Quantifying the Nonconservative Production of Conservative Temperature, Potential Temperature, and Entropy

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ABSTRACT

The evolution equation of potential temperature has to date been treated as an approximation to the oceanic version of the first law of thermodynamics. That is, oceanographers have regarded the advection and diffusion of potential temperature as the advection and diffusion of “heat.” However, the nonconservative source terms that arise in the evolution equation for potential temperature are estimated to be two orders of magnitude larger than the corresponding source terms for Conservative Temperature. In this paper the nonconservative source terms of potential temperature, Conservative Temperature, and entropy are derived for a stratified turbulent fluid, then quantified using the output of a coarse-resolution ocean model and compared to the rate of dissipation of mechanical energy, epsilon. It is shown that the error incurred in ocean models by assuming that Conservative Temperature is 100% conservative is approximately 120 times smaller than the corresponding error for potential temperature and at least 1200 times smaller than the corresponding error for entropy. Furthermore, the error in assuming that Conservative Temperature is 100% conservative is approximately 6 times smaller than the error in ignoring epsilon. Hence Conservative Temperature can be quite accurately regarded as a conservative variable and can be treated as being proportional to the “heat content” per unit mass of seawater, and therefore it should now be used in place of potential temperature in physical oceanography, including as the prognostic temperature variable in ocean models.

1. Introduction

The problem of how best to model advection and diffusion of “heat” in the ocean is not an easy one to solve. First, it is difficult to define what “heat” actually is in the ocean. Second, it is not a trivial task to derive a variable whose advection and diffusion can be regarded as the advection and diffusion of “heat.” It is common practice in oceanography to regard the first law of thermodynamics as the difference between the conservation equation of total energy and the evolution equation for kinetic energy plus gravitational potential energy. What is left is an expression that at leading order can be construed as an evolution equation for “heat” [Landau and Lifshitz 1959; McDougall 2003; Griffies 2004; Intergovernmental Oceanographic Commision (IOC) et al. 2010].

It would be highly desirable to find a thermodynamic variable with the following properties: (i) the advection and diffusion of the variable can be regarded as the advection and diffusion of heat; (ii) the evolution equation of the variable is derived through consideration of the first law of thermodynamics; and (iii) the nonconservative source terms that arise in the evolution equation of the variable are “small,” so that the evolution equation of the variable can be approximated by the following conservation equation (IOC et al. 2010):

\[
\left(\rho C\right)_t + \nabla \cdot \left(\rho u C\right) = \frac{DC}{Dt} = -\nabla \cdot F^C, 
\]
where $p$ is density, $C$ is the thermodynamic variable in question, $\mathbf{V}$ is the divergence operator, $\mathbf{u}$ is the three-dimensional velocity vector, $D/Dt = \partial t / \partial t + \mathbf{u} \cdot \mathbf{V}$ is the material derivative operator following the fluid motion, and $\mathbf{F}^C$ is the flux of $C$ caused by molecular diffusive processes. The subscript $t$ denotes a partial derivative with respect to time.

Since its introduction to the field of oceanography by Helland-Hansen (1911), potential temperature has been treated as the variable whose advection and diffusion can be interpreted as the advection and diffusion of heat. Ocean models have to date treated potential temperature as if it were a conservative property; however, when fluid parcels mix at fixed pressure, nonconservative source terms of potential temperature arise, mostly because the isobaric heat capacity of seawater, which appears in the evolution equation of potential temperature, varies by up to 5% with salinity, and also because enthalpy depends nonlinearly not only on potential temperature but also on salinity (McDougall 2003). If the nonconservative source terms of potential temperature were not ignored, then the errors in ocean models carrying potential temperature as the default temperature variable would be eliminated (although, in this instance, ocean models would need to carry the isobaric heat capacity in the form $c_p(S_A, \theta, p = 0 \text{ dbar})$, which is used at the sea surface to relate the air–sea heat flux to the flux of potential temperature and which varies by 5% at the sea surface because it is a function of $S_A$ and $\theta$, rather than the constant heat capacity $c_p^0$). However, the full evolution equation of potential temperature including its nonconservative production terms have not yet been explicitly derived for a turbulent ocean. Even if they had been derived, including these source terms in ocean models would not be ideal for models based on conservation equations such as Eq. (1).

McDougall (2003) defined an oceanic “heatlike” variable called potential enthalpy $h^0$, referenced to the pressure $p = 0$ as

$$ h^0 = h(S_A, \Theta, 0) = h(S_A, \Theta, p) - \int_0^p \nu(S_A, \Theta, p') \, dp' , \quad (2) $$

where $h$ is specific enthalpy, $S_A$ is Absolute Salinity, $\Theta$ is Conservative Temperature (see below), $p$ is the excess of the absolute pressure over the fixed pressure $p_0 = 0.101325 \text{ MPa}$, $\int$ is the integral operator, and $\nu$ is specific volume. The overhat notation is used to denote a variable that is a function of Conservative Temperature. Values for the arbitrary constants that arise in the Gibbs function definition of the variables in Eq. (2) are listed in IOC et al. (2010). We choose potential enthalpy referenced to the pressure $p = 0$ so that the error in equating the air-sea heat flux with the flux of $h^0$ is minimized. Referring potential enthalpy to $p = 0$ is also appropriate because enthalpy is unknown up to a linear function of salinity, and since there is no flux of salt at the sea surface, the choice of that linear function of salinity will not affect the air–sea heat flux of $h^0$. A temperature variable called Conservative Temperature, denoted $\Theta$, was defined to be proportional to potential enthalpy such that

$$ \Theta = h^0 / c_p^0 , \quad (3) $$

Here, the constant $c_p^0 = 3991.867957 \text{ J kg}^{-1} \text{ K}^{-1}$ (IOC et al. 2010). Although it is possible to reference potential enthalpy to pressures other than the sea surface, Conservative Temperature is always defined in terms of potential enthalpy referenced at the sea surface. The evolution equation for potential enthalpy almost exactly satisfies the first law of thermodynamics, and since the air–sea heat flux is equal to the air–sea flux of potential enthalpy, potential enthalpy can be accurately treated as the “heat content” of seawater (IOC et al. 2010).

By treating potential temperature as if it were conservative, ocean models have in some sense inadvertently interpreted their prognostic temperature variable as Conservative Temperature. McDougall (2003) and Tailleux (2010) have done early work in quantifying the errors introduced into ocean models by ignoring the nonconservative source terms of potential temperature. In particular, McDougall (2003) found that typical errors in ocean models in ignoring the nonconservative source terms of $\theta$ are $\pm 0.1^\circ$C, although the errors can be as large as $1.4^\circ$C (with $\Theta > \theta$) in areas that are warm and fresh, such as where the fresh Amazon River water enters the ocean. This behavior can be seen from Fig. 1, which shows contours of the difference between $\theta$ and $\Theta$ in degrees Celsius at the sea surface. IOC et al. (2010) estimated that Conservative Temperature is about 100 times more conservative than potential temperature. This was deduced through careful examination of their Figs. A.17.1 and A.18.1. More recent work by Tailleux (2010) found that Conservative Temperature is about 20 times more conservative than potential temperature. However, in the literature to date, namely in Tailleux (2010) and McDougall (2003), the relative errors in ignoring the nonconservative source terms of potential temperature and Conservative Temperature have been estimated either from generalizing the laminar evolution equations of each variable to the turbulent ocean, or by using parcel
2. The First Law of Thermodynamics in terms of $\theta$, $\Theta$, and $\eta$

Following IOC et al. (2010), Batchelor (1970), and Gill (1982), the first law of thermodynamics can be expressed in the following forms:

$$\rho \left( \frac{Dh}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} \right) = \rho \left( \frac{Du}{Dt} - (p_0 + p) \frac{1}{\rho^2} \frac{Dp}{Dt} \right) \tag{4}$$

where $\rho$ is density, $Dh/Dt = \partial h/\partial t + \mathbf{v} \cdot \nabla h$ is the material derivative operator following the fluid motion, $h$ is specific enthalpy, $p$ is the excess of the absolute pressure over the fixed pressure, $p_0 = 0.101325$ MPa, $u$ is specific internal energy, $T_0 = 273.15$ K, $t$ is in-situ temperature, $\eta$ is specific entropy, $\mu$ is the relative chemical potential, $S_A$ is Absolute Salinity, $F^R$ is the flux of heat at the ocean boundaries and by radiation, $F^Q$ is the molecular diffusion of heat, $\varepsilon$ is the rate of dissipation of kinetic energy, and $\rho h_{S_A} S_A^S$ is the nonconservative production of enthalpy due to biogeochemical processes. The dissipation of kinetic energy in this equation is almost always ignored since it is very small. Furthermore, while the effect of the source term $\rho S_A^S$ is significant for the evolution of Absolute Salinity, fortunately, this small nonconservative source term has a negligible impact on other variables such as $\eta$, $\theta$, and $\Theta$ (IOC et al. 2010). The first law of thermodynamics can be regarded as the difference between the conservation equation of total energy and the evolution equation for the sum of kinetic energy and potential energy, leaving what can be approximately interpreted as an evolution equation for heat in the ocean (Landau and Lifshitz 1959; McDougall 2003; Griffies 2004; IOC et al. 2010). The physical interpretation of the first law of thermodynamics is that the specific internal energy $u$ of a fluid parcel can change due to (McDougall 2003) (i) the work in changing the fluid parcel’s volume at some pressure $(p_0 + p)$; (ii) the divergence of the flux of heat $\mathbf{v} \cdot \nabla h$; (iii) the dissipation of kinetic energy $\varepsilon$; and (iv) nonconservative biogeochemical processes.

The first law of thermodynamics can be expressed in the following equivalent forms:

$$\rho \left( \frac{Dh}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} \right) = \rho \left( \frac{D\eta}{Dt} + \frac{DS_A}{Dt} \frac{\partial h_A}{\partial \eta} + \frac{Dp}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} \right) \tag{7}$$

$$= \rho \left( \frac{D\theta}{Dt} + \frac{DS_A}{Dt} \frac{\partial h_A}{\partial \theta} + \frac{Dp}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} \right) \tag{8}$$

$$= \rho \left( \frac{D\Theta}{Dt} + \frac{DS_A}{Dt} \frac{\partial h_A}{\partial \Theta} + \frac{Dp}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} \right) \tag{9}$$

$$= -\nabla \cdot \mathbf{F}^R - \mathbf{u} \cdot \mathbf{F}^Q + \rho \varepsilon, \quad \tag{10}$$
where notation has been introduced for the different functional forms of specific enthalpy by using accents such that \( h = \hat{h}(S_A, \eta, p) \), \( h = \hat{h}(S_A, \theta, p) \), and \( h = \hat{h}(S_A, \Theta, p) \). The subscript notation denotes a partial derivative with respect to the variable in the subscript (e.g. \( \hat{h}_\eta \)). We consider the fundamental thermodynamic relation in the following form (Warren 2006):

\[
dh - \frac{1}{\rho} dp = (T_0 + t) d\eta + \mu dS_A. \tag{11}
\]

