A Thermodynamic Potential of Seawater in terms of Conservative Temperature

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Abstract. A thermodynamic potential is found for seawater as a function of Conservative Temperature, Absolute Salinity and pressure. From this thermodynamic potential, all the equilibrium thermodynamic properties of seawater can be derived, just as all these thermodynamic properties can be found from the TEOS-10 Gibbs function (which is a function of *in situ* temperature, Absolute Salinity and pressure). Present oceanographic practice in the Gibbs SeaWater Oceanographic Toolbox uses a polynomial expression for specific volume (and enthalpy) in terms of Conservative Temperature (as well as of Absolute Salinity and pressure), whereas the relationship between in situ temperature and Conservative Temperature is based on the Gibbs function. This mixed practice introduces (numerically small) inconsistencies and superfluous conversions between variables. The proposed thermodynamic potential of seawater, being expressed as an explicit function of Conservative Temperature, overcomes these small numerical inconsistencies, and in addition, the new approach allows for greater computational efficiency in the evaluation of sea surface temperature from Conservative Temperature.

1 Introduction

1.1 Present Practice

The TEOS-10 (the International Thermodynamic Equation of Seawater – 2010, IOC *et al.*, 2010) Gibbs function of seawater is a thermodynamic potential whose arguments are Absolute Salinity, *in situ* temperature and pressure. The adoption in 2010 of TEOS-10 as the official description of the thermodynamic properties of seawater came with the recommendation that the observed variables Practical Salinity S_P, and *in situ* temperature, together with longitude, latitude and pressure, are used to form Absolute Salinity S_A and Conservative Temperature Θ, and it is these variables, S_A and Θ, that take the place of Practical Salinity S_P and potential temperature θ in our oceanographic research and in the publication of our results in journals (IOC *et al.*, 2010, Valladares et al., 2011a,b, McDougall and Barker, 2011, Pawlowicz *et al.*, 2012, Spall *et al*, 2013).

The Absolute Salinity variable of TEOS-10 is defined on the Reference-Composition Salinity Scale of Millero *et al.* (2008) as an approximation to the mass fraction of dissolved material in seawater. As described in Pawlowicz (2010, 2011), and Wright *et al.* (2011), while the Gibbs function of a multi-component solution such as seawater should depend on the concentrations of all its constituents, Absolute Salinity on the Reference-Composition Salinity Scale is defined so that its use yields accurate values of the specific volume of seawater. Conservative Temperature is proportional to the potential enthalpy of seawater referenced to the pressure of the standard atmosphere (McDougall, 2003, IOC et al., 2010, Graham and McDougall, 2013).

This paper was motivated by the question "is it possible to define a thermodynamic potential in terms of Conservative Temperature rather than, for example, in terms of *in situ* temperature, as is the case for the TEOS-10 Gibbs function of seawater (Feistel, 2008, IAWPS, 2008)?". Some progress was already made towards answering this question in appendix P of the TEOS-10 Manual (IOC *et al*., 2010) where it was shown that if expressions were available for both the enthalpy and the entropy of seawater as functions of Absolute Salinity, Conservative Temperature, and pressure, then all the thermodynamic properties of seawater could be derived.

While in situ temperature is a measured variable, its dependence on pressure (even for adiabatic variations of pressure at constant salinity) and its non-conservative nature under turbulent mixing processes, has led to the adoption of Conservative Temperature in order to approximate the "heat content" per unit mass of seawater. It is Conservative Temperature that is now used as the temperature axis of "salinity-temperature" diagrams and as the model's temperature variable in ocean models (McDougall et al., 2021) because it is approximately conserved under mixing processes; the amount of non-conservation is typically two orders of magnitude less than that of potential temperature. In order to facilitate the use of Conservative Temperature in oceanography, Roquet et al. (2015) provided a 75-term polynomial for specific volume, $\hat{v}(S_A, \Theta, P)$, as a function of Absolute Salinity, S_A, Conservative Temperature Θ and pressure P, and this polynomial underlies approximately 75 of the 280 algorithms in the Gibbs Seawater (GSW) Oceanographic Toolbox. While this polynomial expression is as accurate in the oceanographic range of salinity as our present knowledge of seawater properties, it does not give exactly the same values for specific volume as are obtained by using the original TEOS-10 Gibbs function. One consequence of this approximation is that there is at present a slight inconsistency in the conversions between different types of temperature variables using the Gibbs function compared with using the Roquet et al. (2015) polynomial $\hat{v}(S_A, \Theta, P)$. For example, the in situ and potential temperatures, t and θ respectively, are related through the Gibbs function through the implicit relationship $g_T(S_A, T_0 + t, P) = g_T(S_A, T_0 + \theta, P_r)$ (where subscripts denote partial differentiation, P_r is the reference pressure of the potential temperature, and $g(S_A, T_0 + t, P)$ is the Gibbs function), whereas they are related through the forward expression $(T_0 + t)/(T_0 + \theta) = \hat{h}_\Theta(S_A, \Theta, P)/c_p^0$ in terms of the pressure integral of the $\hat{v}(S_A, \Theta, P)$ polynomial of Roquet et al., 2015, with c_p^0 and T_0 being constants, noting that $\hat{h}_P(S_A, \Theta, P) = \hat{v}(S_A, \Theta, P)$. While the inconsistencies in temperature are small, being no larger than 10^{-4}K, we would prefer if they did not exist, and the use of the thermodynamic potential of this paper in place of the Gibbs function eliminates both these small inconsistencies as well as the need for superfluous conversions between different temperatures.

1.2 Thermodynamic fundamentals

85   The First Law of Thermodynamics (Appendix B of IOC et al., 2010)

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + P\frac{\mathrm{d}v}{\mathrm{d}t}\right) = -\nabla\cdot\boldsymbol{F}^Q + \rho\epsilon, \tag{1}$$

expresses how the material derivatives of internal energy, u, and specific volume, v, are related, and how they respond to the local rate of heating by the divergence of the heat flux $\nabla\cdot\boldsymbol{F}^Q$ and by the dissipation of turbulent kinetic energy per unit mass ϵ. The middle part of Eqn. (1) illustrates how the work performed by the environment on the fluid parcel due to its change in

90   volume, $-P\mathrm{d}v$, at pressure P, changes the internal energy $\mathrm{d}u$, while the first part of the equation follows since specific enthalpy is defined by $h = u + Pv$. The molecular, boundary and radiative fluxes of heat are represented by $\boldsymbol{F}^Q$, and the contribution of the non-conservative nature of Absolute Salinity to the First Law is ignored here (this is discussed in the two paragraphs following Eqn. (A.21.13) in Appendix A.21 of the TEOS-10 Manual, IOC et al., 2010, where this contribution was shown to be negligible). The detailed derivation of the First Law (starting from the conservation of total energy) can be found in

95   Appendix B of IOC et al., 2010.

Clausius (1876) considered the cyclic reversible exchange of heat between a control volume and the environment and deduced that there must be a state variable, which he named entropy, η, whose total derivative satisfies the following differential relationship,

$$\mathrm{d}h - v\mathrm{d}P = \mathrm{d}u + P\mathrm{d}v = T\mathrm{d}\eta + \mu\mathrm{d}S_\mathrm{A}. \tag{2}$$

100   This relationship is now called the Fundamental Thermodynamic Relationship (FTR), and importantly, the total differentials represent differences between local equilibrium states (de Groot and Mazur, 1984) that are separated by vanishingly small differences of state variables. This restriction is satisfied for infinitesimally small reversible changes of infinitesimally small seawater parcels, ensuring that, for example, the in-situ temperature T of the seawater parcel is unambiguously defined at all times. Bearing in mind this restriction, the First Law, Eqn. (1), and the FTR, Eqn. (2), may be combined into the following

105   form of the First Law,

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + P\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(T\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right) = -\nabla\cdot\boldsymbol{F}^Q + \rho\epsilon. \tag{3}$$

This version of the First Law may be rearranged into the form,

$$\rho\frac{\mathrm{d}\eta}{\mathrm{d}t} = \frac{\partial}{\partial t}(\rho\eta) + \nabla(\rho\boldsymbol{u}\eta) = -\nabla\cdot\left(\frac{1}{T}\boldsymbol{F}^Q - \frac{\mu}{T}\boldsymbol{F}^S\right) + \boldsymbol{F}^Q\cdot\nabla\left(\frac{1}{T}\right) + \boldsymbol{F}^S\cdot\nabla\left(-\frac{\mu}{T}\right) + \frac{\rho\epsilon}{T}. \tag{4}$$

In doing this rearrangement we have used the evolution equation of Absolute Salinity

110

$$\rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = \frac{\partial}{\partial t}(\rho S_\mathrm{A}) + \nabla(\rho\boldsymbol{u}S_\mathrm{A}) = -\nabla\cdot\boldsymbol{F}^S, \tag{5}$$

where $\boldsymbol{F}^S$ is the flux of Absolute Salinity caused by molecular diffusion. This form (5) of an evolution equation for a variable is the "conservative" form, because the right-hand side of this equation is minus the divergence of a molecular flux (see the formal definition of a conservative variable, Eqn. (A.8.1) of the TEOS-10 Manual, IOC et al., 2010). Using Gauss' integral theorem, it is concluded that the total amount of such a variable in the ocean is then set only by the flux of the variable at the

115   ocean boundaries. A test of the conservative nature (or otherwise) of an oceanographic variable is to consider the turbulent

mixing of two seawater parcels. If the total amount of the variable in the final mixed product is the sum of the amounts in the two original parcels, then the variable is conservative. This is rigorously true for enthalpy in an isobaric mixing process (apart from the dissipation of turbulent kinetic energy which needs to be budgeted separately) and is close to being true of Conservative Temperature (McDougall, 2003, Graham and McDougall, 2013).

120   The entropy evolution equation in the form (4) shows that entropy is not a conservative variable because of the three terms $\boldsymbol{F}^{\mathrm{Q}} \cdot \nabla(1/T)$, $\boldsymbol{F}^{\mathrm{S}} \cdot \nabla(-\mu/T)$, and $\rho\epsilon/T$. The Second Law of Thermodynamics can be stated in many forms, and when considering the mixing of a pair of fluid parcels, the Second Law requires that the entropy of the final mixture must be not less than the sum of the entropies contained in the initial two fluid parcels. This is clearly true for the last term in Eqn. (4) because the dissipation of turbulent kinetic energy, ϵ, is always non-negative. The non-negative production of entropy means that the

125   terms in Eqn. (4) involving the molecular fluxes of heat $\boldsymbol{F}^{\mathrm{Q}}$ and salt $\boldsymbol{F}^{\mathrm{S}}$, namely $\boldsymbol{F}^{\mathrm{Q}} \cdot \nabla(1/T)$ and $\boldsymbol{F}^{\mathrm{S}} \cdot \nabla(-\mu/T)$, also need to be non-negative, and this requirement is shown by Landau and Lifshitz (1959) to be satisfied when the Gibbs function, g, satisfies $g_{TT} < 0$ and $g_{S_A S_A} > 0$. The TEOS-10 Gibbs function of seawater satisfies this thermodynamic stability condition.

To understand and quantify the non-conservative production of entropy when turbulent mixing occurs between different seawater parcels, a different approach is required because the production terms $\boldsymbol{F}^{\mathrm{Q}} \cdot \nabla(1/T)$ and $\boldsymbol{F}^{\mathrm{S}} \cdot \nabla(-\mu/T)$ in Eqn. (4)

130   involve complicated products of the gradients of in situ temperature, of pressure, and of salinity, bearing in mind that the molecular fluxes of heat and salt contain contributions from baro-diffusion, and the Soret and Dufour effects (see Appendix B of IOC et al., 2010). These products of gradients would need to be averaged over the time and space of the turbulent mixing event. Such a formidable averaging task has never been undertaken. Fortunately, there is a much simpler way of evaluating the non-conservative production of entropy due to turbulent mixing, namely, to exploit the fact that entropy is a state function,

135   so that it can be expressed as a function of salinity, enthalpy, and pressure, $\breve{\eta}(S_A, h, P)$. Graham and McDougall (2013) used this approach to show that the production of entropy, $\delta\eta$, that occurs when two seawater parcels of equal mass mix to completion is

$$\delta\eta = -\tfrac{1}{8}\{\breve{\eta}_{hh}(\Delta h)^2 + 2\breve{\eta}_{hS_A}\Delta h \Delta S_A + \breve{\eta}_{S_A S_A}(\Delta S_A)^2\},\qquad(6)$$

where Δh and ΔS_A are the differences between the values of enthalpy and Absolute Salinity of the initial seawater parcels.

