5 cm/s</td>
<td>3.5 cm/s</td>
</tr>
<tr>
<td>$\nu$</td>
<td>CM76</td>
<td>5-40</td>
<td>0-40</td>
<td>0-100</td>
<td>558</td>
<td>10 ppm</td>
<td>11.0 ppm</td>
<td>11.2 ppm</td>
</tr>
<tr>
<td>$\nu^S$</td>
<td>BS70</td>
<td>30-40</td>
<td>-2-30</td>
<td>1-100</td>
<td>221</td>
<td>4 ppm</td>
<td>2.6 ppm</td>
<td>2.6 ppm</td>
</tr>
<tr>
<td>$t_f$</td>
<td>DK74</td>
<td>4-40</td>
<td>-2-0</td>
<td>0</td>
<td>32</td>
<td>2 J/kg</td>
<td>1.8 J/kg</td>
<td>1.9 J/kg</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>B68</td>
<td>0-33</td>
<td>25</td>
<td>0</td>
<td>24</td>
<td>4 J</td>
<td>2.4 J</td>
<td>2.4 J</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>MHH73</td>
<td>1-41</td>
<td>0-30</td>
<td>0</td>
<td>95</td>
<td>0.4 J/kg</td>
<td>0.5 J/kg</td>
<td>0.5 J/kg</td>
</tr>
</tbody>
</table>

i The original value in Table 9 of Feistel (2003) was 11.3 ppm, which apparently was a typographical error.

ii The original value in Table 9 of Feistel (2003) was 0.54 J/(kg K), which apparently was a typographical error.

Table L2. Summary of extra datasets used in the regression to determine the coefficients of the Feistel (2008) Gibbs potential.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Source</th>
<th>$S_A$ (g kg$^{-1}$)</th>
<th>$T$/°C</th>
<th>$p$/MPa</th>
<th>Points</th>
<th>Resulting r.m.s.</th>
<th>Verifying r.m.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$c_p$</td>
<td>BDCW67</td>
<td>11-117</td>
<td>2-80</td>
<td>0</td>
<td>221</td>
<td>3.46 J/(kg K)</td>
<td>3.46 J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>MPD73</td>
<td>1-40</td>
<td>5-35</td>
<td>0</td>
<td>48</td>
<td>0.57 J/(kg K)</td>
<td>0.57 J/(kg K)</td>
</tr>
<tr>
<td>$c_p$</td>
<td>MP05</td>
<td>1-35</td>
<td>10-40</td>
<td>0</td>
<td>41</td>
<td>1.30 J/(kg K)</td>
<td>1.30 J/(kg K)</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>B68</td>
<td>0-97</td>
<td>25</td>
<td>0</td>
<td>33</td>
<td>0.75 J/kg</td>
<td>0.75 J/kg</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>C70</td>
<td>35-36</td>
<td>2-25</td>
<td>0</td>
<td>19</td>
<td>7.2 J/kg</td>
<td>7.1 J/kg</td>
</tr>
<tr>
<td>$\Delta h$</td>
<td>MHH73</td>
<td>1-35</td>
<td>0-30</td>
<td>0</td>
<td>120</td>
<td>3.3 J/kg</td>
<td>3.3 J/kg</td>
</tr>
<tr>
<td>$t_f$</td>
<td>DK74</td>
<td>4-40</td>
<td>-0.2(-2.2)</td>
<td>0</td>
<td>32</td>
<td>1.6 mK</td>
<td>1.6 mK</td>
</tr>
<tr>
<td>$t_f$</td>
<td>FM07</td>
<td>5-109</td>
<td>-0.3(-6.9)</td>
<td>0</td>
<td>22</td>
<td>1.2 mK</td>
<td>1.0 mK</td>
</tr>
<tr>
<td>$p_{vap}$</td>
<td>R54</td>
<td>18-40</td>
<td>25</td>
<td>0</td>
<td>13</td>
<td>2.8 J/kg</td>
<td>2.8 J/kg</td>
</tr>
<tr>
<td>$t_{boil}$</td>
<td>BSRSR74</td>
<td>6-70</td>
<td>60-80</td>
<td>0</td>
<td>32</td>
<td>9.1 J/kg</td>
<td>9.3 J/kg</td>
</tr>
<tr>
<td>$g^{\perp}$</td>
<td>F08</td>
<td>35</td>
<td>-5-95</td>
<td>0</td>
<td>21</td>
<td>0.091 J/kg</td>
<td>0.092 J/kg</td>
</tr>
</tbody>
</table>
Acknowledgements

This work reviews and summarizes the work of the SCOR/IAPSO Working Group 127 on the Thermodynamics and Equation of State of Seawater. TJMcD and DRJ wish to acknowledge partial financial support from the Wealth from Oceans National Flagship. This work contributes to the CSIRO Climate Change Research Program. This document is based on work partially supported by the U.S. National Science Foundation to SCOR under Grant No. OCE-0608600. FJM wishes to acknowledge the Oceanographic Section of the National Science Foundation and the National Oceanic and Atmospheric Association for supporting his work.
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