Following directly from this fundamental thermodynamic relation, it can be shown that \( \eta = \hat{\eta}(S_A, \theta) \) and \( \Theta = \hat{\Theta}(S_A, \theta) \) with no separate dependence on pressure (see appendix A.10 of IOC et al. 2010) and that

\[
\hat{h}|_{S_A, \eta} = \hat{h}|_{S_A, \theta} = \frac{1}{\rho} = \nu, \tag{12}
\]

where \( \nu \) is specific volume. Hence, Eqs. (7)–(10) become

\[
\rho \left( \frac{Dh}{Dt} - \frac{1}{\rho} \frac{Dp}{Dt} \right) = \rho \left( \frac{D\eta}{Dt} + \hat{h}_\eta \frac{DS_A}{Dt} \right) \tag{13}
\]

\[
= \rho \left( \frac{D\theta}{Dt} + \hat{h}_\theta \frac{DS_A}{Dt} \right) \tag{14}
\]

\[
= \rho \left( \frac{D\Theta}{Dt} + \hat{h}_\Theta \frac{DS_A}{Dt} \right) \tag{15}
\]

\[
= - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon. \tag{16}
\]

Furthermore, when enthalpy is in the functional form \( h = \hat{h}(S_A, \eta, p) \), at general pressure, the partial derivatives of enthalpy with respect to \( S_A \) and \( \eta \) are

\[
\hat{h}_{S_A}|_{\eta, \rho} = \hat{\mu}(S_A, \eta, p), \quad \hat{h}_{\eta}|_{S_A, \rho} = (T_0 + t). \tag{17}
\]

It follows that the first law of thermodynamics can be expressed as a function of \( \eta \) by substituting the relations from Eq. (17) into Eq. (13), obtaining

\[
\rho \left[ (T_0 + t) \frac{D\eta}{Dt} + \hat{\mu}(S_A, \eta, p) \frac{DS_A}{Dt} \right] = - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon. \tag{18}
\]

As entropy can be expressed in the functional form \( \eta = \hat{\eta}(S_A, \theta) \), then enthalpy can be expressed in the form \( h = \hat{h}[S_A, \eta(S_A, \theta), p] \). Differentiating this functional form of enthalpy with respect to \( \theta \), holding \( S_A \) and \( p \) constant, we obtain

\[
\hat{h}_\theta|_{S_A, \rho} = \hat{h}_\eta|_{S_A, \rho} \hat{\eta}_\theta|_{S_A}. \tag{19}
\]

At the reference pressure \( p = 0 \), we see that \( \hat{\eta}_\theta|_{S_A} = \hat{c}_p(S_A, \theta, 0)/(T_0 + \theta) \) (IOC et al. 2010), where \( \hat{c}_p \) is the specific isobaric heat capacity, and using the expression for \( \hat{h}_\eta|_{S_A, \rho} \) in Eq. (17) above, it follows that \( \hat{h}_\theta|_{S_A, \rho} \) can be written as

\[
\hat{h}_\theta|_{S_A, \rho} = \frac{(T_0 + t)}{(T_0 + \theta)} \hat{c}_p(S_A, \theta, 0). \tag{20}
\]

Similarly, by differentiating enthalpy in the functional form \( h = \hat{h}[S_A, \eta(S_A, \theta), p] \) with respect to \( S_A \), holding \( \theta \) and \( p \) constant, we obtain

\[
\hat{h}_{S_A}|_{\eta, \rho} = \hat{h}_\eta|_{S_A, \rho} \hat{\eta}_{S_A}|_{\theta}. \tag{21}
\]

Taking into account the relations from Eq. (17) and that from the Gibbs function \( \hat{h}_{S_A} = \mu_T(S_A, \theta, 0) \) the following expression for \( \hat{h}_{S_A} \) is obtained:

\[
\hat{h}_{S_A}|_{\theta, \rho} = \mu(S_A, t, p) - (T_0 + t) \mu_T(S_A, \theta, 0). \tag{22}
\]

These partial derivatives are substituted into Eq. (14) so that the first law of thermodynamics in terms of \( \theta \) can be expressed as

\[
\rho \left\{ \frac{(T_0 + t)}{(T_0 + \theta)} \hat{c}_p(S_A, \theta, 0) \frac{D\theta}{Dt} + \left[ \mu(S_A, t, p) - (T_0 + t) \mu_T(S_A, \theta, 0) \right] \frac{DS_A}{Dt} \right\} = - \nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon, \tag{23}
\]

which is the same form as that derived by Bacon and Fofonoff (1996) via a different route.

Enthalpy can also be expressed in the functional form \( h = \hat{h}[S_A, \eta(S_A, \Theta), p] \). Differentiating this functional form of enthalpy with respect to \( \Theta \), holding \( S_A \) and \( p \) constant, we obtain

\[
\hat{h}_\Theta|_{S_A, \rho} = \hat{h}_\eta|_{S_A, \rho} \hat{\eta}_\Theta|_{S_A}. \tag{24}
\]

At the reference pressure \( p = 0 \), we see that \( \hat{\eta}_\Theta|_{S_A} = \hat{c}_p^0/(T_0 + \theta) \) (IOC et al. 2010), and using the expression for \( \hat{h}_\eta|_{S_A, \rho} \) in Eq. (17) above, it follows that \( \hat{h}_\Theta|_{S_A, \rho} \) can be written as
Now enthalpy is differentiated with respect to $S_A$, holding $\Theta$ and $p$ constant, and taking into account the relations from Eq. (17) and that from the fundamental thermodynamic relation $\hat{\eta}_{S_A} = -\mu(S_A, \theta, 0)/(T_0 + \theta)$, the following expression results

$$
\hat{h}_{S_A|\eta, p} = \hat{h}_{S_A|\eta, 0} + \hat{h}_{S_A|\eta, p} \hat{\eta}_{S_A|\theta},
$$

(26)

$$
= \mu(S_A, t, p) - (T_0 + t)/(T_0 + \theta) \mu(S_A, \theta, 0).
$$

(27)

Substituting these partial derivatives into Eq. (15), the first law of thermodynamics can be written in terms of $\Theta$ as follows (McDougall 2003):

$$
\rho \left[ \frac{(T_0 + t)}{(T_0 + \theta)} c_\theta \frac{D\Theta}{Dt} + \left[ \mu(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(S_A, \theta, 0) \right] \frac{DS_A}{Dt} \right]
$$

$$
= -\mathbf{v} \cdot \mathbf{F}^R - \mathbf{v} \cdot \mathbf{F}^C + \rho e.
$$

(28)

By inspecting the above forms of the first law of thermodynamics, an approximate ranking of the nonconservative natures of $\eta$, $\theta$, and $\Theta$ can be made. The ocean circulation can be viewed as a series of adiabatic and isohaline movements of seawater parcels followed by isolated turbulent mixing events, which occur at fixed pressure. Note that we assume that mixing between parcels occurs when the parcels have the same spatial location, that is, at some fixed pressure. The final irreversible part of a turbulent mixing event involves molecular diffusion which destroys tracer variance. We are ignoring pressure perturbations, for example due to sound waves, during this irreversible molecular diffusion. As each of $\eta$, $\theta$, and $\Theta$ are conserved during the adiabatic and isohaline movements, the nonconservation of $\eta$, $\theta$, and $\Theta$ will depend upon the extent to which the coefficients that multiply the material derivatives of $\eta$, $\theta$, $\Theta$, and $S_A$ in Eqs. (18), (23), and (28) vary at fixed pressure (McDougall 2003). These coefficients, namely $\hat{h}_{\eta}$ and $\hat{h}_{S_A}$, $\hat{h}_{\Theta}$ and $\hat{h}_{S_A}$, and $\hat{h}_{\Theta}$ and $\hat{h}_{S_A}$, are quantified using model output from a standard configuration of version 4 of the Modular Ocean Model (MOM4) (see section 4). Their standard deviations at each pressure in the cast from 0 to 500 dbar are illustrated in Fig. 2. From the variations of the first-order partial derivatives of enthalpy as a function of $\eta$, $\theta$, and $\Theta$ respectively, at each pressure in the cast, we can infer that the source terms of $\eta$ and $\theta$ vary considerably more than the source terms of $\Theta$ and that the greatest variation occurs at the sea surface (in fact, it will be shown that the source terms of $\Theta$ are exactly equal to 0 at the sea surface, whereas the source terms of $\theta$ and $\eta$ achieve their maximums at the sea surface). Hence we conclude that $\Theta$ is the most conservative variable, followed by $\theta$ and $\eta$.

3. Turbulent evolution equations

The preceding discussion shows that nonconservative source terms of $\Theta$, $\theta$, and $\eta$ exist during mixing events. It follows that to derive the full evolution equations for $\Theta$, $\theta$, and $\eta$, including their nonconservative source terms, it is first necessary to obtain the turbulently averaged...
forms of the evolution equations for Absolute Salinity and enthalpy at fixed pressure. These are derived using a similar approach to the one undertaken in IOC et al. (2010).

\( a. \) The evolution equation for \( S_A \)

The instantaneous conservation equation for Absolute Salinity is

\[
\frac{D S_A}{D t} = (\rho S_A)_t + \mathbf{v} \cdot (\rho \mathbf{u} S_A) = -\nabla \cdot \mathbf{F} + \rho \delta S_A. \tag{29}
\]

This is first density-weighted averaged, obtaining

\[
\left( \frac{\overline{\rho S_A^\rho}}{\rho_0} \right)_t + \mathbf{v} \cdot (\overline{\rho S_A^\rho} \mathbf{u}) = \frac{\overline{\rho \delta S_A^\rho}}{\rho_0} + \overline{\mathbf{u} \cdot \nabla S_A^\rho} = -\frac{1}{\rho_0} \mathbf{F} \cdot \mathbf{F} - \frac{1}{\rho_0} \mathbf{v} \cdot \rho S_A^\rho \mathbf{u}^\rho + \frac{\overline{\rho S_A^\rho}}{\rho_0}. \tag{30}
\]

Here, \( \mathbf{u} = \rho \mathbf{u} / \rho_0 \), which is proportional to the averaged mass flux of seawater per unit area and \( \rho_0 \) is constant density, usually assigned a value of 1035 kg m\(^{-3}\) (Griffies 2004). The overbar notation indicates temporally averaged variables, and the double-prime notation indicates deviations of the instantaneous quantity from its density-weighted averaged value. Absolute Salinity has been density-weighted averaged, so that \( S_A^\rho = \overline{\rho S_A} / \rho \). The averaging process used here was derived by McDougall et al. (2002) and represents an average over many small-scale mixing processes over several hours, but not over mesoscale time and space scales. Next, the subsequent isopycnal averaging process performed by Greibach and McDougall (2003) over the mesoscale (of order 100 km) is applied, yielding the following evolution equation for Absolute Salinity

\[
\left( \frac{\overline{\rho S_A^\rho}}{\rho_0} \right)_{\overline{\rho}} + \mathbf{v} \cdot \left( \frac{\overline{\rho S_A^\rho} \mathbf{u}}{\rho_0} \right) + \frac{\overline{\rho \delta S_A^\rho}}{\rho_0} = \frac{\gamma_z}{\rho_0} \mathbf{v} \cdot (\gamma_z^{-1} K \mathbf{v} S_A) + \frac{\overline{\rho S_A^\rho}}{\rho_0}. \tag{31}
\]

The overhat notation introduced here means that the variable has been averaged in a thickness-and-density-weighted manner between a pair of neutral tangent planes a small distance apart in the vertical. Here, \( \mathbf{v} \) is the thickness-and-density-weighted horizontal velocity, \( \mathbf{e} \) is the dianeutral velocity, and \( \mathbf{e} \) is the temporal average of \( e \) on the neutral tangent plane (that is, \( e \) is not thickness weighted). The turbulent fluxes in Eq. (31) have been parameterized by the epineutral diffusivity \( K \) and the dianeutral diffusivity \( D \). The height at which Eq. (31) is evaluated is the average height of the density value \( \rho \). Now invoking the Boussinesq approximation, Eq. (31) is simplified to

\[
\frac{\delta S_A}{\delta t} + \mathbf{v} \cdot \nabla S_A + \frac{\delta S_A}{\delta z} = \frac{DS_A}{Dt} = \gamma_z \mathbf{v} \cdot (\gamma_z^{-1} K \mathbf{v} S_A) + \left( D \frac{\delta S_A}{\delta z} \right) + \overline{\mathbf{u} \cdot \nabla S_A}. \tag{32}
\]

This is the turbulently averaged evolution equation for Absolute Salinity that will be used to derive the corresponding evolution equations for \( \Theta \), \( \theta \), and \( \eta \) in a turbulent ocean. The left-hand side is the derivative following the motion of the thickness-weighted \( S_A \) with respect to the thickness-weighted horizontal velocity \( \mathbf{v} \) and the temporally averaged dianeutral velocity \( \mathbf{e} \) of density coordinates. The right-hand side contains the divergence of the turbulent fluxes of \( S_A \), where \( \gamma_z \) is the vertical gradient of a suitable density variable (such as neutral density, or locally referenced potential density). The overhat notation is not used in what follows to avoid confusion with notation denoting whether a property is a function of \( \Theta \). However, it should be kept in mind that the quantities in the subsequent expressions are turbulently-averaged quantities.