140   Graham and McDougall (2013) also developed the evolution equation for entropy in the presence of turbulent epineutral and dianeutral turbulent mixing (their Eqn. 48). This work is summarised in section A.16 of IOC et al. 2010. There it is shown that the sign-definite production of entropy for the turbulent mixing process places exactly the same requirements on the Gibbs function of seawater as does molecular diffusion, namely that $g_{TT} < 0$ and $g_{S_A S_A} > 0$.

The $Td\eta$ term in Eqn. (2) describes the exchange of heat and constitutes the original definition of entropy by Clausius

145   (1876), so that, for example, if a seawater parcel is heated reversibly at constant pressure and salinity, this input of heat is equal to both dh and $Td\eta$. The last term, μdS_A, describes the influence of changes in Absolute Salinity on enthalpy at constant entropy and pressure, that is, μ is the relative chemical potential defined by $\mu = \partial h/\partial S_A|_{\eta,P}$, which is also given by $\mu = \partial u/\partial S_A|_{v,P}$. While the FTR relates the total derivatives of the several thermodynamic quantities only for thermodynamically

reversible processes, importantly all of enthalpy, internal energy, specific volume, entropy, and relative chemical potential are
150   state variables so that they can be expressed as functions of, for example, (S_A, T, P). That is, after a series of irreversible
processes (such as events in which turbulent kinetic energy is dissipated), the differences in these variables are still given by
the differences in their functional expressions; specifically, the difference in entropy after an irreversible process is given by
the difference in the values of $\eta(S_A, T, P)$ that occur over the time interval of the process (the final value of $\eta(S_A, T, P)$ minus
the initial value) if and only if the sample under consideration is at equilibrium before and after that process. In practice the
155   FTR is used extensively in the construction of the thermodynamic potential that describes seawater, so that all the
thermodynamic variables are related to each other using equations that apply for reversible processes. Because each of these
thermodynamic variables are state variables, the use of the FTR is justified; its use essentially finds a route through parameter
space caused by a series of reversible processes, even though there are other ways of traversing between two (S_A, T, P) states
that involve irreversible processes. Thermodynamic state variables, by definition, never depend on the process history that
160   has led to the actual state. Rather, "the actual state of the world depends only on the most recent past, without being directly
influenced, so to speak, by the memory of the distant past" wrote Henri Poincaré in a report to the International Congress of
Physics in 1900 (Poincaré and Goroff, 1993, pI18).

Two important characteristics of oceanographic variables are (i) whether they are "potential" variables, and (ii) whether
they are "conservative" variables; these characteristics are discussed at length in sections A.8 and A.9 of IOC et al., 2010. A
165   "potential" variable is independent of pressure when the pressure change occurs isentropically and without change in Absolute
Salinity. For example, Absolute Salinity is a potential variable since if the salt flux divergence $\nabla \cdot \boldsymbol{F}^S$ is zero then the salinity
of a fluid parcel is unchanged even though its pressure may vary; this follows from the conservation equation of Absolute
Salinity, $\rho dS_A/dt = -\nabla \cdot \boldsymbol{F}^S$ of Eqn. (5) (where, again, we are neglecting the influence of the non-conservative source term
of Absolute Salinity). Similarly, from Eqn. (3) if in addition to being isohaline, if both $\nabla \cdot \boldsymbol{F}^Q = 0$ and $\epsilon = 0$ so that there is
170   no flux of heat across the boundaries of the fluid parcel and no dissipation of turbulent kinetic energy inside the parcel, then
entropy η is also constant, showing that entropy also has the "potential" property. Potential enthalpy, potential density, and
potential temperature, θ, all have the "potential" property, by construction.

Since Conservative Temperature Θ is defined as being proportional to potential enthalpy, $h(S_A, T_0 + \theta, P_0)$, it is also a
potential variable and can be regarded as a function $\widetilde{\Theta}(S_A, \theta)$, of only S_A and θ. It follows that entropy $\eta = \eta(S_A, T_0 + t, P) = $
175   $\eta(S_A, T_0 + \theta, P_0) = -g_T(S_A, T_0 + \theta, P_0)$ can be expressed as a function of S_A and Θ only, $\eta = \hat{\eta}(S_A, \Theta)$, and is not a separate
function of in-situ pressure. The hat over a variable indicates that it is being expressed as a function of Conservative
Temperature (rather than in situ temperature $T = T_0 + t$). Note that molecular diffusion fluxes heat down the temperature
gradient (up the gradient of $1/T$) and, in the presence of gravity, does not act to eliminate entropy gradients. In contrast,
turbulent mixing acts to flux "potential" properties down the gradients of these "potential" variables, but, in the presence of
180   gravity, establishes a gradient of in situ temperature.

The Fundamental Thermodynamic Relationship of Eqn. (2) can be regarded as an expression for the total derivative of enthalpy when it is expressed as a function of (S_A, η, P) and the three partial derivatives with respect to these variables are μ, T and v. Thermodynamically speaking, this form of enthalpy, namely $\breve{h}(S_A, \eta, P)$, is the most natural thermodynamic potential of seawater (here the cup over a variable's name indicates that it is being expressed as a function of entropy). Its "heat-like"

185   argument, entropy, is a "potential" variable, and this property leads to simple expressions for quantities such as the adiabatic and isentropic compressibility, $\kappa = -\breve{h}_P^{-1}\breve{h}_{PP}$. But entropy, η, is neither a measured quantity (c.f. in situ temperature T), nor is it an almost conservative quantity (c.f. Conservative Temperature Θ). The Gibbs function $g(S_A, T, P)$ has proven to be a practically more useful thermodynamic potential than $\breve{h}(S_A, \eta, P)$ because its "heat-like" argument, T, is a measured quantity, even though T is neither a "potential" variable nor is it an almost conservative variable. We note, from the FTR, that an

190   alternative to $\breve{h}(S_A, \eta, P)$ as a thermodynamic potential is internal energy as a function of (S_A, η, v) where specific volume (or density) takes the place of pressure as an independent variable and the partial derivates are μ, T and $-P$. For completeness it may be mentioned that the thermodynamic potential of pure water, which is part of TEOS-10, is a Helmholtz function expressed as a function of (T, v) which permits the joint description of liquid and gaseous water by a single mathematical expression (Wagner and Pruß, 2002).

195   Importantly, all of those thermodynamic potentials obey the three general criteria which characterise axiomatic systems (Feistel, 2008, 2018). The potentials, by their definition, intrinsically exhibit *consistency* (that is, they exclude the possibility of deducing two different mathematical expressions for the same property), *independence* (that is, they prevent any derived function from being deducible from another one) and *completeness* (that is, they provide an equation for every equilibrium thermodynamic bulk property). For an arbitrary given thermodynamic property equation, the validity of these criteria is not

200   trivially fulfilled and needs to be demonstrated in order to regard that equation a thermodynamic potential.

In this paper we derive a new thermodynamic potential of seawater, $\hat{\phi}(S_A, \Theta, P)$, whose "heat-like" variable is Conservative Temperature, Θ, which, while not being a measured quantity, is a "potential" variable, and is also close to being 100% conservative. That is, of the three desirable attributes of the "heat-like" argument of a thermodynamic potential, namely (i) being a measured quantity, (ii) being a "potential" variable, and (iii) being nearly conservative, Θ has two of these attributes,

205   while both T and η have only one attribute each.

2 Thermodynamic potentials versus knowledge of both enthalpy and entropy

2.1 The case of $h(S_A, T, P)$ and $\eta(S_A, T, P)$

The Gibbs function $g(S_A, T, P)$ is given by enthalpy minus the product of entropy and the absolute temperature, $g = h - T\eta$. The total differential of the Gibbs function, $dg = dh - \eta dT - T d\eta$, can be found from the FTR (Eqn. 2) to be

210
$$dg = \mu dS_A - \eta dT + v dP, \tag{7}$$

with the three partial derivatives of $g(S_A, T, P)$ being μ, $-\eta$ and v. We can think of the Gibbs function being formed from laboratory-derived measurements of these three partial derivatives. Note that the FTR follows from this expression for the total derivative of the Gibbs function *if and only if* one also knows that $g = h - T\eta$; we will return to this later.

This discussion of the derivation, definition and use of the Gibbs function can be approached via a slightly different line of reasoning. We introduce this alternative line of reasoning because it resonates with the same line of reasoning that we use to derive/justify the thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ of this paper. In this alternative way of approaching the Gibbs function, one again takes $\mu(S_A, T, P)$, $\eta(S_A, T, P)$ and $v(S_A, T, P)$ to be known functions of seawater, but instead of forming a Gibbs function $g(S_A, T, P)$ according to its total differential, Eqn. (7), we instead form the total derivative of enthalpy in the functional form (S_A, T, P), by substituting the total differential of entropy, $d\eta = \eta_{S_A} dS_A + \eta_T dT + \eta_P dP$, into the FTR, obtaining,

$$\mathrm{d}h = \left(\mu + T\eta_{S_A}\right)\mathrm{d}S_A + T\eta_T \mathrm{d}T + (v + T\eta_P)\mathrm{d}P. \tag{8}$$

with the three partial derivatives of $h(S_A, T, P)$ being $\left(\mu + T\eta_{S_A}\right) = (\mu - T\mu_T)$, $T\eta_T$ and $(v + T\eta_P) = (v - Tv_T)$ respectively. We can think of enthalpy being formed from these three partial derivatives using laboratory-derived measurements of $\mu(S_A, T, P)$, $\eta(S_A, T, P)$ and $v(S_A, T, P)$. Note that the FTR, $\mathrm{d}h - v\mathrm{d}P = T\mathrm{d}\eta + \mu\mathrm{d}S_A$, follows directly from this expression for the total derivative of enthalpy by using the total differential of entropy, $d\eta = \eta_{S_A} dS_A + \eta_T dT + \eta_P dP$. Having formed $h(S_A, T, P)$ by integrating its differential definition, Eqn. (8), and also knowing $\eta(S_A, T, P)$, all the thermodynamic properties can be found. Despite that, however, the combination of $h(S_A, T, P)$ and $\eta(S_A, T, P)$ is not fully equivalent to a thermodynamic potential as the function pair violates the criterion of *independence*. This is evident from the heat capacity for which two different equations can be found,

$$c_P = \left(\frac{\partial h}{\partial T}\right)_{S,P} = T\left(\frac{\partial \eta}{\partial T}\right)_{S,P}. \tag{9}$$

Therefore, any suitable thermodynamic potential must intrinsically ensure the validity of the consistency condition,

$$\left(\frac{\partial h}{\partial T}\right)_{S,P} \equiv T\left(\frac{\partial \eta}{\partial T}\right)_{S,P}. \tag{10}$$

It is easily verified that this identity in fact holds for the TEOS-10 Gibbs function.

The last step in this alternative narrative that leads to the Gibbs function is to note that it is more convenient to combine the knowledge contained in $h(S_A, T, P)$ and $\eta(S_A, T, P)$ into the single function, $g = h - T\eta$, whose T derivative gives $-\eta$ (using $h_T = T\eta_T$), and enthalpy can then be found by simply adding $T\eta$ to $g = h - T\eta$.