\( b. \) The evolution equation for potential enthalpy \( h^m \) referenced to the general pressure \( p^m \), at \( p^m \)

Potential enthalpy \( h^m \) referenced to the pressure \( p^m \) is defined by

\[
h^m(S_A, \Theta, p) = \hat{h}(S_A, \Theta, p^m)
\]

\[
= \hat{h}(S_A, \Theta, p) - \int_{\rho}^{p} \hat{v}(S_A, \Theta, p') dp'. \tag{33}
\]

It is clear then that once the reference pressure \( p^m \) is chosen, \( h^m \) is a function of only \( S_A \) and \( \Theta \) [actually \( h^m(S_A, \Theta, p) = \hat{h}(S_A, \Theta, p^m) = \hat{h}(S_A, \Theta, p^m) = \hat{h}(S_A, \Theta, p^m) \)]. Taking the material derivative of potential enthalpy \( h^m \), from Eq. (33) we find

\[
\frac{D h}{D t} - \frac{1}{\rho} \frac{D p}{D t} = \frac{D h^m}{D t}, \text{ at } p = p^m, \tag{34}
\]

so that at \( p = p^m \) the first law of thermodynamics, Eq. (10), becomes
\[
\rho \frac{Dh^m}{Dt} = (\rho h^m)_t + \nabla \cdot (\rho u h^m) \\
= -\nabla \cdot F^R - \nabla \cdot F^Q + \rho e, \quad \text{at} \quad p = p^m. \tag{35}
\]

The important point to note about this evolution equation for \( h^m \) is that at \( p = p^m \), the evolution equation for \( h^m \) is of the conservative form except for the term \( \rho e \) in the dissipation of kinetic energy. Because \( h^m \) is a “potential” variable in that it is unchanged under adiabatic and isothermal changes in pressure, it is possible to undertake the same two-stage-averaging process as used in the previous subsection and to take the turbulent fluxes of \( h^m \) to be down the respective mean gradients of \( h^m \). Performing this two-stage averaging process, we find that the Boussinesq form of the mesoscale averaged equation is

\[
\frac{\partial h^m}{\partial t} + \mathbf{v} \cdot \nabla h^m + \dot{e} \frac{\partial h^m}{\partial z} = \frac{Dh^m}{Dt} = \gamma \frac{V}{n} \cdot (\gamma^{-1} K V h^m) \\
+ (Dh^m)_z + \dot{e}, \quad \text{at} \quad p = p^m. \tag{36}
\]

Here, the molecular flux of heat has been ignored because it is small in comparison with the turbulent fluxes, but it is trivial to retain the averaged molecular flux here if desired. Note that we have left out the averaged form of the divergence of the radiative heat flux, for convenience, given that it is a conservative term. The left-hand side of the above equation is the derivative following the motion of the thickness-weighted enthalpy (where, for simplicity, the overhat notation denoting thickness-weighted averaging has been removed from \( h^m \)) with respect to the thickness-weighted horizontal velocity \( \mathbf{v} \) and the temporally averaged dianeutral velocity \( \dot{e} \) of density coordinates. The right-hand side contains the divergence of the turbulent fluxes of \( h^m \), where \( \gamma \) is the vertical gradient of a suitable density variable. Having derived the evolution equations for \( S_A \) and \( h^m \), the full evolution equations for \( \Theta, \theta, \) and \( \eta \) in a turbulently mixed ocean are now derived.

c. The evolution equation for \( \Theta \)

If potential enthalpy referenced to \( p^m, h^m \), is expressed in the form \( h^m = \hat{h}(S_A, \Theta, p^m) \) at the fixed pressure \( p = p^m \) [recall that Conservative Temperature \( \Theta \) is defined with respect to \( \frac{\partial}{\partial} \text{dbar} \), see Eqs. (2) and (3)], it follows that the spatial and temporal gradients in Eq. (36) can be written in terms of the spatial and temporal gradients of \( S_A \) and \( \Theta \), namely

\[
\dot{h}_\Theta = \bar{h}_\Theta D\Theta + \bar{h}_{S_A} D S_A = \gamma \frac{V}{n} \cdot [\gamma^{-1} K V \Theta] \\
+ [D(\hat{h}_\Theta \Theta) + \bar{h}_{S_A} S_{A\zeta}]_z + \dot{e}, \quad \text{at} \quad p = p^m. \tag{37}
\]

Substituting the expression for the turbulently averaged conservation equation for Absolute Salinity from Eq. (32), Eq. (37) is rearranged to become

\[
\frac{D\Theta}{Dt} = \gamma \frac{V}{n} \cdot (\gamma^{-1} K V \Theta) + (D\Theta)_z + \frac{\dot{e}}{\hat{h}_\Theta} \\
+ \frac{1}{\hat{h}_\Theta} [K V \Theta \cdot V h^m + K V S_A \cdot V S^m_h] \\
+ \frac{1}{\hat{h}_\Theta} [D(\hat{h}_\Theta \Theta) + D S_A \Theta \hat{h}_{S_A} S_{A\zeta}], \quad \text{at} \quad p = p^m. \tag{38}
\]

Because \( \hat{h}_\Theta \) and \( \hat{h}_{S_A} \) are functions of Absolute Salinity and Conservative Temperature, not of pressure [remember that \( \hat{h}_\Theta = h_\Theta(S_A, \Theta, p^m) \) and \( \hat{h}_{S_A} = h_{S_A}(S_A, \Theta, p^m) \)], the spatial gradients in Eq. (38) can be expanded to give the following evolution equation for \( \Theta \):

\[
\frac{D\Theta}{Dt} = \gamma \frac{V}{n} \cdot (\gamma^{-1} K V \Theta) + (D\Theta)_z + \frac{\dot{e}}{\hat{h}_\Theta} + \frac{K \hat{h}_\Theta \Theta \cdot V \Theta \cdot V S_A}{\hat{h}_\Theta} + \frac{\hat{h}_{S_A} S_A \Theta S_{A\zeta}}{D_3} \\
+ \frac{\hat{h}_\Theta \Theta \cdot V \Theta \cdot V S_A}{D_1} + \frac{2 D_{12} \Theta S_{A\zeta}}{D_1} + \frac{\hat{h}_\Theta \Theta \cdot V \Theta \cdot V S_A}{D_2} \tag{39}
\]

This evolution equation for \( \Theta \) in a turbulent ocean, and in particular, the form of the nonconservative source terms, is one of the key results of this paper. Note that the superscript \( m \) is no longer needed on the partial derivatives of enthalpy here because this equation applies at all pressures. The epineutral fluxes in Eq. (39)
can be written in terms of the turbulent epineutral mesoscale fluxes rather than their parameterized versions as follows:

\[
K \nabla \cdot \mathbf V_n = - \mathbf F^\phi \cdot \mathbf V_n, \quad \text{(40)}
\]

\[
K \nabla S_A \cdot \mathbf V_n S_A = - \mathbf F^S \cdot \mathbf V_n S_A, \quad \text{and} \quad \text{(41)}
\]

\[
2K \nabla \cdot \mathbf V_n S_A = - \mathbf F^\phi \cdot \mathbf V_n S_A - \mathbf F^S \cdot \mathbf V_n, \quad \text{(42)}
\]

where \( \mathbf F^\phi \) and \( \mathbf F^S \) are the epineutral fluxes of \( \Phi \) and \( S_A \) respectively.

Note that in this subsection we have taken the averaged enthalpy to be a function of the averaged Absolute Salinity and the averaged Conservative Temperature in the form \( h^m = \hat h(S_A, \Theta, p^m) \). More correctly, we should be averaging the enthalpy as a function of the instantaneous values of Absolute Salinity and Conservative Temperature. In appendix A we explore the consequences of the subtly different forms of averaging and conclude that the more correct form of averaging adds a spatially rich pattern to the source terms, which averages to zero. In what follows we continue to regard thermodynamic variables as a function of their averaged independent variables.

d. The evolution equation for \( \theta \)

We consider \( \theta \) in the functional form \( \theta = \hat \theta(S_A, \Theta) \), that is, as a function of Absolute Salinity and Conservative Temperature only and not dependent on pressure. The conservation equation of \( \theta \) following the appropriately averaged mean velocity is the sum of the conservation equation for \( \Theta \) following the appropriately averaged mean velocity, Eq. (39), multiplied by \( \hat \theta \), and the conservation equation of \( S_A \) following the appropriately averaged mean velocity, Eq. (32), multiplied by \( \hat \theta S_A \), and is given by

\[
\frac{D\theta}{Dt} = \mathcal D_{\Theta} \frac{DS_A}{Dt} + \hat \theta \left[ \hat \theta \gamma z \mathbf V_n \cdot \mathbf V_n \Theta + \frac{\hat \theta}{\hat h_\Theta} \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n \Theta \cdot \mathbf V_n S_A + \hat \theta S_A \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n S_A \cdot \mathbf V_n S_A \right],
\]

\[
\text{where } \mathcal D_{\Theta} = \frac{\hat \theta}{\hat h_\Theta} \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n S_A \cdot \mathbf V_n S_A + \hat \theta S_A \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n S_A \cdot \mathbf V_n S_A.
\]

Equation (43) can be expressed in terms of diffusion of potential temperature by using

\[
\frac{D\theta}{Dt} = \gamma z \mathbf V_n \cdot \left( \gamma z^{-1} K \mathbf V_n \Theta \right) + (D\hat \theta) z + \frac{\hat \theta}{\hat h_\Theta} \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n \Theta \cdot \mathbf V_n S_A + \hat \theta S_A \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n S_A \cdot \mathbf V_n S_A,
\]

\[
\text{where } \gamma z \mathbf V_n \cdot \left( \gamma z^{-1} K \mathbf V_n \Theta \right) + (D\hat \theta) z + \frac{\hat \theta}{\hat h_\Theta} \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n \Theta \cdot \mathbf V_n S_A + \hat \theta S_A \left( \frac{\hat \theta S_A}{\hat h_\Theta} \right)^2 \mathbf V_n S_A \cdot \mathbf V_n S_A.
\]

This evolution equation for \( \theta \) in a turbulent ocean, and in particular, the form of the nonconservative source terms, is one of the key results of this paper.

We now consider enthalpy in the functional form \( h^m = \hat h(S_A, \theta, p^m) \). Using a similar method to that presented in section c to derive Eq. (39), the following alternative for the evolution equation of \( \theta \) is derived:
\[
\frac{D\theta}{Dt} = \gamma_z \nabla_n \cdot (\gamma_z^{-1} K \nabla_n \theta) + (D \theta_z) + \frac{e}{h_\theta} K \left( \tilde{h}_{\theta\theta} \nabla_n \theta \cdot \nabla_n \theta + 2 \tilde{h}_{\theta\theta} \nabla_n \theta \cdot \nabla_n S_A + \tilde{h}_{S\theta} \nabla_n S_A \cdot \nabla_n S_A \right) \\
+ D \left( \frac{\tilde{h}_{\theta\theta}}{h_\theta} \theta_z^2 + 2 \frac{\tilde{h}_{\theta\theta}}{h_\theta} \theta_z S_{AZ} + \frac{\tilde{h}_{S\theta}}{h_\theta} S_{AZ}^2 \right).
\]

The differences between the turbulent evolution Eqs. (39) and (45) and the respective laminar equations are discussed in appendix B.

e. The evolution equation for \( \eta \)

Regarding \( \eta \) in the form \( \eta = \hat{\eta}(S_A, \Theta) \), an evolution equation for specific entropy is derived by multiplying \( \hat{\eta}_\theta \) by the conservation equation for \( \Theta \) following the appropriately averaged mean velocity, Eq. (39), and adding \( \hat{\eta}_S \) multiplied by the conservation equation of \( S_A \) following the appropriately averaged mean velocity, Eq. (32); namely,

\[
\frac{D\eta}{Dt} = \hat{\eta}_\theta \frac{D\Theta}{Dt} + \hat{\eta}_S \frac{DS_A}{Dt}
\]

Using the identities \( \nabla_n \eta = \hat{\eta}_S \nabla_n S_A + \hat{\eta}_\theta \nabla_n \Theta \) and \( \eta_z = \hat{\eta}_S S_A + \hat{\eta}_\theta \Theta_z \), Eq. (47) can be expressed in terms of diffusion of specific entropy. Then the evolution equation for \( \eta \) in a turbulent ocean becomes

\[
\frac{D\eta}{Dt} = \gamma_z \nabla_n \cdot (\gamma_z^{-1} K \nabla_n \eta) + (D \eta_z) + \frac{e}{(T_0 + t)} + K \left( \frac{\tilde{h}_{\theta\theta}}{h_\theta} - \hat{\eta}_\theta \right) \nabla_n \Theta \cdot \nabla_n \Theta \\
+ 2K \left( \frac{\tilde{h}_{\theta\theta}}{h_\theta} - \hat{\eta}_\theta S_A \right) \nabla_n \Theta \cdot \nabla_n S_A + K \left( \frac{\tilde{h}_{S\theta}}{h_\theta} \Theta_z - \hat{\eta}_S S_A \right) \nabla_n S_A \cdot \nabla_n S_A + D \left( \frac{\tilde{h}_{\theta\theta}}{h_\theta} - \hat{\eta}_\theta \right) \Theta_z^2 \\
+ 2D \left( \frac{\tilde{h}_{\theta\theta}}{h_\theta} - \hat{\eta}_\theta S_A \right) \Theta_z S_{AZ} + D \left( \frac{\tilde{h}_{S\theta}}{h_\theta} \Theta_z - \hat{\eta}_S S_A \right) S_{AZ}^2.
\]

The second law of thermodynamics requires that the nonconservative production of \( \eta \) is positive definite. This is further discussed in appendix C.

4. Quantifying the nonconservative source terms

a. Dataset

For our calculations, we require a dataset with salinity, temperature, and pressure as well as credible values of the turbulent diffusivities \( K \) and \( D \). We use the same model output from a standard configuration of version 4 of the Modular Ocean Model (MOM4; Griffies et al. 2004) as used in Klocker and McDougall (2010a,b), with a resolution of \( 1^\circ \times 1^\circ \). This model carries Conservative Temperature rather than potential temperature, practical salinity, an isopycnal diffusivity \( K \) of 1000 m$^2$ s$^{-1}$, and uses the vertical mixing scheme by Bryan and Lewis (1979). The evolution equations for \( \Theta, \theta, \) and \( \eta \) in both...
the laminar and turbulent cases are developed here in terms of Absolute Salinity. This is the salinity argument of the modern Gibbs function, and although the MOM4 dataset used in this section carries practical salinity rather than Absolute Salinity, for consistency with the notation used throughout the paper so far and for laying the foundation for future work in this area, the model’s salinity variable will be interpreted as Absolute Salinity, denoted $S_A$ which we have simply calculated as practical salinity times $35.165 \, 04 \, g \, kg^{-1}/35$. The model uses the Jackett et al. (2006) equation of state. This equation of state has been superseded by the more accurate and comprehensive Thermodynamic Equation of Seawater 2010 (TEOS-10), described in IOC et al. (2010); however, for consistency with the model data, all calculations are performed using the earlier definition for the equation of state.

Since potential temperature was not carried in the model, we use the inverse function $\theta = \theta(S_A, \Theta)$, gsw_pt_from_CT, of the Gibbs Sea Water (GSW) Oceanographic Toolbox [McDougall and Barker (2011), found at www.TEOS-10.org] to calculate potential temperature. The turbulent rate of dissipation of kinetic energy $\varepsilon$ is calculated using the Osborn (1980) relation between the diapycnal diffusivity $D$ and the square of the buoyancy frequency $N^2$; namely,

$$\varepsilon = \frac{DN^2}{\Gamma}, \quad (49)$$

where the mixing efficiency $\Gamma$ is the ratio of the turbulent buoyancy flux to the turbulent kinetic energy dissipation rate. Following Klocker and McDougall (2010a), a value of $\Gamma = 0.2$ is used, which is an upper bound for $\Gamma$ in the context of shear flow instability (Osborn 1980). Although it has been suggested that this value is oversimplified and a little too large for some regions of the ocean (see for example Smyth et al. 2001; Arnebord 2002), due to a lack of consensus and for ease of comparison with earlier work, $\Gamma = 0.2$ is appropriate for our purposes.

b. **Quantifying the nonconservative source terms of $\Theta$, $\theta$, and $\eta$**

The nonconservative source terms in Eqs. (39), (44), and (48) are quantified and then integrated with respect to depth. The depth integrals of the source terms are defined by (in units of mW m$^{-2}$)

$$I_{\Theta}(z_r) = \frac{c_0}{\rho_0} \int_{z_b}^{z_r} P_{\Theta} \, dz', \quad (50)$$

$$I_{\theta}(z_r) = \frac{c_0}{\rho_0} \int_{z_b}^{z_r} P_{\theta} \, dz', \quad (51)$$

$$I_{\eta}(z_r) = \frac{1}{\eta_0} \int_{z_b}^{z_r} P_{\eta} \, dz', \quad \text{and} \quad (52)$$

$$I_{\varepsilon}(z_r) = 5\rho_0 \int_{z_b}^{z_r} DN^2 \, dz', \quad (53)$$

and illustrated in Fig. 3. Here, the subscript on $I$ denotes the variable whose source terms are being integrated, and $z_r$ denotes the fixed reference depth to which the integrals are evaluated. $P_{\Theta}$, $P_{\theta}$, and $P_{\eta}$ represent the source terms of $\Theta$, $\theta$, and $\eta$ respectively in Eqs. (39), (44), and (48). Unless otherwise indicated, the integrals are evaluated from the sea floor (where $z_b \approx -5000$ m). Also, $\rho_0$ is the constant density $1035 \, kg \, m^{-3}$, and $\eta_0$ is the scaling constant of $\eta_0 = 14 \, J \, kg^{-1} \, K^{-2}$.

We consider the integrals of the source terms of $\Theta$, $\theta$, and $\eta$, as per Eqs. (50)–(53), from the sea floor ($z_b \approx -5000$ m) to the sea surface ($z_r \approx 0$ m). In the cases of $\Theta$, $\theta$, and $\eta$, the resulting expressions are $I_{\Theta}(0)$, $I_{\theta}(0)$, and $I_{\eta}(0)$, which can be interpreted as the errors in the air–sea heat flux (mW m$^{-2}$) in assuming that the variables $\Theta$, $\theta$, and $\eta$ are conservative. In the case of $\varepsilon$, the resulting expression is $I_{\varepsilon}(0)$, which represents the air–sea heat flux that warms the water column at the same rate as does the interior turbulent rate of dissipation of kinetic energy. For this study, an arbitrary depth of 300 m is applied globally such that above 300 m the horizontal gradients $\nabla z$ of temperature and salinity are used in place of the epineutral gradients $\nabla z$, while below
300 m, epineutral gradients of temperature and salinity are used. Given the model data used is of coarse resolution, it is sufficient for our purposes to choose a fixed value for the mixed layer depth and a depth of 300 m is chosen to encapsulate the dynamics of the mixed layer. Deep convection regions where the slope might usually be infinite are not encountered in this study, also due to the coarse resolution of the model data.

1) MAP OF $I_Q(0)$

The magnitude of the depth-integrated source terms, namely $I_Q(0)$, is shown in Fig. 4. The mean of $I_Q(0)$ is 0.318 mW m$^{-2}$, and the maximum value is 13.8 mW m$^{-2}$. In general, the largest values of $I_Q(0)$ are found in areas where strong currents are present [for example, the Gulf Stream, the Antarctic Circumpolar Current (ACC) region,
and the Kuroshio Current], whereas smaller values of \( I_{\theta}(0) \) occur at high latitudes in the Southern Hemisphere and in the Bering Sea. The dominant terms contributing to \( I_{\theta}(0) \) are the \( K_1 \) and \( D_1 \) terms in Eq. (39), taking into account that horizontal gradients rather than epineutral gradients are calculated in the mixed layer (the upper 300 m). It is clear that \( K_1 \) and \( D_1 \), integrated with respect to depth from the sea floor to the sea surface, represent the error in the air–sea heat flux due to ignoring the effect of cabbeling since \( \theta_{\theta h} = \alpha_{\theta \theta} p / \rho_0 \), where \( \alpha_{\theta \theta} \) is the first-order derivative of the thermal expansion coefficient with respect to \( \Theta \) and is the dominant term in the expression for the cabbeling coefficient (IOC et al. 2010). The depth-integrated \( K_1 \) and \( D_1 \) terms are here and henceforth denoted \( K_1(0) \) and \( D_1(0) \) and are illustrated in Figs. 4b and 4c. The mean of \( K_1(0) \) is 0.176 mW m\(^{-2}\), the mean of \( D_1(0) \) is 0.127 mW m\(^{-2}\), and both \( K_1(0) \) and \( D_1(0) \) are strictly positive. The second terms in the expressions that are multiplied by \( K \) and \( D \) in Eq. (39) are integrated with respect to depth from the sea floor to the sea surface and are denoted \( K_2(0) \) and \( D_2(0) \). These terms can be negative since the horizontal gradients of \( S_A \) and \( \Theta \) can be of opposite sign in the upper ocean. However, the magnitude of \( K_2(0) + D_2(0) \) is up to 20 times smaller than \( K_1(0) + D_1(0) \), which means that the overall sign of \( I_{\theta}(0) \) is positive. The third terms in the expressions that are multiplied by \( K \) and \( D \) in Eq. (39), integrated with respect to depth and denoted \( K_3(0) \) and \( D_3(0) \) (these terms are sometimes called the “heat of mixing” terms), are on average 278 and 224 times smaller than \( K_1(0) \) and \( D_1(0) \) respectively, although the spatial patterns are similar.