Comparing the traditional with the alternative reasoning surrounding the Gibbs function, we see that via the traditional approach, in order to arrive at the FTR one needs to know both (i) how the Gibbs function is found from the observed data, namely, the differential expression Eqn. (7), as well as (ii) the definition of the Gibbs function in terms of enthalpy and entropy, $g = h - T\eta$. In contrast, the alternative approach uses the same observed data of of $\mu(S_A, T, P)$, $\eta(S_A, T, P)$ and $v(S_A, T, P)$ to define specific enthalpy according to Eqn. (8), which is already the FTR. In this alternative approach both entropy

$\eta(S_A, T, P)$ and enthalpy $h(S_A, T, P)$ are now known and all the thermodynamic variables follow. That is, having formed enthalpy $h(S_A, T, P)$ from its partial derivatives (Eqn. 8) there is no need for an additional definition; the Gibbs function and its definition do not need to be introduced. Rather, the two functions $h(S_A, T, P)$ and $\eta(S_A, T, P)$ can be regarded as a pair of functions that together define all the thermodynamic properties of seawater. In this alternative reasoning, the Gibbs function $g(S_A, T, P)$ is introduced as the last step, for the sole purpose that all the thermodynamic quantities can be derived from a single function rather than having to carry along the two separate functions $h(S_A, T, P)$ and $\eta(S_A, T, P)$.

2.2 The case of $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$

Now we discuss the case of Conservative Temperature Θ taking the place of in situ temperature T as the independent temperature variable. Appendix P of IOC et al., 2010 has shown that if expressions for both enthalpy and entropy are known in the functional forms $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$, this information is sufficient to derive all the thermodynamic quantities. This can be understood from realizing that $\eta = \hat{\eta}(S, \Theta,)$ is equivalent to providing the implicit definition of $\Theta = \breve{\Theta}(S, \eta)$ so that knowledge of $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ is equivalent to knowing $\breve{h}(S_A, \eta, P) = \hat{h}(S, \breve{\Theta}(S, \eta), P)$ so that the three partial derivatives of $\breve{h}(S_A, \eta, P)$ (from which the FTR can be written down) can be written in terms of the partial derivatives of $\hat{h}(S, \Theta, P)$ and $\hat{\eta}(S, \Theta,)$ (see Table 1 for these expressions). IOC et al., 2010 stopped short of finding a single thermodynamic potential in terms of (S_A, Θ, P); this is done in the present paper.

First, there are two useful features that follow directly from the definition of Conservative Temperature as being proportional to potential enthalpy referenced to P_0, i.e. $c_p^0 \Theta \equiv \hat{h}(S_A, \Theta, P_0)$. The first feature is that that entropy has the functional form $\eta = \hat{\eta}(S_A, \Theta)$ and is not a function of pressure; this feature is due to Conservative Temperature possessing the "potential" property (as does both entropy and Absolute Salinity). The second feature is the very simple form of the first derivatives of enthalpy at P_0, namely that $\hat{h}_\Theta(S_A, \Theta, P_0) = c_p^0$ and $\hat{h}_{S_A}(S_A, \Theta, P_0) = 0$. Specific enthalpy is now defined in terms of (S_A, Θ, P) from its total differential,

$$\mathrm{d}h = \left(\mu + T\hat{\eta}_{S_A}\right)\mathrm{d}S_A + T\hat{\eta}_\Theta \mathrm{d}\Theta + v\mathrm{d}P, \tag{11}$$

which is simply a rearranged version of the Fundamental Thermodynamic Relation (FTR), $\mathrm{d}h - v\mathrm{d}P = \mu \mathrm{d}S_A + T\mathrm{d}\eta$, since $\mathrm{d}\eta = \hat{\eta}_{S_A}\mathrm{d}S_A + \hat{\eta}_\Theta \mathrm{d}\Theta$. Knowledge of $\hat{\mu}(S_A, \Theta, P)$, $\hat{T}(S_A, \Theta, P)$ and $\hat{v}(S_A, \Theta, P)$ are needed to find these partial derivatives in Eqn. (11), while $\hat{\eta}(S_A, \Theta)$ can be found from integrating the first two partial derivatives of Eqn. (11) evaluated at P_0, namely $0 = \hat{\mu}(S_A, \Theta, P_0) + (T_0 + \theta)\hat{\eta}_{S_A}$ and $c_p^0 = (T_0 + \theta)\hat{\eta}_\Theta$, where $(T_0 + \theta) = \hat{T}(S_A, \Theta, P_0)$, together with the arbitrary assignment $\hat{\eta}(S_{SO}, 0°C) = 0$. After having formed both $\hat{\eta}(S_A, \Theta)$ and $\hat{h}(S_A, \Theta, P)$ from the differential form Eqn. (11), we know from Appendix P of IOC et al. (2010) that all the thermodynamic variables of seawater follow, so that if one is willing to define seawater properties using these two functions, no more work is required. However it is convenient to define all the thermodynamic properties from a single thermodynamic potential function, and in this paper we have found such a function,

$\hat{\phi}(S_A, \Theta, P)$, given by Eqns. (13) or (14) below, which contains the information of both $\hat{\eta}(S_A, \Theta)$ and $\hat{h}(S_A, \Theta, P)$ and from which these two functions can be found. Having a thermodynamic potential ensures not only that every thermodynamic

275   property can be derived from it, but also, importantly, that there is only one expression for each thermodynamic quantity.

Note that in the (S_A, Θ, P) case, specific volume, $v = \hat{h}_P$, internal energy, $u = \hat{h} - P\hat{h}_P$, and the isentropic compressibility, $\kappa = -\hat{h}_{PP}/\hat{h}_P$, depend only on enthalpy, $\hat{h}(S_A, \Theta, P)$, and are independent of entropy, $\hat{\eta}(S_A, \Theta)$. This contrasts with the (S_A, T, P) case where specific volume, $v = h_P - T\eta_P$, internal energy, $u = h - Ph_P + TP\eta_P$, and the isentropic compressibility, $\kappa = -(h_{PP}\eta_T - h_T\eta_{PP} + \eta_P^2)/(h_P\eta_T - h_T\eta_P)$, depend not only on enthalpy, $h(S_A, T, P)$, but also on

280   entropy, $\eta(S_A, T, P)$. The simpler expressions for specific volume, internal energy, the isentropic compressibility and the sound speed in the (S_A, Θ, P) case compared with the (S_A, T, P) case is also a feature of the $\check{h}(S_A, \eta, P)$ thermodynamic potential and is due to the Conservative Temperature variable being a "potential" variable.

In the next section we introduce the new thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ and then compare its derivation and properties with the corresponding derivation and properties of the Gibbs function. This leads to a discussion of whether

285    $\hat{\phi}(S_A, \Theta, P)$ is as thermodynamically fundamental as the Gibbs function $g(S_A, T, P)$.

3 A thermodynamic potential of seawater in terms of Conservative Temperature

3.1 Defining the thermodynamic potential $\widehat{\phi}(S_A, \Theta, P)$

Since Conservative Temperature Θ is the temperature variable that is recommended for use in marine science under TEOS-10

290   (taking the place of potential temperature θ) it is of interest to determine if a thermodynamic potential of seawater can be found in terms of Θ. From Appendix P of IOC et al. (2010), and section 2 above, we know that if we can find a single function from which enthalpy and entropy can be found in the functional forms $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$, our aim will have been achieved. It is possible to find several such functions from which $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ can be derived, and some of these are described in Appendix A. The one we suggest, Eqn. (13) below, is motivated from section 5 of Feistel (2008) (the paper that

295   derived the Gibbs function of seawater as incorporated into TEOS-10), where the differential expression for the Gibbs function, Eqn. (3), was integrated along an arbitrary but convenient path through (S_A, T, P) space, first with respect to Absolute Salinity from the Absolute Salinity of Standard Seawater S_{SO} at $T = T_0$ and $P = P_0$, then with respect to in situ temperature at the given Absolute Salinity and at $P = P_0$, and finally with respect to pressure at the given values of Absolute Salinity and in situ temperature, so that the Gibbs function can be written as

300    $$g(S_A, T, P) = \int_{S_{SO}}^{S_A} \mu(S_A', T_0, P_0) \, dS_A' - \int_{T_0}^{T} \eta(S_A, T', P_0) \, dT' + \int_{P_0}^{P} v(S_A, T, P') \, dP'. \qquad (12)$$

where $g(S_{SO}, T_0, P_0)$ was chosen to be zero with no loss of generality. This integration method results in a path-independent function $g(S_A, T, P)$ if and only if the three integrands satisfy the integrability conditions (Maxwell relations) $\mu_T = -\eta_{S_A}$, $\mu_P = v_{S_A}$ and $-\eta_P = v_T$.

In this paper we adopt a similar integration of entropy and specific volume, but now with respect to Conservative Temperature (rather than in situ temperature) to define the new thermodynamic potential of seawater $\hat{\phi}(S_A, \Theta, P)$ as

$$\hat{\phi}(S_A, \Theta, P) = -\int_0^{\Theta} \hat{\eta}(S_A, \Theta')d\Theta' + \int_{P_0}^{P} \hat{v}(S_A, \Theta, P')dP'. \tag{13}$$

or equivalently (since we know that $v = \hat{h}_P$ and $c_p^0 \Theta \equiv \hat{h}(S_A, \Theta, P_0)$)

$$\hat{\phi}(S_A, \Theta, P) = -\int_0^{\Theta} \hat{\eta}(S_A, \Theta')d\Theta' + \hat{h}(S_A, \Theta, P) - c_p^0 \Theta. \tag{14}$$

Note that (i), entropy $\hat{\eta}(S_A, \Theta)$ is not a function of pressure, and (ii), unlike in Eqn. (12), we find that in Eqn. (13) we do not need to perform a salinity integral of relative chemical potential μ in order to fully define the thermodynamic properties of seawater from $\hat{\phi}(S_A, \Theta, P)$. Expressions for $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ are obtained from $\hat{\phi}(S_A, \Theta, P)$ as follows,

$$\hat{h}(S_A, \Theta, P) = c_p^0 \Theta + \hat{\phi}(S_A, \Theta, P) - \hat{\phi}(S_A, \Theta, P_0) = c_p^0 \Theta + \int_{P_0}^{P} \hat{\phi}_P(S_A, \Theta, P')dP', \tag{15}$$

$$\hat{\eta}(S_A, \Theta) = -\hat{\phi}_{\Theta}(S_A, \Theta, P_0) = -\hat{\phi}_{\Theta}(S_A, \Theta, P) + \int_{P_0}^{P} \hat{\phi}_{P\Theta}(S_A, \Theta, P')dP', \tag{16}$$

and from Appendix P of IOC et al., 2010, we know that all the thermodynamic variables follow once we have expressions for $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$. For example, the conversion formula of Conservative to in-situ temperature follows from $\hat{\phi}(S_A, \Theta, P)$ to be

$$T(S, \Theta, P) = \frac{\hat{h}_{\Theta}}{\hat{\eta}_{\Theta}} = -\frac{c_p^0 + \hat{\phi}_{\Theta}(S_A, \Theta, P) - \hat{\phi}_{\Theta}(S_A, \Theta, P_0)}{\hat{\phi}_{\Theta\Theta}(S_A, \Theta, P_0)}. \tag{17}$$

Hence, we conclude that $\hat{\phi}(S_A, \Theta, P)$, defined by Eqn. (13 or 14), is a thermodynamic potential of seawater. The expressions for several thermodynamic variables in terms of $\hat{\phi}(S_A, \Theta, P)$ can be found in Appendix C.

In summary, we are using polynomial fits to entropy and enthalpy (or equivalently, specific volume), as functions of Conservative Temperature, knowing from Appendix P of IOC et al. 2010 that these fits in the forms $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ are sufficient to define all the thermodynamic variables of seawater. We have then found a way, Eqns. (13) or (14), to combine these two polynomial functions into one function from which both $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ can be found.

3.2 Is the thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ equivalent to the Gibbs function?

In section 2 we suggested that enthalpy in the functional form $\breve{h}(S_A, \eta, P)$ is the most natural thermodynamic potential, because its total differential expression is the Fundamental Thermodynamic Relationship (FTR), Eqn. (2). In contrast, forming the Gibbs function from "observations" (that is, knowledge) of $\mu(S_A, T, P)$, $\eta(S_A, T, P)$ and $v(S_A, T, P)$, using the total

differential $\mathrm{d}g = \mu\mathrm{d}S_A - \eta\mathrm{d}T + v\mathrm{d}P$ is not equivalent to the FTR since there is no link to the total differentials of either
330   enthalpy or internal energy. Rather, to proceed from knowledge of the total differential of the Gibbs function to the FTR one
needs the additional knowledge that $g = h - T\eta$.

     In section 2 we introduced an alternate route to deriving the Gibbs function, using knowledge/observations of $\mu(S_A, T, P)$,
$\eta(S_A, T, P)$ and $v(S_A, T, P)$ together with the differential form Eqn. (8) of enthalpy to find enthalpy in the form $h(S_A, T, P)$,
which embodies the FTR. The combination of the information in $h(S_A, T, P)$ and $\eta(S_A, T, P)$ serves to define all the
335   thermodynamic quantities of seawater, and the FTR follows from Eqn. (8) without the need to introduce another function. The
last step in this discussion of the Gibbs function is to introduce it as $g(S_A, T, P) = h(S_A, T, P) - T\eta(S_A, T, P)$ for the sole
purpose that all the thermodynamic quantities can be derived from a single function.

     Similarly, we showed that in the (S_A, Θ, P) case, knowledge/observations of $\hat{\mu}(S_A, \Theta, P)$, $\hat{T}(S_A, \Theta, P)$ and $\hat{v}(S_A, \Theta, P)$
together with the differential form Eqn. (11) gives both enthalpy and entropy in the forms $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ which also
340   embody the FTR. Again, a single thermodynamic potential is not needed either to arrive at the FTR, or to be able to derive all
the thermodynamic quantities of seawater. In both the (S_A, T, P) and (S_A, Θ, P) cases a single thermodynamic potential can be
found; in one case as $g(S_A, T, P) = h(S_A, T, P) - T\eta(S_A, T, P)$ and in the other as (Eqn. 14), $\hat{\phi}(S_A, \Theta, P) = \hat{h}(S_A, \Theta, P) -$
$c_p^0\Theta - \int_0^\Theta \hat{\eta}(S_A, \Theta')\mathrm{d}\Theta'$.

     We conclude that the new thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ and the Gibbs function $g(S_A, T, P)$ are equivalent
345   thermodynamic potentials of seawater. Both thermodynamic potentials are found from "observations" of, in one case μ, η and
v, and in the other case μ, T and v, to constrain various derivatives of either $h(S_A, T, P)$ or $\hat{h}(S_A, \Theta, P)$, from which the FTR
immediately follows. All the thermodynamic properties of seawater can be derived from these expressions for enthalpy along
with their corresponding expressions for entropy. Given these pairs of expressions for enthalpy and entropy, corresponding
thermodynamic potential functions can be found in the form of the Gibbs function or in the form of $\hat{\phi}(S_A, \Theta, P)$. This
350   summarizes the identical nature of the derivations of the two thermodynamic potentials from the viewpoint of the slightly
different derivation of the thermodynamic potentials as described in section 2. In Appendix D we describe the equivalence of
the two potential functions on the basis of their differential expressions and their definitions.

     Having argued that the two thermodynamic potentials, $g(S_A, T, P)$ and $\hat{\phi}(S_A, \Theta, P)$ are equivalent, we add a practical caveat
regarding how $\hat{\phi}(S_A, \Theta, P)$ has actually been found; that is, how we formed the polynomial expressions for $\hat{v}(S_A, \Theta, P)$ and
355    $\hat{\eta}(S_A, \Theta)$, that appear in the definition of $\hat{\phi}(S_A, \Theta, P)$ in Eqn. (13). First, all the most accurate data of thermodynamic quantities
(such as specific volume, sound speed, isobaric specific heat capacity, "heat of mixing", temperature of maximum density,
freezing point depression, etc.) were absorbed into the TEOS-10 Gibbs function of seawater $g(S_A, T_0 + t, P)$ (Feistel 2003,
2008). It is natural to absorb this information into a Gibbs function because all the laboratory data were obtained at measured
values of in situ temperature, and the Gibbs function has in situ temperature as its "heat-like" independent variable. Second,

360   the conversion between in situ and potential temperature used the implicit relationship $g_T(S_A, T_0 + t, P) = g_T(S_A, T_0 + \theta, P_0)$ which involves the Gibbs function. Third, the conversion between potential temperature and Conservative Temperature used the Gibbs function-based equation of potential enthalpy, $h(S_A, T_0 + \theta, P_0)$, which is equated to $c_p^0 \Theta$. Fourth, using this conversion between t and Θ we were able, in Roquet et al. (2015), to form a polynomial expression for $\hat{v}(S_A, \Theta, P)$ from the Gibbs function-based values of $v = g_P(S_A, T_0 + t, P)$. Fifth, and lastly, using the now known conversion between θ and Θ,

365   we are able in this paper to form an algorithm for $\hat{\eta}(S_A, \Theta)$ from the Gibbs function-based values of $\tilde{\eta}(S_A, \theta) = -g_T(S_A, T_0 + \theta, P_0)$. In summary, we have used the TEOS-10 Gibbs function of seawater to relate the different temperature variables and to evaluate both specific volume and entropy, which were then fitted with polynomials in the three independent variables S_A, Θ, P. In performing these polynomial fits, we ensured that in the oceanographic range of salinity, the $\hat{v}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ polynomials fitted the Gibbs function-derived values of specific volume and entropy more accurately than these

370   variables are known from the underlying laboratory measurements. In this way we claim that the thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ and the TEOS-10 Gibbs function $g(S_A, T_0 + t, P)$ are equally accurate in representing the thermodynamic properties of seawater in the oceanographically relevant range of salinity.

4   An approximate polynomial expression for entropy

4.1 Beginning with an analogy with a perfect gas

375   In order to construct an accurate polynomial expression for the thermodynamic potential of seawater $\hat{\phi}(S_A, \Theta, P)$ of Eqn. (13) we will integrate the 75-term polynomial expression for specific volume $\hat{v}(S_A, \Theta, P)$ of Roquet *et al.* (2015) with respect to pressure to obtain $\hat{h}(S_A, \Theta, P)$ (using the fact that $\hat{h}_P = v$), and we also need to find an accurate expression for entropy, $\hat{\eta}(S_A, \Theta)$, which we will develop in this section.

     The specific entropy of a perfect gas can be expressed in terms of the Celsius potential temperature θ (with reference sea

380   pressure of $p_r = 0$ dbar; that is, reference absolute pressure of $P_r = P_0 \equiv 101\,325$ Pa) by

$$\eta^{gas} = c_p^{gas} \ln(1 + \theta/T_0) \tag{18}$$

where entropy is defined so that it is zero at a Celsius temperature of 0℃ (see Eqn. (J.6) and (J.7) of IOC *et al.* (2010)). In general, the enthalpy and internal energy of a perfect gas is a general function of (only) temperature, but here we have restricted attention to the "calorically perfect gas" where the specific isobaric heat capacity c_p^{gas} is a constant. The enthalpy of a perfect

385   gas (e.g. dry air) is also defined to be zero at a Celsius temperature of 0℃, so the potential enthalpy of a perfect gas is $h^0 = c_p^{gas} \theta$ and if a "conservative temperature of a perfect gas" were to be defined, then it would be simply equal to potential temperature θ.

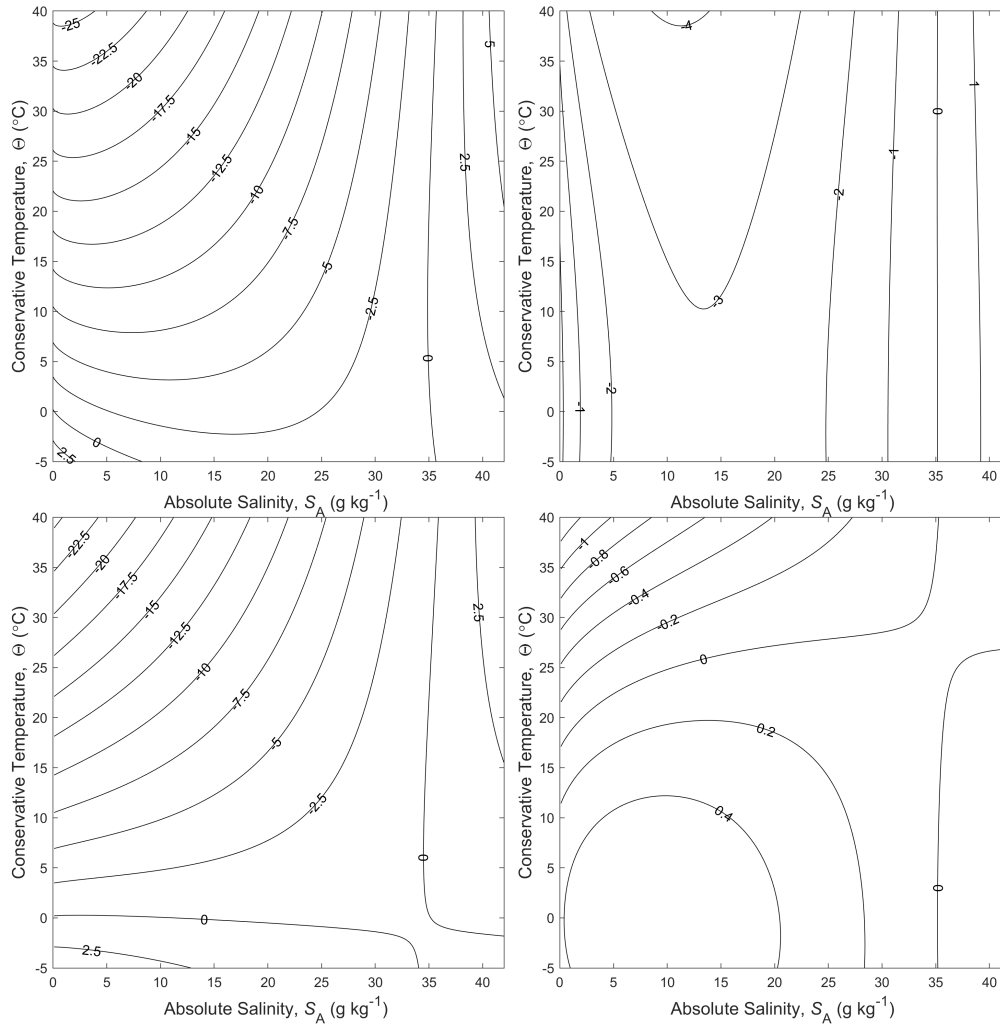



Figure 1. Panels (a) and (b) are contour plots of $c_p^0 \ln(1 + \theta/T_0) - \eta$ and $c_p^0 \ln(1 + \Theta/T_0) - \eta$ respectively, while panels (c) and (d) show $c_p^0 \ln(1 + \theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO}) - \eta$ and $c_p^0 \ln(1 + \Theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO}) - \eta$ respectively. All panels in this figure are in the units of entropy, namely $\mathrm{J\,kg^{-1}\,K^{-1}}$.

One wonders how accurate a correspondingly simple logarithm expression would be for the entropy of seawater, defined by either $c_p^0 \ln(T_0 + \theta) + \text{constant}$ or by $c_p^0 \ln(T_0 + \Theta) + \text{constant}$. The constants can be chosen so that it makes the estimate of entropy zero if $\theta = 0°C$ or $\Theta = 0°C$ in the two cases respectively, since entropy is zero for Standard Seawater ($S_A = S_{SO}$) at this temperature. That is, we examine the two estimates $c_p^0 \ln(1 + \theta/T_0)$ and $c_p^0 \ln(1 + \Theta/T_0)$ as approximations to the entropy of seawater. (Note that for seawater, c_p^0 is approximately four times as large as the isobaric specific heat capacity of

air, c_p^{gas}). The errors in using these two approximate expressions can be seen in Figure 1 (a) and (b). It is seen that the expression involving Conservative Temperature, $c_p^0 \ln(1 + \Theta/T_0)$, is a better approximation to entropy than is the one involving potential temperature, $c_p^0 \ln(1 + \theta/T_0)$, with the maximum error being less by approximately an order of magnitude.