Figures 4d and 4e show the integral of the nonconservative source terms of \( \Theta \) from \(-5000 \) to \(-1800 \) m, denoted \( I_{\theta}(\init{5000}) \) and \( I_{\theta}(\init{1800}) \), and from \(-1800 \) to \(-500 \) m, denoted \( I_{\theta}(\init{-500}) \) and \( I_{\theta}(\init{-1800}) \), respectively. The relative magnitude of the values of each of these plots is of the same order as in \( I_{\theta}(0) \); however, the mean value of \( I_{\theta}(\init{-1800}) \) is \( 3.20 \times 10^{-2} \) mW m\(^{-2}\) and the mean value of \( I_{\theta}(\init{-500}) - I_{\theta}(\init{-1800}) \) is \( 7.73 \times 10^{-2} \) mW m\(^{-2}\), so it can be seen that the production of \( \Theta \) in the upper 500 m of the ocean dominates \( I_{\theta}(0) \). Both \( I_{\theta}(\init{-1800}) \) and \( I_{\theta}(\init{-500}) - I_{\theta}(\init{-1800}) \) are dominated by the vertical flux terms in Eq. (39).

2) Map of \( I_{\theta}(0) \)

Figure 5 illustrates the error in the air–sea heat flux in assuming that \( \theta \) is conservative. The mean value of \( I_{\theta}(0) \) is \(-9.62 \) mW m\(^{-2}\), the magnitude of which is approximately 30 times greater than the mean value of \( I_{\theta}(0) \), the maximum value is 678 mW m\(^{-2}\), and the minimum value is \(-1465 \) mW m\(^{-2}\). So, the maximum absolute error in assuming \( \theta \) is conservative is approximately 106 times greater than the maximum absolute error in assuming \( \Theta \) is conservative. In general, negative values occur at high latitudes and in the equatorial regions, whereas larger, positive values dominate the mid-latitudes.

Similarly to the previous section, we denote the depth-integrated terms from the expression for the source terms of \( \theta \) in Eq. (44) as \( K_1(0) \), \( K_2(0) \), \( K_3(0) \), \( D_1(0) \), \( D_2(0) \), and \( D_3(0) \), where horizontal rather than epineutral gradients are calculated in the top 300 m of the ocean. It can be seen that the \( K_1(0) \) and \( D_1(0) \) terms are positive definite and the \( K_3(0) \) and \( D_3(0) \) terms are negative definite, while the \( K_2(0) \) and \( D_2(0) \) terms can take both positive and negative values due to the sign of the temperature and salinity gradients in each term and hence \( \theta \) can be alternatively produced and consumed in turbulent mixing. The “heat of mixing” terms, \( K_3(0) \) and \( D_3(0) \), are smaller than the remaining terms in the expression for the evolution of \( \theta \) by up to 16 times. Unlike in the \( \Theta \) case, cabbeling is not the dominant term contributing to \( K_1(0) \) and \( D_1(0) \); rather, the magnitude of the \( \theta_{\theta h} \) term is much greater than the magnitude of the \( \theta_{\Theta h_{\Theta h}}/h_{\Theta h} \) term. Figures 5b–e illustrate the contribution of the \( K_1(0) \) and \( D_1(0) \) terms and the \( K_2(0) \) and \( D_2(0) \) terms to \( I_{\theta}(0) \).

3) Map of \( I_{\eta}(0) \)

The error in assuming that \( \eta \) is conservative \( I_{\eta}(0) \) is illustrated in Fig. 6. An approximate conversion factor of 14 J kg\(^{-1}\) K\(^{-2}\) has been used to express entropy in the same units as \( \Theta \) and \( \theta \). We have done this so that the nonconservative source terms of entropy can be expressed in units of W m\(^{-2}\). The mean value of \( I_{\eta}(0) \) is 379 mW m\(^{-2}\) and the maximum value is 7290 mW m\(^{-2}\), which are approximately 1191 times the mean and 528 times the maximum values in \( I_{\theta}(0) \) respectively. The spatial patterns in \( I_{\eta}(0) \) are similar to those in the production of \( \Theta \), including that the majority of the contribution to \( I_{\eta}(0) \) occurs in the upper 500 m of the ocean, along the intensified boundary currents and in the ACC. The \( K_1(0) \) and \( D_1(0) \) terms are the depth-integrated \( K_1 \) and \( D_1 \) terms as defined in Eq. (48) and are the dominant terms contributing to \( I_{\eta}(0) \). Furthermore, the \( \eta_{\theta h} \) term in Eq. (48) dominates the patterns in \( K_1(0) \) and \( D_1(0) \). The contribution of \( K_3(0) \) and \( D_3(0) \) to the overall production of \( \eta \) is small. \( K_2(0) \) and \( D_2(0) \) alternatively attain positive and negative values due to the fact that \( V_S S_A \cdot V_\zeta \Theta \) can be negative in the upper ocean, as \( h_{S_A \Theta} / h_{\theta \Theta}, \eta_{\theta} \) and \( \eta_{S_A \Theta} \) are all positive definite.

4) Map of \( I_{\zeta}(0) \)

Figure 7 shows the magnitude of \( I_{\zeta}(0) \), the dissipation of kinetic energy into heat, integrated to the sea surface.
The mean value of $I_\phi(0)$ is 2.99 mW m$^{-2}$, and the maximum is 18.5 mW m$^{-2}$, which occurs in the Arctic Ocean. $I_\phi(0)$ shows a strong dependence on latitude, with low values between 50$^\circ$ latitude and 70$^\circ$ latitude and below approximately −50$^\circ$ latitude, and high values around 30$^\circ$ latitude and −30$^\circ$ latitude. These patterns are predominantly due to the square of the buoyancy frequency $N^2$, although the diapycnal diffusivity $D$ dominates the spatial patterns in the equatorial region.

**Fig. 5.** (a) $I_u(0)$ referenced at the sea surface (mW m$^{-2}$); (b) $K_1(0)$ (mW m$^{-2}$); (c) $K_2(0)$ (mW m$^{-2}$); (d) $D_1(0)$ (mW m$^{-2}$); and (e) $D_2(0)$ (mW m$^{-2}$). Note the different range relative to $I_\phi(0)$ in Fig. 4.

5) **Comparison of the Maps of $I_\phi(0)$, $I_\theta(0)$, $I_q(0)$, and $I_e(0)$**

From these maps it can be concluded that $I_\phi(0)$ is the smallest of the variables $\Theta$, $\theta$, and $\eta$. The mean values of $I_\phi(0)$, $I_\theta(0)$, $I_q(0)$, and $I_e(0)$ can be compared to the mean geothermal heat flux, which is approximately 86.4 mW m$^{-2}$ (Emile-Geay and Madec 2009). So, the error in assuming that $\Theta$ is conservative is of the order of 270
times smaller than the mean geothermal heat flux. By contrast, the nonconservative production of $\theta$ is approximately 9 times smaller than the geothermal heat flux, and the nonconservative production of $\eta$ is approximately 4 times larger than the mean geothermal heat flux. Ignoring the turbulent kinetic energy dissipation rate in ocean models introduces an error approximately 29 times smaller than the error in ignoring the geothermal heat flux.

6) FREQUENCY DISTRIBUTIONS

Another way of expressing the nonconservation of $Q$, $u$, and $h$ and the magnitude of $\varepsilon$ is to plot the frequency distributions of $I_{Q}(0)$, $I_{u}(0)$, $I_{h}(0)$, and $I_{\varepsilon}(0)$. For convenience of comparison, the log$_{10}$ of each of these variables has been calculated and its frequency plotted in Fig. 8. Here, 95% of the values of $I_{Q}(0)$ occur within the range 0 to 0.892 mW m$^{-2}$. By comparison, 95% of the values of $I_{\varepsilon}(0)$ occur within the range 0 to 5.37 mW m$^{-2}$ and 95% of the values of $I_{h}(0)$ occur within the range 0 to 1070 mW m$^{-2}$. $I_{u}(0)$ is the only variable that is not positive definite, with a mean of $\sim9.62$ mW m$^{-2}$ and a standard deviation of 59.8 mW m$^{-2}$ so that approximately 95% of $I_{u}(0)$ occurs within the range $\sim130$ to $110$ mW m$^{-2}$.

The approach in Tailleux (2010) used to estimate the magnitude of the nonconservative source terms of $\Theta$ and $\theta$ involved replacing the laminar fluxes of the evolution equations for $\Theta$ and $\theta$ (derived in appendix B along with the laminar evolution equation for $\eta$) with turbulent fluxes so that an extra term approximately $1/\ell$ the magnitude of $\varepsilon$ was subtracted from the respective nonconservative source terms on the right-hand side of Eqs. (39) and (44). Hence, this approach would change the mean value of the nonconservative source terms of $\Theta$ and $\theta$ by approximately 0.598 mW m$^{-2}$. This term is larger.

FIG. 6. (a) $I_{\varepsilon}(0)$ referenced at the sea surface (mW m$^{-2}$); (b) $K_{1}(0)$ (mW m$^{-2}$); and (c) $D_{1}(0)$ (mW m$^{-2}$). Note the different range relative to $I_{\varepsilon}(0)$ in Fig. 4 and $I_{u}(0)$ in Fig. 5.

FIG. 7. $I_{\varepsilon}(0)$ referenced at the sea surface (mW m$^{-2}$).
than the mean value of $I_\theta(0)$, which is 0.318 mW m$^{-2}$.

We conclude that the substitution of turbulent fluxes into the laminar evolution equation for $Q$ is inappropriate at leading order.

In summarizing the 95th percentiles for the depth integrals to the sea surface in Eqs. (50)–(53), it can be seen that Conservative Temperature is approximately 120 times more conservative than potential temperature and 1200 times more conservative than entropy. Of particular note is the fact that treating Conservative Temperature as being conservative in a model is of less concern (by a factor of 6) than neglecting the turbulent rate of dissipation of kinetic energy.

7) MERIDIONAL HEAT FLUXES

The meridional heat fluxes for $\Theta$, $\theta$, $\eta$, and $\epsilon$, shown in Fig. 9, are calculated by taking the area integral of $I_\theta(0)$, $I_\eta(0)$, $I_\epsilon(0)$, and $I_\eta(0)$ at each latitude. These heat fluxes represent the error in the heat budget from assuming that $\Theta$, $\theta$, and $\eta$ are conservative variables. For the three sign definite variables $I_\theta(0)$, $I_\eta(0)$, and $I_\epsilon(0)$, the gradient of increase in the heat fluxes is always positive. The plots show a strong dependence on latitude, with distinct changes in the rate of increase at about $-50^\circ$ latitude and $50^\circ$ latitude, corresponding to sharp changes in the magnitude of $I_\theta(0)$, $I_\eta(0)$, $I_\epsilon(0)$, and $I_\eta(0)$. The meridional heat flux for $I_\eta(0)$ is also a strong function of latitude. It is informative to compare the ratios of the maximum values of the meridional heat fluxes for $I_\theta(0)$, $I_\eta(0)$, $I_\epsilon(0)$, and $I_\eta(0)$. Then it can be seen that the magnitude of $I_\theta(0)$ is approximately 9.8 times smaller than for $I_\eta(0)$, 17 times smaller than for $I_\epsilon(0)$ and over 1200 times smaller than for $I_\eta(0)$.