400 The relative accuracies of these approximate expressions to the specific entropy of seawater can be understood from the following expressions for the total differential of entropy in terms of θ and Θ (see Eqns. (A.12.7) and (A..12.8) of IOC et al. 2010),

$$ \mathrm{d}\eta \;=\; c_p(S_A, \theta, P_0)\, \mathrm{d}(\ln[1 + \theta/T_0]) \;-\; \mu_T(S_A, \theta, P_0)\, \mathrm{d}S_A, \qquad (19) $$

$$ \mathrm{d}\eta \;=\; c_p^0 \frac{(T_0+\Theta)}{(T_0+\theta)}\, \mathrm{d}(\ln[1 + \Theta/T_0]) \;-\; \frac{\hat{\mu}(S_A, \Theta, P_0)}{(T_0+\theta)}\, \mathrm{d}S_A. \qquad (20) $$

405 The partial derivative with respect to Absolute Salinity that has been used in Eqn. (19), namely $\tilde{\eta}_{S_A} = \eta_{S_A}(S_A, \theta, P_0)$, is also given by $-\mu_T(S_A, \theta, P_0)$ since both expressions are $-g_{TS_A}(S_A, \theta, P_0)$, while the other partial derivative, $\tilde{\eta}_\theta = c_p(S_A, \theta, P_0)/(T_0 + \theta)$, can be gleaned from $h_T = T\eta_T$ (from Eqn. 8) evaluated at P_0, noting that $c_p(S_A, \theta, P_0) = h_T(S_A, \theta, P_0)$ is the specific isobaric heat capacity of seawater evaluated at P_0 and at the potential temperature θ. The partial derivatives $\hat{\eta}_{S_A}$ and $\hat{\eta}_\Theta$ used in Eqn. (20) can be gleaned from Eqn. (11) evaluated at P_0, noting that $\hat{h}_{S_A}(S_A, \Theta, P_0) = 0$. The contributions of

410 the terms in $\mathrm{d}S_A$ are small in comparison to the leading terms on the right-hand sides of Eqns. (19) and (20), and the specific heat capacity $c_p(S_A, \theta, P_0)$ varies by 5.5% in the ocean whereas the ratio $(T_0 + \Theta)/(T_0 + \theta)$ varies by no more than 0.67%, and this explains why the approximate expression $\eta \approx c_p^0 \ln(1 + \Theta/T_0)$ outperforms $\eta \approx c_p^0 \ln(1 + \theta/T_0)$ by about an order of magnitude.

While the fit to entropy in better in Fig. 1(b) than in Fig. 1(a), neither is particularly accurate for our purposes. For example,

415 in determining potential temperature θ from $\hat{\eta}_\Theta = c_p^0/(T_0 + \theta)$, the remaining error in Fig. 1(b) amounts to an error in potential temperature of approximately 0.5°C while that in Fig 1(a), using $\tilde{\eta}_\theta = c_p(S_A, \theta, P_0)/(T_0 + \theta)$, amounts to about 10°C.

4.2 Adding a simple function of Absolute Salinity

420 The Second Law of Thermodynamics requires that entropy must be produced when mixing occurs, and the approximation $c_p^0 \ln(1 + \Theta/T_0)$ does not allow for the production of entropy when mixing occurs between seawater parcels of different Absolute Salinities but the same value of Conservative Temperature. The TEOS-10 Gibbs-function-derived expression for specific entropy contains the term $a(S_A/S_{SO}) \ln(S_A/S_{SO})$ with the coefficient a being $a = -9.310\,292\,413\,479\,596 \,\mathrm{J\,kg^{-1}\,K^{-1}}$ (this is the value of the coefficient derived from the g_{110} coefficient of the Gibbs

425 function (appendix H of IOC *et al.* (2010)), allowing for our version of the normalization of salinity, (S_A/S_{SO})). This term

was derived by Feistel (2008) to be theoretically correct at very small Absolute Salinities, relying on Plank's theory of ideal solutions and the now-exact value of the molar gas constant. Here we use the slightly different value $a = -9.309\ 495\ 003\ 228\ 781\ J\ kg^{-1}\ K^{-1}$ that comes from a least-squares fit incorporating a particular polynomial form, as described below, and tabulated in appendix B. This slightly different value of a allows a more accurate fit to the entropy data over the whole range of oceanographic salinities rather than only at vanishingly small salinities.

430

The accuracy of the approximate expression $c_p^0 \ln(1 + \Theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO})$ is shown in Figure 1(d). There is no improvement over $c_p^0 \ln(1 + \Theta/T_0)$ near zero Absolute Salinity, but at intermediate salinity values the fit is improved over that of $c_p^0 \ln(1 + \Theta/T_0)$ by approximately an order of magnitude. Over the whole (S_A, Θ) plane this simple theoretically inspired estimate of entropy, illustrated in Figure 1(d) is in error by no more than 0.2% of the full range of entropy. In contrast, when the same expression is used with potential temperature (as in Figure 1(c)) in place of Conservative Temperature, the relative error is 4% of the full range of entropy.

435

4.3 The full expression for $\hat{\eta}(S_A, \Theta)$

In order to obtain an expression for $\hat{\eta}(S_A, \Theta)$ suitable for combining with the 75-term polynomial for specific volume $\hat{v}(S_A, \Theta, P)$ of Roquet *et al.* (2015) to form the thermodynamic potential of seawater $\hat{\phi}(S_A, \Theta, P)$ of Eqn. (13), we have added a polynomial in powers of $s = [S_A/S_{SO}]^{0.5}$ and $\tau = \Theta/40°C$ with the highest power of each being eight, so that our final approximate expression for $\hat{\eta}(S_A, \Theta)$ is

440

$$\hat{\eta}(S_A, \Theta) = c_p^0 \ln(1 + \Theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO}) + P\{8,8\}(s, \tau),\tag{21}$$

and the 45 coefficients of the eighth order bi-polynomial $P\{8,8\}$ are listed in Appendix B. The error of Eqn. (21) in approximating $\hat{\eta}(S_A, \Theta)$ is shown in Fig. 2(a), from which we see that the typical errors are $2 \times 10^{-6}\ J\ kg^{-1}\ K^{-1}$.

445

When the thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ of Eqn. (13 or 14) is used to obtain all the thermodynamic properties of seawater, one of the key variables that is obtained from entropy in the form $\hat{\eta}(S_A, \Theta)$ is the potential temperature θ referenced to P_0, and this is found from the derivative of entropy with respect to Conservative Temperature, namely

$$\hat{\eta}_\Theta = \frac{c_p^0}{(T_0 + \theta)}.\tag{22}$$

450

This relationship was originally derived from the FTR by McDougall (2003) and can be deduced from Eqn. (11); see also Eqn. (A.12.8) of the TEOS-10 Manual (IOC *et al.* (2010)). When the polynomial-based approximate form of $\hat{\eta}(S_A, \Theta)$, Eqn. (21), is used to evaluate the potential temperature from Eqn. (22), the error is as shown in Fig. 2(b), where we see that the typical error is $10\mu K$, with maximum errors of $60\mu K$ at $S_A = 0\ g\ kg^{-1}$. Since this error seems acceptable in oceanographic applications, and since the 75-term polynomial for $\hat{v}(S_A, \Theta, P)$ of Roquet *et al.* (2015) is as accurate as the data to which the

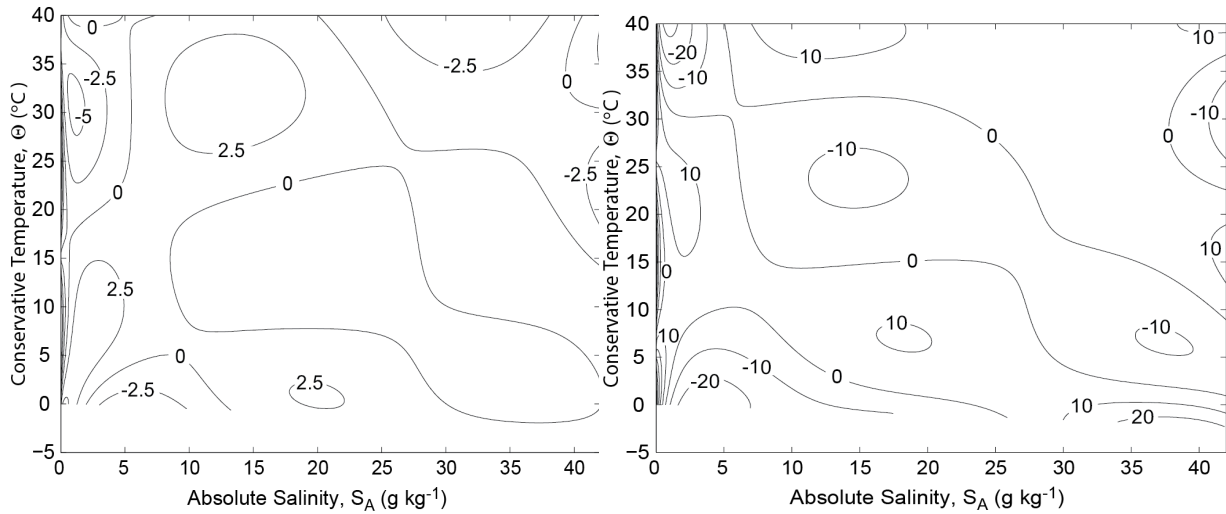
455 original Gibbs function of Feistel (2008) was fitted, we conclude that the thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$ of Eqn. (13 or 14), which is written in terms of Conservative Temperature, is equally as accurate as the Gibbs function $g(S_A, T, P)$, and will therefore prove sufficiently accurate for use in physical oceanography as the thermodynamic potential of seawater in the oceanographic range of salinity.

460

Figure 2. (a) The error in the fit Eqn. (21) to entropy (in units of 10^{-6} J kg^{-1} K^{-1}). (b) The error in evaluating potential temperature θ (in μK) from Eqns. (21) and (22).

5 Numerical Implementation

465 When calculating Conservative Temperature Θ from observations of in situ temperature t using the Gibbs function approach, the first step is to calculate the potential temperature θ at the reference pressure P_0 by equating the values of entropy at the in situ pressure P and at the reference pressure P_0, that is, by solving the implicit relationship $g_T(S_A, T_0 + t, P) = g_T(S_A, T_0 + \theta, P_0)$. The second step is to evaluate the parcel's potential enthalpy, $h(S_A, T_0 + \theta, P_0)$, being $g(S_A, T_0 + \theta, P_0) - (T_0 + \theta)g_T(S_A, T_0 + \theta, P_0)$, and the third step is to divide potential enthalpy by c_p^0. The computationally expensive step is the

470 first, typically involving a Newton-type iterative procedure.

When adopting the approach of the present paper, the conversion from in situ temperature t to Conservative Temperature Θ is also computationally expensive, since, from Eqn. (11), Θ is obtained by finding the zero of the function $\hat{h}_\Theta / \hat{\eta}_\Theta - (T_0 + t)$. This is done by first evaluating both an approximate polynomial for Θ as a function of $(S_A, T_0 + t, P)$, and an approximation to the second derivative of Θ with respect to in situ temperature, by differentiating the polynomial. Then only one pass though

475 the accelerated Newton method of McDougall et al. (2019) is needed to evaluate Θ to machine precision. This code takes approximately the same time to compute Θ as does using the Gibbs function approach described in the previous paragraph.

Having converted observations of in situ temperature into Conservative Temperature, other calculations are more computationally efficient when using the thermodynamic potential function, $\hat{\phi}(S_A, \Theta, P)$, of the present paper rather than using the Gibbs function $g(S_A, T, P)$. For example, during the running of an ocean model, the sea surface temperature is needed as

480 the input temperature for bulk air-sea flux formulae. With the $\hat{\phi}(S_A, \Theta, P)$ approach this is a forward calculation requiring only the evaluation of $\hat{\eta}_\Theta$ since in this case the sea surface temperature, θ, is given by the simple forward expression $(T_0 + \theta) = c_p^0/\hat{\eta}_\Theta$. This calculation is a factor of three less computationally expensive than the corresponding calculation based on the Gibbs function (where an iterative Newton-based algorithm is required).