In appendix C, we deduce, from parcel mixing arguments, that the nonconservative source terms of $\Theta$, $\eta$, and $\epsilon$ are sign definite if the following three inequalities are satisfied:

$$h_{\theta\theta} > 0, \quad h_{\eta\eta} > 0, \quad h_{\theta\eta}^2 < h_{\theta\theta} h_{\eta\eta}.$$  (54)
These three inequalities have been examined throughout the full cube in $S_A - \Theta - p$ space in which TEOS-10 is defined. Note the following exact expressions for $\hat{h}_{\Theta\Theta}$ and $\hat{h}_{S_A S_A}$ are

$$\hat{h}_{\Theta\Theta}|_{S_A, p} = \int_0^{p_m} \nu_{\Theta\Theta}(S_A, \Theta, p') dp',$$

$$\hat{h}_{S_A S_A}|_{\Theta, p} = \int_0^{p_m} \nu_{S_A S_A}(S_A, \Theta, p') dp'. \tag{55}$$

We have found that all three inequalities of Eq. (54) hold with our particular choice of fixed reference pressure (i.e. 0 dbar) in the definition of $\Theta$. Hence, in our case, $\Theta$ is produced for any turbulent mixing process in the ocean, whether it is vertical or horizontal turbulent mixing or turbulent mixing along neutral tangent planes. However, this does not imply that the nonconservative source terms of potential enthalpy are positive definite for any choice of its fixed reference pressure $p^m$.

The sign definite nature of the nonconservative production terms has also been found for specific volume; in this case the production terms are negative definite. It is interesting to note that the nonconservative source terms of density, related to specific volume by $\rho = 1/\nu$, are not necessarily sign definite. This can easily be seen from inspection of the second-order partial derivatives of $\rho$ derived in terms of $\nu$, as there is no requirement for $\rho$ or its second-order partial derivatives to be sign definite, and in fact, the nonconservative source terms of $\rho$ are not sign definite using the TEOS-10 equation of state. The conditions on the sign definiteness of specific volume are derived in appendix C.

5. Discussion and conclusions

A key finding of this paper is that the error in the air–sea heat flux incurred by ocean models in assuming that Conservative Temperature $\Theta$ is a conservative thermodynamic property is approximately 120 times smaller than the corresponding error for potential temperature. This factor of 120 applies to the rms of the depth-integrated source terms. Furthermore, the error in the air–sea heat flux incurred by ocean models in assuming $\Theta$ is conservative is approximately 6 times smaller than the error incurred by ocean models in ignoring the rate of dissipation of turbulent kinetic energy in the conservation equation for “heat.” Entropy is the least conservative of the three variables $\Theta$, $\theta$, and $\eta$, and the error in the air–sea heat flux in ignoring the source terms of entropy is approximately 1200 times greater than the corresponding error for Conservative Temperature. Figure 10 summarizes the ratios of the upper bound of the 95th percentiles of the depth-integrated source terms for $\epsilon$, $\theta$, and $\eta$ compared with that of $\Theta$. Even at great depth in the ocean (for example 4000 dbar), Fig. 2 implies that $\Theta$ is more locally conservative than $\theta$ by approximately an order of magnitude. Of course, given that at depth the salinity and temperature gradients are small, the magnitude of the source terms is considerably smaller at depth than closer to the sea surface. This issue is discussed in further detail in IOC et al. (2010) in their appendix A.18. It is well known, from the second law of thermodynamics, that entropy is produced during irreversible mixing processes, hence the error in assuming that entropy is conservative is positive definite. By definition, the dissipation of kinetic energy is also positive definite. Conversely, the error in assuming that potential temperature is a conservative thermodynamic property is not sign definite; potential temperature is alternatively produced and consumed during turbulent mixing. From examination of the three inequalities in Eq. (54), we find that the source terms of Conservative Temperature are positive definite for our choice of its fixed reference pressure, 0 dbar. This is true for the full TEOS-10 Gibbs function as well as for the 48-term approximation of IOC et al. (2010) and is true over the full range of applicability of each equation of state. However, this does not imply that the nonconservative source terms of potential enthalpy are always positive definite; rather, for different choices of fixed reference pressure $p^m$, potential enthalpy may be alternatively produced and consumed during turbulent mixing. Since Conservative Temperature is defined as being proportional to potential enthalpy referenced to $p = 0$ dbar, then we can say that the nonconservative source terms of Conservative Temperature are positive definite.

Conservative temperature can be regarded as a conservative variable with a high degree of accuracy. Furthermore, because potential enthalpy possesses the “potential” property and because the air–sea heat flux is equal to the air–sea flux of potential enthalpy, then potential enthalpy is the most accurate variable to represent the “heat content” per unit mass of seawater. Warren (1999, 2006) argues that because enthalpy is unknown up to a linear function of salinity, it is only possible to talk of a flux of “heat” through an ocean section if the fluxes of mass and salt through that section are both zero. This
argument is incorrect; it is perfectly valid to regard the flux of potential enthalpy across an ocean section as "heat flux" irrespective of whether there are nonzero fluxes of mass and salt across the section. This issue is discussed at greater length in McDougall (2003) and IOC et al. (2010). Some model components of coupled models, such as the atmosphere and rivers, carry enthalpy rather than potential enthalpy as heat content. In such cases, when heat is transferred from the atmosphere or from rivers to the ocean, if the ocean is not carrying potential enthalpy as heat content, then a bias in the air–sea heat flux is introduced. This bias is removed if potential enthalpy is regarded as "heat content" by all model components in coupled models.

If Eq. (C12) for the nonconservative production of $\delta \theta$ of appendix C were to be used to quantify the errors in oceanographic practice incurred by assuming that $\theta$ is a conservative variable, one might select property contrasts that were typical of a prominent oceanic front and decide that because $\delta \theta$ is small at this one front, then the issue can be ignored. But the observed properties in the ocean result from a large and indeterminate number of such prior mixing events and the nonconservative production of $\theta$ accumulates during each of these mixing events, often in a sign definite fashion. How can we possibly estimate the error that is made by treating potential temperature as a conservative variable during all of these unknowably many past individual mixing events? As explained in IOC et al. (2010), the difference between $\theta$ and $\Theta$ (as seen in Fig. 1), is the error caused by ignoring the nonconservative source terms in $\theta$ in all these past mixing events.

Since we have shown that potential enthalpy can be accurately regarded as "heat content" per unit mass of seawater, it follows that the turbulent diffusive flux of heat is more accurately directed down the gradient of $\Theta$ rather than of $\theta$. The ratio of the mean gradients of $\theta$ and $\Theta$ can be expressed as (see appendix A.14 IOC et al. 2010)

$$\frac{\nabla_{n} \theta}{\nabla_{n} \Theta} = \frac{\alpha^{\theta} / \beta^{\theta}}{\alpha^{\Theta} / \beta^{\Theta}} = \frac{\alpha^{\theta}}{\beta^{\theta}} \frac{\partial S_{A}}{\partial \Theta} \frac{\partial \Theta}{\partial \theta}, \tag{56}$$

where the partial derivatives $\partial \Theta / \partial \theta$ and $\partial S_{A} / \partial \Theta$ are both independent of pressure, while $\alpha^{\theta} / \beta^{\theta}$ is a function of pressure. It can also be shown that $\alpha^{\Theta} / \alpha^{\theta} = \theta_{\Theta}$ and $\beta^{\Theta} / \beta^{\theta} = 1 + (\alpha^{\Theta} / \beta^{\theta}) \partial S_{A} / \partial \theta$. These ratios, along with the ratio in Eq. (56), are illustrated at $p = 0$ in Fig. 11. Figure 11a shows that the epineutral gradient of $\theta$ can be 1.2% less and 1.6% greater than that of $\Theta$ for typical $S_{A}$ and $\Theta$ ranges in the oceans.

Tailleux (2010) estimated the nonconservative production of $\Theta$ and $\theta$ by replacing the laminar fluxes of the instantaneous evolution equations for $\Theta$ and $\theta$ with turbulent fluxes. Because of the pressure dependence of enthalpy in the laminar forms, this approach contributes an extra term to the turbulent evolution equations for $\Theta$ and $\theta$ with turbulent fluxes. Because of the pressure dependence of enthalpy in the laminar forms, this approach contributes an extra term to the turbulent evolution equations for $\Theta$ and $\theta$ approximately $1/5$ of the size of $\varepsilon$ as shown in appendix B. The extra term is relatively small in the $\theta$ equation but dominates the true nonconservation of $\Theta$ in the $\Theta$ evolution equation. The substitution of a turbulent diffusivity in place of a laminar one is a potentially dangerous thing to do, as we demonstrate in appendix B where we find that doing this does not guarantee that entropy is always produced under turbulent mixing processes.
Garrett (1992) found a corresponding difference between the behavior of molecular and turbulent fluxes, namely that the molecular flux divergences of heat and salt contribute to the divergence of the three-dimensional velocity vector, while the corresponding turbulent heat and salt flux divergences do not. We are thus comfortable with finding a different expression for the irreversible nonconservative production of Conservative Temperature than that of Tailleux (2010). The results of this paper rely heavily on the physical idea that for turbulent mixing to occur, the fluid parcels must be in contact with each other, sharing the same location in latitude, longitude, and pressure. This seems a robust concept and we are encouraged that our results show a striking similarity to the more standard results of mixing between two water parcels at fixed pressure [compare Eqs. (39) and (C9)]. However, this idea of mixing taking place at a series of constant pressures is indeed an assumption that we have no independent way of checking. For example, we have ignored the small variations of pressure that occur as the turbulent motion occurs all the way down to the molecular scale. However, it must be realized that these same small pressure variations occur in the standard thought experiment when two parcels are mixed in a laboratory situation, leading to Eq. (C9). So, while the idea of turbulent mixing occurring at a fixed pressure is indeed an assumption, it seems a convincing one, and we prefer it to simply replacing a molecular flux with a turbulent one; an approach that does not guarantee that the second law of thermodynamics is obeyed (see appendix B).

R. Tailleux (2012, personal communication) and Tailleux (2012) have made the point that, in a steady-state ocean, the volume integrated nonconservative production of Conservative Temperature is very nearly equal to minus the volume integrated thermodynamic work by expansion/contraction. Conservative Temperature has this special property because the flux of heat through the sea surface is exactly proportional to the flux of Conservative Temperature (whereas this proportionality is not true of potential temperature or of specific entropy). Here, we generalize the derivation of Tailleux to the case where there is a geothermal heat flux into the ocean (as well as there being heat fluxes both into and out of the ocean at the sea surface).

Take the first law of thermodynamics in the form of Eqs. (4) and (6), namely,

$$\frac{\partial (pu)}{\partial t} + \mathbf{V} \cdot (\rho\mathbf{u}\mathbf{u}) + (p_0 + p)\frac{D\mathbf{u}}{Dt} = -\mathbf{V} \cdot \mathbf{F}^R - \mathbf{V} \cdot \mathbf{F}^Q + \rho e,$$

(57)

where we have ignored the term in the production of salinity $h_s\rho S^{\infty}$, and the rate of change of internal energy $u$ has been written in the divergence form. Integrating this equation over the whole ocean volume, while assuming a steady state, and taking the mass flux of water across the air–sea interface to be zero, we find that

$$\int_V \left( p_0 + p \right) \frac{Du}{Dt} dV = \int_A F^{geo} dA - \int_A F^{surf} dA + \int_V \rho e dV,$$

(58)

where $F^{geo}$ is the geothermal heat flux into the ocean at the sea floor and $F^{surf}$ is the air–sea heat flux exchanged with the atmosphere (defined positive when the heat flux is upwards, leaving the ocean, and hence cooling the ocean). This air–sea heat flux $F^{surf}$ includes radiation as well as sensible and latent heat. Note that the material derivative $Du/Dt$ in the integrand of Eq. (58) is the instantaneous material derivative; it is not the coarsely-grained version that we usually use in oceanographic practice.

Next, we turn attention to our Eqs. (38) or (39), except that here we do not make the Boussinesq approximation. Multiplying Eq. (39) by $\rho_0$ and integrating over the volume of the ocean we find

$$0 = \int_A \frac{(T_0 + \theta)}{(T_0 + t)} F^{geo} dA - \int_A F^{surf} dA + \int_V \frac{(T_0 + \theta)}{(T_0 + t)} \rho e dV + \int_V \rho_0 \frac{\partial}{\partial t} \rho \theta_{irr} dV.$$

(59)

Here, $\theta_{irr}$ is the last two lines of Eq. (38), namely, the irreversible nonconservative production terms of Conservative Temperature due to diffusion. Note that the geothermal heat flux $F^{geo}$ at an individual point on the sea floor is $h_\theta = c^0_\theta (T_0 + t)/(T_0 + \theta)$ times the flux of Conservative Temperature, so explaining the geothermal flux term in the above equation.

Now, we eliminate the sea surface heat flux term between Eqs. (58) and (59), finding

$$\int_V \rho_0 \frac{\partial}{\partial t} \rho \theta_{irr} dV = -\int_V \left( p_0 + p \right) \frac{Du}{Dt} dV + \int_V \frac{(t - \theta)}{(T_0 + t)} F^{geo} dA + \int_V \frac{(t - \theta)}{(T_0 + t)} \rho e dV.$$

(60)

The ratio $(t - \theta)/(T_0 + t)$ is very small in the ocean (never much more than $10^{-3}$) so that the last term in Eq. (60) is unlikely to be important. The term in the geothermal heat flux cannot be so easily dismissed because the geothermal heat flux occurs at the sea floor.
where \((t - \theta)/(T_0 + t)\) is the largest (whereas the largest values of \(\epsilon\) occur shallower in the water column where \((t - \theta)/(T_0 + t)\) is very small indeed). We have shown in this paper that the irreversible production \(\dot{\Theta}_{\text{irr}}\) is positive definite in the ocean and if it were true that the geothermal heat flux made a negligible contribution to Eq. (60), then this equation shows that the volume integrated thermodynamic work done by contraction/ expansion, being the global integral over the mass of the ocean of \((p_0 + p)Dv/Dt\), is always negative.

Since the nonconservative production of Conservative Temperature \(\dot{\Theta}_{\text{irr}}\) is very closely related to the “cabbeling” nonlinearity of the equation of state and independent of the “thermobaric” nonlinearity (see section 4c above), it is interesting that Eq. (60) provides a rather direct connection between what is essentially a pressure-weighted volume integral of the contraction-on-mixing due to the “cabbeling” nonlinearity [the left-hand side of Eq. (60); see Eq. (55)] and the volume-integrated thermodynamic work done by expansion/contraction throughout the ocean in steady state.

The results of this paper highlight some of the deficiencies in present ocean modeling practice regarding the use of potential temperature, namely, that potential temperature \(\theta\) is not a conservative property and the evolution equation for potential temperature that is currently carried in ocean models mistakenly neglects the nonconservative source terms. Nonconservative source terms also arise in the evolution equation of Conservative Temperature; however, they are significantly smaller in magnitude than the corresponding source terms of potential temperature. To minimize the errors incurred by ocean models in neglecting the nonconservative source terms, it is therefore recommended that the default temperature variable becomes Conservative Temperature \(\Theta\) rather than potential temperature \(\theta\) and the output temperature of the model be compared to observed Conservative Temperature data rather than to potential temperature data.

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APPENDIX A

Alternative Derivation of Evolution Equations

In this paper we have assumed relations such as \(h^m = \dot{h}(S_A, \Theta, p^m)\) where \(S_A\) and \(\Theta\) are the appropriately averaged Absolute Salinity and Conservative Temperature (thickness-weighted mean values, averaged in density coordinates). Recall that \(h^m\) is potential enthalpy referenced to pressure \(p^m\). However, evaluating enthalpy with the instantaneous values of \(S_A\) and \(\Theta\) and then averaging enthalpy will give a different average enthalpy than evaluating enthalpy with the pre-averaged values of \(S_A\) and \(\Theta\). Here we explore whether this distinction is important in the context of this paper. As a preliminary observation, we note the encouraging similarity between the nonconservative source terms in the parcel-mixing approach of appendix C to those in the evolution equation approach in the bulk of the paper [i.e. compare Eqs. (39) and (39)]. This observation suggests that any differences that arise from the different forms of averaging discussed in this appendix will be small.

At the pressure \(p = p^m\), making the Boussinesq approximation and ignoring the molecular and radiative heat fluxes, the instantaneous first law of thermodynamics is [from Eq. (35)]

\[
\frac{Dh^m}{Dt} = h^m_{\Theta} \frac{D\Theta}{Dt} + h^m_{S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

in terms of the instantaneous material derivative \(D/Dt = \partial/\partial t + u \cdot \nabla\). Now, we expand the partial derivatives \(h^m_{\Theta}\) and \(h^m_{S_A}\) in a Taylor series about the Eulerian-averaged values of Absolute Salinity and Conservative Temperature, \(\bar{S}_A\) and \(\bar{\Theta}\), so that

\[
h^m_{\Theta} = h^m_{\Theta}(\bar{S}_A, \bar{\Theta}, p^m) + h^m_{\Theta\Theta}(\bar{S}_A, \bar{\Theta}, p^m)\Theta' + h^m_{\Theta S_A}(\bar{S}_A, \bar{\Theta}, p^m)S_A' \quad \text{and} \quad (A2)
\]

\[
h^m_{S_A} = h^m_{S_A}(\bar{S}_A, \bar{\Theta}, p^m) + h^m_{S_A S_A}(\bar{S}_A, \bar{\Theta}, p^m)S_A' + h^m_{S_A S_A}(\bar{S}_A, \bar{\Theta}, p^m)\Theta', \quad (A3)
\]

where the second order partial derivatives are also evaluated at \((\bar{S}_A, \bar{\Theta}, p^m)\). The first law of thermodynamics, Eq. (A1), is now time averaged at constant pressure (i.e. an Eulerian average) giving

\[
\frac{Dh^m}{Dt} = h^m_{\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

\[
+ h^m_{\Theta\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

\[
+ h^m_{\Theta\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

\[
+ h^m_{\Theta\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

\[
+ h^m_{\Theta\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

\[
+ h^m_{\Theta\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]

\[
+ h^m_{\Theta\Theta} \frac{D\bar{\Theta}}{Dt} + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon = h^m_{\Theta\Theta} + \Theta \cdot \nabla \Theta + \nabla \cdot (u \Theta') + h^m_{\Theta S_A} \frac{DS_A}{Dt} = \epsilon \quad \text{at} \quad p = p^m, \quad (A1)
\]
When this expression is rearranged into an evolution equation for mean Conservative Temperature, the four terms in Eq. (A4) involving the scalar product of an eddy flux and a mean gradient (such as the term $\mathbf{u}\vec{\mathbf{\Theta}} \cdot \nabla \mathbf{\Theta}$) are recognized as the nonconservative source terms in Eq. (39). Where Eq. (A4) differs from the approach taken in the bulk of this paper is in the following additional terms in Eq. (A5), which do not appear in Eq. (39),

$$D\left(\frac{1}{2} \frac{D^{m}}{D t} \nabla \mathbf{\Theta}^{2}\right) + h_{\Omega \Theta}^{m} D\left(\frac{D \mathbf{\Theta}}{D t}\right) + h_{\theta \Theta}^{m} D\left(\frac{1}{2} \frac{D^{m}}{D t} \nabla \mathbf{\Theta}^{2}\right).$$  \hspace{1cm} (A5)

These terms express the difference between considering enthalpy as a function of averaged Absolute Salinity and Conservative Temperature versus the more correct interpretation as simply being the averaged enthalpy. These differences arise when the perturbation variances are unsteady, and also due to the advection of such variances. The terms in Eq. (A5) make a local difference to Eq. (A4) but spatially integrate to zero over any region of high variance. In this way, it is seen that these terms act as spatially fluctuating source terms, which do not contribute to an area average.

The averaging in this appendix has been Eulerian averaging at fixed pressure. The same additional source terms, Eq. (A5), are obtained by thickness-weighted averaging in density coordinates. We have chosen to illustrate this effect using Eulerian averages simply because it requires less algebra in the Eulerian averaging case.

**APPENDIX B**

**The Laminar Evolution Equations**

Tailleux (2010) estimated the magnitudes of the nonconservative source terms of Conservative Temperature and potential temperature from the respective laminar evolution equations by taking down-gradient turbulent flux formulations for $\mathbf{F}^\Theta$, $\mathbf{F}^\phi$, and $\mathbf{F}^S$. This appendix compares the laminar evolution equations for $\Theta$ and $\theta$ with their turbulent evolution equations, Eqs. (39) and (45), to check the validity of the approach in Tailleux (2010).

The forms of the first law of thermodynamics in terms of $\Theta$, $\theta$, and $\eta$, namely, Eqs. (28), (23), and (18) can be rearranged to be expressed as

$$\rho \frac{D\Theta}{Dt} = (-\nabla \cdot \mathbf{F}^R - \mathbf{F}^Q) + \mathbf{F}^\Theta \cdot \nabla \mathbf{h} \Theta + \mu \mathbf{V} \cdot \mathbf{F}^S + \mu \mathbf{V} \cdot \rho e)/(T_0 + t).$$  \hspace{1cm} (B3)

where the conservation equation of Absolute Salinity is given by $\rho \partial \mathbf{S}/\partial t = -\nabla \cdot \mathbf{F}^S$, ignoring the nonconservative source of Absolute Salinity due to biogeochemistry $\rho S \partial \mathbf{S}/\partial t$, These equations are rearranged by collecting terms that are the divergence of a flux plus other nonconservative source terms that are not the divergence of a flux to obtain

$$\rho \frac{D\Theta}{Dt} = (-\nabla \cdot \mathbf{F}^R - \mathbf{F}^Q) + \mathbf{F}^\Theta \cdot \nabla \mathbf{h} \Theta + \mu \mathbf{V} \cdot \mathbf{F}^S + \mu \mathbf{V} \cdot \rho e)/(T_0 + t).$$  \hspace{1cm} (B4)

$$\rho \frac{D\theta}{Dt} = (-\nabla \cdot \mathbf{F}^R - \mathbf{F}^Q) + \mathbf{F}^\phi \cdot \nabla \mathbf{h} \phi + \mu \mathbf{V} \cdot \mathbf{F}^S + \mu \mathbf{V} \cdot \rho e)/(T_0 + t).$$  \hspace{1cm} (B5)

$$\rho \frac{D\eta}{Dt} = (-\nabla \cdot \mathbf{F}^R - \mathbf{F}^Q - \mu \mathbf{F}^\phi) + \mathbf{F}^\Theta \cdot \nabla \mathbf{h} \Theta + \mu \mathbf{V} \cdot \mathbf{F}^S + \mu \mathbf{V} \cdot \rho e)/(T_0 + t).$$  \hspace{1cm} (B6)

Now we prove that the flux terms inside the divergence operators on the right-hand side of the above equations can be expressed simply as the fluxes of $\Theta$, $\theta$, and $\eta$ respectively. The first law of thermodynamics in the form Eq. (35) at $p = p^m$ shows that the molecular diffusive flux of $h^m = h(S_A, \Theta, p^m)$ is $\mathbf{F}^R + \mathbf{F}^Q$ (the molecular viscosity also affects the evolution of $h^m$ through the $\varepsilon$ term). The functional form of $h^m = h(S_A, \Theta, p^m)$ means that the molecular diffusive flux of $h^m$ is also given by $\mathbf{F}^S + \frac{\mu}{T_0 + t} \mathbf{F}^\Theta$ and equating this with $\mathbf{F}^R + \mathbf{F}^Q$ gives

$$\mathbf{F}^\Theta = \frac{\mathbf{F}^R + \mathbf{F}^Q - \mathbf{h} S_A \mathbf{F}^S}{\mathbf{h} \Theta}.$$  \hspace{1cm} (B7)