Similar gains in computational efficiency occur when evaluating potential density at a variety of reference pressures when

485 using $\hat{\phi}(S_A, \Theta, P)$ compared with the Gibbs function approach. These computational gains occur because the potential specific volume, referenced to an arbitrary reference pressure P_r, is available from the forward calculation $\hat{v}(S_A, \Theta, P_r)$, whereas with the Gibbs function approach, the in situ temperature has to be first evaluated at P_r, and this involves an iterative calculation.

6 Conclusions

490 While in situ temperature is relatively simple to measure in the ocean, it is neither a "potential" property, nor is it a "conservative" property, and these deficiencies of in situ temperature have led to the adoption of Conservative Temperature Θ for use in physical oceanography. This switch to Conservative Temperature, since the introduction of TEOS-10 in 2010, has motivated the quest of this paper; to find a thermodynamic potential of seawater in terms of Conservative Temperature, Absolute Salinity and pressure. Roquet et al. (2015) have provided a 75-term polynomial for specific volume in the form

495 $\hat{v}(S_A, \Theta, P)$ and this is the basis for many of the functions in the Gibbs Seawater (GSW) Oceanographic Toolbox of TEOS-10. But to date the conversions between in situ temperature and Conservative Temperature have been done using the TEOS-10 Gibbs function, and this is not 100% consistent with the use of the Roquet et al. polynomial for $\hat{v}(S_A, \Theta, P)$.

When the Roquet et al. (2015) 75-term polynomial for specific volume, $\hat{v}(S_A, \Theta, P)$, is integrated with respect to pressure (noting that $\hat{v} = \hat{h}_P$) and the resulting polynomial for enthalpy is used in the expression for the ratio of the in situ and potential

500 temperatures, $(T_0 + t)/(T_0 + \theta) = \hat{h}_\Theta(S_A, \Theta, P)/c_p^0$, the difference between these temperatures, $|t - \theta|$, compared with evaluating this temperature difference using the Gibbs function, is typically less than 10^{-4}K (the standard deviation of the temperature difference is 4×10^{-5}K; see Table 3 of Roquet et al., 2015). From Figure 2(b) above we see that the use of the $\hat{\eta}(S_A, \Theta)$ expression of the present paper has errors when relating potential and Conservative temperatures of 10^{-5}K. The sum of these tiny temperature differences amounts to less than 10^{-4}K, representing the difference in evaluating Conservative

505 Temperature from in situ temperature using the Gibbs function versus using the Roquet et al. (2015) expression for $\hat{v}(S_A, \Theta, P)$,

together with the present expression for $\hat{\eta}(S_A, \Theta)$. These inconsistencies in temperature between the two approaches are small, being more than an order of magnitude smaller than the underlying experimental error in the laboratory data from which the TEOS-10 Gibbs function was derived. While these differences are small, it is preferable if all the thermodynamic quantities are 100% consistent with each other.

510   In this paper we have provided an accurate expression for entropy as a function of Conservative Temperature, $\hat{\eta}(S_A, \Theta)$, and this can be used in conjunction with Roquet et al.'s $\hat{v}(S_A, \Theta, P)$ to relate in situ temperature and Conservative Temperature. These relationships between the different temperature variables can be performed consistently, to machine precision, and without further reference to the Gibbs function $g(S_A, T, P)$. Appendix P of IOC et al. (2010) has shown that knowledge of both enthalpy and entropy in the functional forms $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ is sufficient to derive all thermodynamic variables,

515 so it seems advisable that when the 75-term polynomial of Roquet et al. 2015 is used, that it is used in conjunction with the expression for $\hat{\eta}(S_A, \Theta)$ of the present paper. The functions in the Gibbs SeaWater (GSW) Oceanographic Toolbox of TEOS-10 (McDougall and Barker, 2011) that need changing are (i) those that calculate one of η, Θ, θ, T from another one, (ii) the adiabatic lapse rate, (iii) the calculation of the three chemical potentials and the Gibbs function, as well as (iv) the new thermodynamic potential $\hat{\phi}(S_A, \Theta, P)$.

520   Converting from observed values of in situ temperature to Conservative Temperature takes a similar amount of computer time using the $\hat{\phi}(S_A, \Theta, P)$ approach of the present paper as when using the Gibbs function, but the subsequent calculations of various temperatures and potential densities are more computationally efficient using the $\hat{\phi}(S_A, \Theta, P)$ approach since these quantities require only simple forward (as opposed to iterative) calculations.

     In the (S_A, Θ, P) case, specific volume, internal energy, the isentropic compressibility and the sound speed depend only on

525 enthalpy, $\hat{h}(S_A, \Theta, P)$, and are independent of entropy, $\hat{\eta}(S_A, \Theta)$, whereas the expressions for the corresponding variables in the (S_A, T, P) case depend not only on enthalpy, $h(S_A, T, P)$, but also on entropy, $\eta(S_A, T, P)$. We conclude that $\hat{h}(S_A, \Theta, P)$ is sufficient to describe the heat-like (enthalpy, internal energy) and buoyancy-like (specific volume, compressibility and sound speed) properties of seawater, while $\hat{\eta}(S_A, \Theta)$ is needed switch between the "temperature-like" variables η, θ, T, Θ and to evaluate the chemical potentials. Thus the $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ pair provides a clean separation of the heat and buoyancy

530 information (derivable from $\hat{h}(S_A, \Theta, P)$ alone) from the information in $\hat{\eta}(S_A, \Theta)$ that is needed to relate the various temperature variables and the chemical potentials. Also, unlike in the (S_A, T, P) case, there is no consistency requirement between $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$.

     Moreover, we have been able to combine the expressions for specific volume and for entropy into a single thermodynamic potential function, $\hat{\phi}(S_A, \Theta, P)$, Eqn. (13), from which all the thermodynamic quantities of seawater can be derived (see

535 Appendix C). This provides a theoretical boost to using Conservative Temperature as the temperature variable in physical oceanography as recommended by TEOS-10 (Valladares et al., 2011a,b). The thermodynamic potential, $\hat{\phi}(S_A, \Theta, P)$, is both complete (in that every thermodynamic property can be derived from it), and consistent (in that there is only one expression for each thermodynamic quantity).

Appendix A: Alternative thermodynamic potentials in terms of Conservative Temperature

540   Eqn. (13) (or Eqn. 14) above is the proposed definition of the thermodynamic potential of seawater defined with respect to Conservative Temperature, but it is not the only possible functional form, and here we present two others. Eqn. (13) resembles the integral definition of the Gibbs function, Eqn. (12), and now we follow an analogy to the $g = h - T\eta$ definition of the Gibbs function which would suggest another form of the thermodynamic potential to be

$$\hat{\varphi}(S_A, \Theta, P) = \hat{h}(S_A, \Theta, P) - [T_0 + \Theta]\hat{\eta}(S_A, \Theta), \tag{A1}$$

545   with the expressions for $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ being found from

$$\hat{h}(S_A, \Theta, P) = c_p^0 \Theta + \hat{\varphi}(S_A, \Theta, P) - \hat{\varphi}(S_A, \Theta, P_0) = c_p^0 \Theta + \int_{P_0}^{P} \hat{\varphi}_P(S_A, \Theta, P') \mathrm{d}P', \tag{A2}$$

$$\hat{\eta}(S_A, \Theta) = -\left[\hat{\varphi}(S_A, \Theta, P_0) - c_p^0 \Theta\right]/[T_0 + \Theta] = -\left[\hat{\varphi}(S_A, \Theta, P) - \int_{P_0}^{P} \hat{\varphi}_P(S_A, \Theta, P') \mathrm{d}P' - c_p^0 \Theta\right]/[T_0 + \Theta]. \tag{A3}$$

Note that the bracket $[T_0 + \Theta]$ in both Eqns. (A1) and (A3) could instead be chosen to be any non-zero function $F(S_A, \Theta)$ of S_A and Θ including a constant such as $T_0 = 273.15°\mathrm{C}$. Such a choice does not affect the way enthalpy is calculated in Eqn.

550   (A2). There seems no fundamental reason to prefer Eqn. (14) over Eqn. (A1), but we offer the following three comments. First, using (14), entropy arises as a temperature derivative of the thermodynamic potential, as it is for the Gibbs function, whereas in (A3) entropy arises as a difference between the thermodynamic potential and $c_p^0 \Theta$. Second, the calculation of entropy from (A3) requires knowledge not only of $\hat{\varphi}(S_A, \Theta, P)$ but also of the function $F(S_A, \Theta)$ (even if this is simply T_0). Third, while we don't imagine that this is relevant, we note in passing that while $\hat{\phi}(S_A, \Theta, P)$ of Eqn. (13 or 14) is not identical

555   to the Gibbs function, $h - T\eta$, it is a little closer than is the function $\hat{\varphi}(S_A, \Theta, P)$ of Eqn. A1, (at $S_A = 0$, it is closer by a factor of two).

Another type of functional from which both enthalpy and entropy can be deduced involves the pressure integral of enthalpy, for example,

$$\hat{\psi}(S_A, \Theta, P) \equiv -P_0 \int_0^{\Theta} \hat{\eta}(S_A, \Theta') \mathrm{d}\Theta' + \int_{P_0}^{P} \hat{h}(S_A, \Theta, P') \mathrm{d}P', \tag{A4}$$

560   with enthalpy and entropy being evaluated as

$$\hat{h}(S_A, \Theta, P) = \hat{\psi}_P(S_A, \Theta, P), \tag{A5}$$

$$\hat{\eta}(S_A, \Theta) = -\hat{\psi}_\Theta(S_A, \Theta, P_0)/P_0 = -\hat{\psi}_\Theta(S_A, \Theta, P)/P_0 + \int_{P_0}^{P} \hat{\psi}_{P\Theta}(S_A, \Theta, P') \mathrm{d}P'/P_0. \tag{A6}$$

This functional form does not seem to offer an advantage over our Eqn. (14). We note in passing that the form Eqn. (A4) of thermodynamic potential works also when potential temperature θ is used in place of Θ as the "heat-like" variable, with the

565   caveat that the $\tilde{\eta}(S_A, \theta)$ and $\tilde{h}(S_A, \theta, P)$ functions need to satisfy the consistency relationship that $(T_0 + \theta) = \tilde{h}_\theta(S_A, \theta, P_0)/\tilde{\eta}_\theta$. In contrast, the use of potential temperature in place of Conservative Temperature in Eqns. (13) and (A1) does not enable the enthalpy and entropy to be deduced in the forms $\tilde{h}(S_A, \theta, P)$ and $\tilde{\eta}(S_A, \theta)$, and hence these forms of seawater thermodynamic potential functions do not work for potential temperature θ. That is, $\tilde{h}(S_A, \theta, P)$ is not a thermodynamic potential, and neither is one found by adopting the forms of either Eqns. (13) or (A1).

Appendix B: The polynomial-based expression for entropy

The polynomial-based expression for specific entropy as a function of Absolute Salinity and Conservative Temperature is given by Eqn. (21) as the sum of the two dominant logarithm terms plus an eighth-order polynomial in the two dimensionless variables $s = [S_A/S_{SO}]^{0.5}$ and $\tau = \Theta/40°C$, where $S_{SO} = 35.165\,04\,\text{g kg}^{-1}$ is the Standard Ocean Reference Salinity (IOC *et al.* (2010)),

$$\hat{\eta}(S_A, \Theta) = c_p^0 \ln(1 + \Theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO}) + P\{8,8\}(s, \tau), \tag{B1}$$

where $T_0 = 273.15\text{K}$ is the Celsius zero point, $c_p^0 = 3991.867\,957\,119\,63\,\text{J kg}^{-1}\,\text{K}^{-1}$, and the least-squares fit gives the constant $a = -9.309\,495\,003\,228\,781\,\text{J kg}^{-1}\,\text{K}^{-1}$ and the eighth order polynomial coefficients given by

$P\{8,8\}(s, \tau) =$
 $(((((((ETA08*\tau+ETA17*s+ETA07)*\tau$
 $+ (ETA26*s+ETA16)*s+ETA06)*\tau$
 $+ ((ETA35*s+ETA25)*s+ETA15)*s+ETA05)*\tau$
 $+ (((ETA44*s+ETA34)*s+ETA24)*s+ETA14)*s+ETA04)*\tau \tag{B2}$
 $+ ((((ETA53*s+ETA43)*s+ETA33)*s+ETA23)*s+ETA13)*s+ETA03)*\tau$
 $+ (((((ETA62*s+ETA52)*s+ETA42)*s+ETA32)*s+ETA22)*s+ETA12)*s+ETA02)*\tau$
 $+ ((((((ETA71*s+ETA61)*s+ETA51)*s+ETA41)*s+ETA31)*s+ETA21)*s+ETA11)*s+ETA01)*\tau$
 $+ (((((((ETA80*s+ETA70)*s+ETA60)*s+ETA50)*s+ETA40)*s+ETA30)*s+ETA20)*s+ETA10)*s+ETA00$

and the 45 constants (each of which has units of $\text{J kg}^{-1}\,\text{K}^{-1}$) are given by

ETA00 = -3.7102436569e-01; ETA10 = 3.0834502223e-04; ETA20 = -3.2916987818e+00;
ETA30 = 7.2818259040e+00; ETA40 = -5.6657256773e+00; ETA50 = 2.8402903938e+00;
ETA60 = -8.9615123138e-01; ETA70 = 1.0035964794e-01; ETA80 = 1.8140964105e-03;
ETA01 = 3.0779211774e-02; ETA11 = 1.5006196848e-03; ETA21 = 1.2029316021e-01;
ETA31 = 3.7464975805e-01; ETA41 = -6.0590428227e-01; ETA51 = 6.4365865093e-02;
ETA61 = 2.4626795446e-02; ETA71 = -1.0335853091e-02; ETA02 = 2.3045093877e+00;
ETA12 = -5.4154968624e-03; ETA22 = -2.5098282844e+00; ETA32 = 1.9163697628e-02;
ETA42 = 9.6230320461e-02; ETA52 = 3.7953034101e-02; ETA62 = -5.1206778774e-04;
ETA03 = -8.4974032876e-01; ETA13 = -1.3727475447e-02; ETA23 = 8.6969911602e-01;
ETA33 = 1.1127539375e-01; ETA43 = -8.7616123860e-02; ETA53 = -1.6250024449e-02;
ETA04 = 4.1807750439e-01; ETA14 = 5.1388181100e-02; ETA24 = -3.1917000611e-01;
ETA34 = -4.4999965986e-02; ETA44 = 3.3822211876e-02; ETA05 = -1.9191736060e-01;
ETA15 = -5.3890029514e-02; ETA25 = 9.3472917957e-02; ETA35 = -4.9779616704e-04;
ETA06 = 6.6066546976e-02; ETA16 = 2.4144978278e-02; ETA26 = -1.2850921670e-02;
ETA07 = -1.3678360946e-02; ETA17 = -4.1337102429e-03; ETA08 = 1.1180283076e-03;

Appendix C: Expressions for thermodynamic variables in terms of $\hat{h}(S_A, \Theta, P)$, $\hat{\eta}(S_A, \Theta)$ and $\hat{\phi}(S_A, \Theta, P)$

C.1 Expressions for entropy and enthalpy in terms of $g(S_A, T, P)$ and $\hat{\phi}(S_A, \Theta, P)$

Eqns. (15) and (16) for entropy η and enthalpy h in terms of $\hat{\phi}(S_A, \Theta, P)$ are compared to the corresponding expressions for these variables in terms of the Gibbs function $g(S_A, T, P)$,

$$\eta \; = \; -\hat{\phi}_\Theta(S_A, \Theta, P_0) \; = \; -\hat{\phi}_\Theta(S_A, \Theta, P) + \int_{P_0}^{P} \hat{\phi}_{P\Theta}(S_A, \Theta, P')\mathrm{d}P'$$

$$= \; -g_T(S_A, T, P) \; = \; -g_T(S_A, T, P_0) - \int_{P_0}^{P} g_{PT}(S_A, T, P')\mathrm{d}P'. \tag{C1}$$

and

$$h \; = \; c_p^0 \Theta + \hat{\phi}(S_A, \Theta, P) - \hat{\phi}(S_A, \Theta, P_0) \; = \; c_p^0 \Theta + \int_{P_0}^{P} \hat{\phi}_P(S_A, \Theta, P')\mathrm{d}P'$$

$$= g(S_A, T, P) - T g_T(S_A, T, P) \; = \; h(S_A, T, P_0) + \int_{P_0}^{P} g_P(S_A, T, P')\mathrm{d}P' - T \int_{P_0}^{P} g_{PT}(S_A, T, P')\mathrm{d}P'. \tag{C2}$$

There are some similarities between these expressions using the two different thermodynamic potentials, and there are differences. When expressed using Conservative Temperature, $\hat{\eta}(S_A, \Theta)$ is not a separate function of pressure, so that in the first line of Eqn. (C1), where $-\hat{\phi}_\Theta(S_A, \Theta, P)$ is evaluated at pressure P, this pressure dependence needs to be subtracted. In Eqn. (C2) note that $h(S_A, T, P_0)$ is not the same as potential enthalpy $c_p^0 \Theta$ except when the in situ pressure P happens to be P_0.

C.2 Variables expressed using $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ compared with $h(S_A, T, P)$ and $\eta(S_A, T, P)$

Considering changes occurring at constant Absolute Salinity and pressure, the FTR in the forms Eqns. (8) and (11) show that in situ temperature $T = T_0 + t$ is given by

$$T = \partial h / \partial \eta |_{S_A, P} = h_T / \eta_T = \hat{h}_\Theta / \hat{\eta}_\Theta. \tag{C3}$$

The h_T/η_T part of this equation is a consistency requirement between the temperature dependence of the $h(S_A, T, P)$ and $\eta(S_A, T, P)$ expressions. That is, expressions for $h(S_A, T, P)$ and $\eta(S_A, T, P)$ cannot be formed independently of each other but rather must satisfy the consistency relationship, $T = h_T/\eta_T$, since T is one of the independent variables. If necessary, however, the required consistency may be established by the integration,

$$\eta(S_A, T, P) = \int_{T_0}^{T} \frac{h_T(S_A, T', P)}{T'} \, dT' + \eta(S_A, T_0, P), \tag{C4}$$

so that already $h(S_A, T, P)$ in combination with an independent function $\eta(S_A, T_0, P)$ taken at an arbitrary reference temperature T_0 provide together the necessary information. The corresponding relationship in the (S_A, Θ, P) case, $T = \hat{h}_\Theta/\hat{\eta}_\Theta$, does not impose any such consistency requirement on $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ because T is not an independent variable in this case.

The expression for specific volume in terms of the Gibbs function is very neat and compact, being $v = g_P$, while the corresponding expression in terms of $h(S_A, T, P)$ and $\eta(S_A, T, P)$ is $v = h_P - (h_T/\eta_T)\eta_P$ (see Eqn. 8). Since S_A, Θ and η are

all "potential" variables, when the material derivative of enthalpy in the FTR is expressed in the form $\hat{h}_{S_A} dS_A + \hat{h}_\Theta d\Theta + \hat{h}_P dP$,
635   one finds (from Eqn. (11) by considering the adiabatic and isohaline situation when $dS_A = d\eta = d\Theta = 0$) that specific volume is given by $\hat{h}_P$, hence we have

$$v = g_P = h_P - (h_T/\eta_T)\eta_P = \hat{h}_P. \tag{C5}$$

Note that specific volume can also be expressed in terms of $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$ as $v = \hat{h}_P - (\hat{h}_\Theta/\hat{\eta}_\Theta)\hat{\eta}_P$ because $\hat{\eta}_P$ is zero, and so the last two equalities in Eqn. (C5) are more similar than they appear.

640   In terms of the Gibbs function, the adiabatic lapse rate (the rate of change of in situ temperature with an adiabatic and isohaline change in pressure, see McDougall and Feistel, 2003) is $\Gamma = -g_{TP}/g_{TT}$, while using the two expressions in terms of enthalpy and entropy gives (by differentiating Eqn. C3 with respect to pressure)

$$\Gamma = -\eta_P/\eta_T = \hat{h}_{P\Theta}/\hat{\eta}_\Theta = v_T/\eta_T = \hat{v}_\Theta/\hat{\eta}_\Theta, \tag{C6}$$

where the last two expressions are written in terms of specific volume and entropy. Another expression for Γ that corresponds
645   to $-\eta_P/\eta_T$ is $-\left(\partial\Theta/\partial P|_{S_A,T}\right)/\left(\partial\Theta/\partial T|_{S_A,P}\right)$.

The relative chemical potential $\mu = g_{S_A} = \partial h/\partial S_A|_{\eta,P} = \check{h}_{S_A}$ can be expressed as (from the partial differentials in Eqn. (8) and (11))

$$\mu = h_{S_A} - (h_T/\eta_T)\eta_{S_A} = \hat{h}_{S_A} - \left(\hat{h}_\Theta/\hat{\eta}_\Theta\right)\hat{\eta}_{S_A}, \tag{C7}$$

and the chemical potential of water in seawater, $\mu^W = g - S_A g_{S_A}$, is

650       $$\mu^W = \left(h - S_A h_{S_A}\right) - (h_T/\eta_T)\left(\eta - S_A\eta_{S_A}\right) = \left(\hat{h} - S_A\hat{h}_{S_A}\right) - \left(\hat{h}_\Theta/\hat{\eta}_\Theta\right)\left(\hat{\eta} - S_A\hat{\eta}_{S_A}\right). \tag{C8}$$

Again, it is interesting these expressions for both μ and μ^W, written in terms of enthalpy and entropy, have the same form whether as functions of (S_A, T, P) or (S_A, Θ, P).

The adiabatic and isohaline compressibility has the following compact expression in terms of $\hat{h}(S_A, \Theta, P)$

$$\kappa = -\hat{h}_{PP}/\hat{h}_P, \tag{C9}$$

655   but because in situ temperature does not possess the "potential" property the expressions in terms of (S_A, T, P) are not as compact, being

$$\kappa = -g_{PP}/g_P + (g_{TP})^2/(g_P g_{TT}) = -(h_{PP}\eta_T - h_T\eta_{PP} + \eta_P^2)/(h_P\eta_T - h_T\eta_P). \tag{C10}$$

It is interesting that κ can also be expressed by the same expressions as in Eqn. (C10) even when enthalpy and entropy are functions of (S_A, Θ, P), namely as $-\left(\hat{h}_{PP}\hat{\eta}_\Theta - \hat{h}_\Theta\hat{\eta}_{PP} + \hat{\eta}_P^2\right)/\left(\hat{h}_P\hat{\eta}_\Theta - \hat{h}_\Theta\hat{\eta}_P\right)$, because $\hat{\eta}_P$ and $\hat{\eta}_{PP}$ are both zero. That is, the
660   last expressions in Eqns. (C9) and (C10) are more similar than they appear.

These expressions for the various thermodynamic variables are summarized in Table 1.

C.3 The constraints on thermodynamic variables revealed by cross-differentiation

When the second order cross derivatives of the thermodynamic potential, $\breve{h}(S_A, \eta, P)$, are taken, we find the following relations between the observed quantities v, T and μ,

$$\breve{T}_P = \breve{v}_\eta, \tag{C11}$$

$$\breve{\mu}_P = \breve{v}_{S_A}, \tag{C12}$$

$$\breve{\mu}_\eta = \breve{T}_{S_A}, \tag{C13}$$

and when the second order cross derivatives of the Gibbs function, $g(S_A, T, P)$, are taken, we find the following relations between the observed quantities $v(S_A, T, P)$, $\eta(S_A, T, P)$, and $\mu(S_A, T, P)$ (these are sometimes called the Maxwell relationships)

$$-\eta_P = v_T, \tag{C14}$$

$$\mu_P = v_{S_A}, \tag{C15}$$

$$\mu_T = -\eta_{S_A}. \tag{C16}$$

For our new thermodynamic potential, $\hat{\phi}(S_A, \Theta, P)$, we write the total differential of $\hat{\phi}(S_A, \Theta, P)$ in the form (using Eqns. (11) and (14))

$$\mathrm{d}\hat{\phi} = \left\{ -\int_0^\Theta \hat{\eta}_{S_A}(S_A, \Theta')\mathrm{d}\Theta' + \hat{\mu} + \hat{T}\hat{\eta}_{S_A} \right\}\mathrm{d}S_A + \left\{ -\hat{\eta} + \hat{T}\hat{\eta}_\Theta - c_p^0 \right\}\mathrm{d}\Theta + \hat{v}\mathrm{d}P \tag{C17}$$

which involves the three partial derivatives,

$$\hat{\phi}_{S_A} = -\int_0^\Theta \hat{\eta}_{S_A}(S_A, \Theta')\mathrm{d}\Theta' + \hat{\mu} + \hat{T}\hat{\eta}_{S_A}, \tag{C18}$$

$$\hat{\phi}_\Theta = -\hat{\eta} + T\hat{\eta}_\Theta - c_p^0, \tag{C19}$$

$$\hat{\phi}_P = \hat{v}. \tag{C20}$$

The three cross-derivatives yield

$$\hat{T}_P \hat{\eta}_\Theta = \hat{v}_\Theta, \tag{C21}$$

$$\hat{\mu}_P + \hat{T}_P \hat{\eta}_{S_A} = \hat{v}_{S_A}, \tag{C22}$$

$$\hat{\mu}_\Theta + \hat{T}_\Theta \hat{\eta}_{S_A} = \hat{T}_{S_A} \hat{\eta}_\Theta. \tag{C23}$$

after subtracting the two terms $-\hat{\eta}_{S_A}$ and $\hat{T}\hat{\eta}_{S_A\Theta}$ that appear in both $\hat{\phi}_{S_A\Theta}$ and $\hat{\phi}_{\Theta S_A}$.

Note that the equality between v_T and $-\eta_P$ in (C14) does not resemble the balance $\hat{T}_P \hat{\eta}_\Theta = \hat{v}_\Theta$ in (C21), and moreover we know that the corresponding pressure derivative, $\hat{\eta}_P$, is zero. Rather, the expression (C21) for the adiabatic lapse rate, $\Gamma = \breve{T}_P = \hat{T}_P = (\hat{v}_\Theta/\hat{\eta}_\Theta)$, resonates with the result $\breve{T}_P = \breve{v}_\eta$ of Eqn. (C11). The additional term $\hat{T}_P \hat{\eta}_{S_A} = (\hat{v}_\Theta/\hat{\eta}_\Theta)\hat{\eta}_{S_A}$ in Eqn. (C22) compared with the corresponding formulae in Eqns. (C12) or (C15) is small (being less than 0.5% of both $\hat{v}_{S_A}$ and $\hat{\mu}_P$). The relationship (C23) that comes from equating $\hat{\phi}_{S_A\Theta}$ and $\hat{\phi}_{\Theta S_A}$ has some similarities with both (C13) and (C16), with $\hat{T}_\Theta \hat{\eta}_{S_A}$ appearing to be an additional term in one case and $\hat{T}_{S_A} \hat{\eta}_\Theta$ in the other case.

695   It can be shown by coordinate transformation that each of (C21) – (C23) contain exactly the same information as (C14) –

(C16). This is, each of the equations (C21) – (C23) can be found by transforming the corresponding equation in (C14) – (C16)

from (S_A, T, P) coordinates into (S_A, Θ, P) coordinates.

700

Appendix D: Deducing the FTR from the differential of a thermodynamic potential and its definition in terms of enthalpy and entropy.

The Fundamental Thermodynamic Relationship (FTR) can be deduced from knowledge of the total differential of the Gibbs function $dg = \mu dS_A - \eta dT + v dP$, together the definition of the Gibbs function in terms of enthalpy and entropy, $g = h - T\eta$. Here we show that the FTR can also be found from knowledge of the total differential of $\hat{\phi}(S_A, \Theta, P)$ as well as its definition in terms of enthalpy and entropy.

We write the total differential of $\hat{\phi}(S_A, \Theta, P)$ in the form (C17)

$$d\phi = \left\{ -\int_0^\Theta \hat{\eta}_{S_A}(S_A, \Theta')d\Theta' + \hat{\mu}(S_A, \Theta, P) + T\hat{\eta}_{S_A} \right\} dS_A + \left\{ -\hat{\eta}(S_A, \Theta) + T\hat{\eta}_\Theta - c_p^0 \right\} d\Theta + \hat{v}(S_A, \Theta, P)dP \tag{D1}$$

and we use the definition of $\hat{\phi}(S_A, \Theta, P)$ in the form Eqn. (14), repeated here,

$$\hat{\phi}(S_A, \Theta, P) = -\int_0^\Theta \hat{\eta}(S_A, \Theta')d\Theta' + \hat{h}(S_A, \Theta, P) - c_p^0\Theta, \tag{D2}$$

and we ask whether the FTR can be deduced from knowledge of Eqns. (D1) and (D2), in direct analogy to what is possible for the Gibbs function.

Because of the definition of Conservative Temperature, $c_p^0 \Theta \equiv \hat{h}(S_A, \Theta, P_0)$, we know that $\eta = \hat{\eta}(S_A, \Theta)$, $\hat{h}_\Theta(S_A, \Theta, P_0) = c_p^0$ and $\hat{h}_{S_A}(S_A, \Theta, P_0) = 0$. Equating the three partial derivatives of Eqn. (D1) with the corresponding expressions from differentiating Eqn. (D2) shows that $\hat{h}_{S_A} = \mu + T\hat{\eta}_{S_A}$, $\hat{h}_\Theta = T\hat{\eta}_\Theta$ and $\hat{h}_P = v$, so that the expression, Eqn. (11), for the total derivative of enthalpy has been found. Using $d\eta = \hat{\eta}_{S_A}dS_A + \hat{\eta}_\Theta d\Theta$, the FTR follows, and the analogy with the Gibbs function is complete.

720

Code availability

Upon acceptance of this paper for publication, the 24 Gibbs SeaWater Oceanographic Toolbox (GSW) subroutines in Matlab that we have prepared will replace existing subroutines of the same name that are presently in the GSW code on the TEOS-10 web site (http://www.teos-10.org/software.htm).

725

Author contribution

TMcD discovered the new thermodynamic potential of seawater as a function of Conservative Temperature, PMB wrote and tested the 24 new computer subroutines that were needed to implement the ideas of this paper into the GSW computer software of TEOS-10, RF ensured that the thermodynamic motivation and reasoning in the paper were precise, while FR performed the

730 fit of entropy to Absolute Salinity and Conservative Temperature. All authors contributed to writing the manuscript.

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785

Figure Captions

Figure 1. Panels (a) and (b) are contour plots of $c_p^0 \ln(1 + \theta/T_0) - \eta$ and $c_p^0 \ln(1 + \Theta/T_0) - \eta$ respectively, while panels (c) and (d) show $c_p^0 \ln(1 + \theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO}) - \eta$ and $c_p^0 \ln(1 + \Theta/T_0) + a(S_A/S_{SO}) \ln(S_A/S_{SO}) - \eta$ respectively. All panels in this figure are in the units of entropy, namely J kg^{-1} K^{-1}.

790

Figure 2. (a) The error in the fit Eqn. (21) to entropy (in units of 10^{-6} J kg^{-1} K^{-1}). (b) The error in evaluating potential temperature θ (in μK) from Eqns. (21) and (22).

Table 1. Expressions for various thermodynamic variables based on different thermodynamic potentials.

	Expressions based on $\hat{h}(S_A, \eta, P)$	Expressions based on $g(S_A, T, P)$	Expressions based on $h(S_A, T, P)$ and $\eta(S_A, T, P)$	Expressions based on $\hat{h}(S_A, \Theta, P)$ and $\hat{\eta}(S_A, \Theta)$
T	$T = \hat{h}_\eta$	T	$T = h_T/\eta_T$ This is a necessary consistency condition between h_T and η_T.	$T = (T_0 + t) = \hat{h}_\Theta/\hat{\eta}_\Theta$
θ	$T_0 + \theta = \hat{h}_\eta(S_A, \eta, P_0)$	$g_T(S_A, T_0 + \theta, P_0) = g_T(S_A, T, P)$ This is an implicit equation for θ.	$\eta(S_A, T_0 + \theta, P_0) = \eta(S_A, T, P)$ This is an implicit equation for θ.	$(T_0 + \theta) = c_p^0/\hat{\eta}_\Theta$
Θ	$\Theta = \hat{h}(S_A, \eta, P_0)/c_p^0$	$\Theta = g(S_A, T_0 + \theta, P_0)/c_p^0$ $- (T_0 + \theta)g_T(S_A, T_0 + \theta, P_0)/c_p^0$	$\Theta = h(S_A, T_0 + \theta, P_0)/c_p^0$	Θ; $\quad \Theta \equiv \hat{h}(S_A, \Theta, P_0)/c_p^0$
h	$\hat{h}(S_A, \eta, P)$	$g - Tg_T$	$h(S_A, T, P)$	$\hat{h}(S_A, \Theta, P)$
g	$\hat{h} - \eta\hat{h}_\eta$	$g(S_A, T, P)$	$h - T\eta$	$\hat{h} - \hat{\eta}\hat{h}_\Theta/\hat{\eta}_\Theta$
η	η	$-g_T$	$\eta(S_A, T, P)$	$\hat{\eta}(S_A, \Theta)$
v	$\hat{h}_P$	g_P	$h_P - T\eta_P$	$\hat{h}_P$
u	$\hat{h} - P\hat{h}_P$	$g - Tg_T - Pg_P$	$h - Ph_P + TP\eta_P$	$\hat{h} - P\hat{h}_P$
μ	$\hat{h}_{S_A}$	g_{S_A}	$h_{S_A} - T\eta_{S_A}$	$\hat{h}_{S_A} - \hat{\eta}_{S_A}\hat{h}_\Theta/\hat{\eta}_\Theta$
μ^W	$\hat{h} - \eta\hat{h}_\eta - S_A\hat{h}_{S_A}$	$g - S_A g_{S_A}$	$(h - S_A h_{S_A}) - T(\eta - S_A\eta_{S_A})$	$(\hat{h} - S_A\hat{h}_{S_A})$ $- (\hat{h}_\Theta/\hat{\eta}_\Theta)(\hat{\eta} - S_A\hat{\eta}_{S_A})$
f	$\hat{h} - \eta\hat{h}_\eta - P\hat{h}_P$	$g - Pg_P$	$(h - T\eta) - P(h_P - T\eta_P)$	$\hat{h} - \hat{\eta}\hat{h}_\Theta/\hat{\eta}_\Theta - P\hat{h}_P$
κ	$-\hat{h}_{PP}/\hat{h}_P$	$-g_{PP}/g_P + (g_{TP})^2/(g_P g_{TT})$	$-(h_{PP}\eta_T - h_{TP}\eta_{PP} + \eta_P^2)/(h_P\eta_T - h_T\eta_P)$	$-\hat{h}_{PP}/\hat{h}_P$
Γ	$\hat{h}_{P\eta}$	$-g_{TP}/g_{TT}$	$-\eta_P/\eta_T$	$\hat{h}_{P\Theta}/\hat{h}_\Theta$
α^Θ	$\dfrac{c_p^0 \hat{h}_{P\eta}}{\hat{h}_P\,\hat{h}_\eta(S_A, \eta, P_0)}$	$-\dfrac{g_{PT}}{g_P}\dfrac{c_p^0}{(T_0 + \theta)g_{TT}}$	$-\dfrac{\eta_P}{(h_P - T\eta_P)}\dfrac{c_p^0}{(T_0 + \theta)\eta_T}$	$\hat{h}_{P\Theta}/\hat{h}_P$
β^Θ	$-\dfrac{\hat{h}_{PS_A}}{\hat{h}_P} + \dfrac{\hat{h}_{P\eta}}{\hat{h}_P}\dfrac{\hat{h}_{S_A}(S_A, \eta, P_0)}{\hat{h}_\eta(S_A, \eta, P_0)}$	Expression too large to fit here	Expression too large to fit here	$-\hat{h}_{PS_A}/\hat{h}_P$