This expression applies at any general pressure $p$ and expresses how the molecular diffusion of Conservative Temperature is related to the molecular (and radiative) fluxes of heat and salt. Using the functional forms $\theta = \theta(S_A, \Theta)$ and $\eta = \eta(S_A, \Theta)$ shows that
\[
F^\theta = \hat{\theta}_S S^\theta + \hat{\theta}_\theta F^\theta, \quad \text{and} \quad F^\eta = \bar{\eta}_S S^\eta + \bar{\eta}_\theta F^\eta. \quad (B8)
\]

Applying the chain rule to the expressions \( h = \hat{h}[S_A, \hat{\theta}(S_A, \Theta), p] \) and \( h = \bar{h}[S_A, \bar{\eta}(S_A, \Theta), p] \), and combining with Eq. (B8) yields the following expressions for the molecular fluxes of potential temperature and entropy

\[
F^\theta = \frac{F^R + F^Q - \hat{h}_S S^\theta + \hat{h}_\theta F^\theta}{\hat{h}_\theta}, \quad \text{and} \quad F^\eta = \frac{F^R + F^Q - \mu S^\eta}{(T_0 + t)}. \quad (B9)
\]

In the latter expression, the fundamental thermodynamic relation has been invoked to yield expressions for the partial derivatives of \( h \) with respect to \( \eta \) and \( S_A \); namely, \( \hat{h}_\eta = (T_0 + t) \) and \( \hat{h}_S = \mu \). Hence, the evolution equations of \( \Theta, \theta \) and \( \eta \) respectively are given by

\[
\rho \frac{D \Theta}{Dt} = -\nabla \cdot F^\Theta - \frac{F^\Theta \cdot \nabla \hat{h}_\Theta}{\hat{h}_\Theta} - \frac{F^S \cdot \nabla \hat{h}_S}{\hat{h}_\Theta} + \rho e \quad (B10)
\]

\[
\rho \frac{D \theta}{Dt} = -\nabla \cdot F^\theta - \frac{F^\Theta \cdot \nabla \hat{h}_\Theta}{\hat{h}_\Theta} - \frac{F^S \cdot \nabla \hat{h}_S}{\hat{h}_\Theta} + \rho e, \quad \text{and}
\]

\[
\rho \frac{D \eta}{Dt} = -\nabla \cdot F^\eta - \frac{\left(F^Q + (T_0 + t) \right) - \hat{h}_\Theta}{(T_0 + t)} - \frac{F^S \cdot \nabla \mu}{(T_0 + t)} + \rho e. \quad (B11)
\]

These are the forms of the nonconservative source terms of \( \Theta, \theta, \) and \( \eta \), corresponding to those derived recently by Tailleux (2010). Note that they are derived by rearranging the first law of thermodynamics using the fundamental thermodynamic relation; the second law of thermodynamics has not been invoked. The second law of thermodynamics states that entropy is always produced during mixing processes. This means that the sum of the last three terms in Eq. (B12) must always be positive. For molecular diffusion this is the case, but we will show at the end of this appendix that this is not the case if the fluxes in Eq. (B12) are simply taken to be turbulent fluxes down their respective gradients.

We now compare the laminar equations (B10) and (B11) with their turbulent equivalents, Eqs. (39) and (45) to check whether replacing the molecular fluxes of \( F^\theta, F^\eta \), and \( F^S \) with their corresponding turbulent fluxes is valid.

It is evident that the laminar and turbulent forms of the evolution equations (B10) and (B11) are only equal if each of the partial derivatives of enthalpy with respect to \( \Theta, \theta, \) or \( \eta \) and \( S_A \) have no separate dependence on pressure. For the case of \( \Theta \), these extra terms are found by evaluating the pressure dependence of \( \hat{\theta}_\Theta \) and \( \hat{\theta}_S \), to the following terms from Eq. (B10):

\[
\frac{F^\Theta \cdot \nabla \hat{h}_\Theta}{\hat{h}_\Theta} - \frac{F^S \cdot \nabla \hat{h}_S}{\hat{h}_\Theta}. \quad (B13)
\]

The lateral turbulent flux of \( \Theta \) along the neutral tangent plane \(-KV_n\Theta\) has the exactly horizontal component \(-KV_n\Theta\) and a vertical component because the neutral tangent plane has a slope \( V_n z \) with respect to the horizontal. In Cartesian coordinates then, the lateral turbulent flux of \( \Theta \) along the neutral tangent plane, \(-KV_n\Theta\), is

\[
-KV_n\Theta - kK V_n \Theta \cdot V_n z, \quad (B14)
\]

where \( k \) is the unit vector in the vertical direction, and the total flux of \( \Theta \) due to both epineutral and vertical diffusion is

\[
F^\Theta = -KV_n\Theta - k(K V_n \Theta \cdot V_n z + D\Theta_z). \quad (B15)
\]

Note that it can be proven that the three-dimensional Cartesian divergence of Eq. (B15), is

\[
-KV_n\Theta - k(K V_n \Theta \cdot V_n z + D\Theta_z), \quad (B16)
\]

by using the relations \( (V_n z)_z = \gamma_z^{-1} V_n \gamma_z \) and \( V_n \cdot b = V_z \cdot b + b_z \cdot V_n z \), for any two-dimensional vector \( b \).

In order to evaluate \( V_n \hat{\Theta} \) in the expression \(-F^\theta \cdot \nabla \hat{\Theta}\), the following three-dimensional Cartesian gradient operator is used:

\[
V \phi = V_z \phi + b \phi_z = V_n \phi - \phi_z V_n z + k \phi_z. \quad (B17)
\]

Using equations (B15) and (B17) to evaluate \(-F^\theta \cdot \nabla \hat{\Theta}\) yields

\[
-F^\theta \cdot \nabla \hat{\Theta} = \left[ KV_n \Theta + k(K V_n \Theta \cdot V_n z + D\Theta_z) \right] \]

\[
\cdot \left[ V_n \hat{\Theta} + \hat{h}_\Theta z V_n z + k \hat{h}_\Theta z \right] \]

\[
= KV_n \Theta \cdot V_n \hat{\Theta} + D\Theta_z \hat{h}_\Theta. \quad (B18)
\]

The corresponding equation for \(-F^S \cdot \nabla \hat{S}_A\) is

\[
-F^S \cdot V_n \hat{S}_A = \left[ KV_n S_A + k(K V_n S_A \cdot V_n z + D S_A z) \right] \]

\[
\cdot \left[ V_n \hat{S}_A + \hat{h}_S z V_n z + k \hat{h}_S z \right] \]

\[
= KV_n S_A \cdot V_n \hat{S}_A + D S_A z \hat{h}_S. \quad (B19)
\]

Now \( V_n \hat{\Theta} \) and \( V_n \hat{S}_A \) are expanded in terms of \( \Theta, S_A \) and \( p \), such that

\[
\begin{align*}
\hat{\Theta}(S_A, \Theta, p) & \quad \text{and} \quad \hat{S}_A(S_A, \Theta, p) \\
\hat{\Theta}(S_A, \Theta, p) & \quad \text{and} \quad \hat{S}_A(S_A, \Theta, p) \\
\hat{\Theta}(S_A, \Theta, p) & \quad \text{and} \quad \hat{S}_A(S_A, \Theta, p) \\
\end{align*}
\]
\[ \mathbf{V}_n \: \hat{h}_\Theta = \hat{h}_\Theta \mathbf{V}_n \: \Theta + \hat{h}_\Theta S_A \: \mathbf{V}_n S_A + \hat{h}_\Theta p \: \mathbf{V}_n p, \quad \text{and} \quad (B20) \]

\[ \mathbf{V}_n \: \hat{h}_S = \hat{h}_S X_A \: \mathbf{V}_n \: \Theta + \hat{h}_S X_A \: \mathbf{V}_n S_A + \hat{h}_S X_A \: \mathbf{V}_n p. \quad (B21) \]

The last term in each of the above expressions arises due to the pressure dependence of \( \hat{h}_\Theta \) and \( \hat{h}_S \), in Eqs. (B18) and (B19), respectively, so that the additional terms in \(-F^\Theta \cdot \mathbf{V} \hat{h}_\Theta \) and \(-F^S \cdot \mathbf{V} \hat{h}_S \), respectively, due to this pressure dependence are

\[ Kh_\Theta \mathbf{V}_n \: \Theta \cdot \mathbf{V}_n p + D \Theta \cdot \mathbf{z} \mathbf{h}_\Theta p \cdot \mathbf{z}, \quad \text{and} \quad (B22) \]

\[ K \hat{h}_S X_A \: \mathbf{V}_n S_A \: \cdot \mathbf{V}_n p + D S_A \: \mathbf{h}_S X_A \: \mathbf{p} \cdot \mathbf{z}. \quad (B23) \]

The partial derivatives of \( \hat{h}_\Theta \) and \( \hat{h}_S X_A \) can be written as (IOC et al. 2010)

\[ \hat{h}_\Theta = \frac{1}{\rho} \frac{\partial \rho}{\partial \Theta}, \quad \text{and} \quad \hat{h}_S = \frac{1}{\rho} \frac{\partial \rho}{\partial S_A}. \quad (B24) \]

\[ \hat{h}_S X_A = \frac{1}{\rho} \frac{\partial \rho}{\partial S_A}. \quad (B25) \]

where \( \alpha^\Theta \) is the thermal expansion coefficient and \( \beta^\Theta \) is the saline contraction coefficient, so the extra terms in Eq. (B13) contribute to \( D \Theta / Dt \) in Eq. (B10) the amount

\[ K \left( \frac{\alpha^\Theta \mathbf{V}_n \: \Theta - \beta^\Theta \mathbf{V}_n S_A}{\rho h_\Theta} \right) \cdot \mathbf{V}_n p + D \left( \frac{\alpha^\Theta \mathbf{z} \mathbf{z} - \beta^\Theta S_A \mathbf{z}}{h_\Theta} \right) p. \quad (B26) \]

Since \( \alpha^\Theta \mathbf{V}_n \Theta = \beta^S \mathbf{V}_n S_A \), the epineutral terms in the above expression cancel. Invoking the hydrostatic relation, the vertical terms become

\[ -gD \left( \frac{\alpha^\Theta \mathbf{z} \mathbf{z} - \beta^S S_A \mathbf{z}}{h_\Theta} \right). \quad (B27) \]

IOC et al. (2010) defines the square of the buoyancy frequency as \( N^2 = g(\alpha^\Theta \mathbf{z} \mathbf{z} - \beta^S S_A \mathbf{z}) \), so in the turbulent case for \( \Theta \), the pressure dependence of \( \hat{h}_\Theta |_{S_A} \) and \( \hat{h}_S \) contribute to the right-hand side of the \( D \Theta / Dt \) equation (B10) the term

\[ -DN^2 \frac{\mathbf{z}}{h_\Theta}. \quad (B28) \]

The expression for the turbulent rate of dissipation of mechanical energy is given by \( \varepsilon = DN^2 / \Gamma \). Substituting this into equations (B28) and (B29) contributes the following terms to Eqs. (B10) and (B11) for \( \Theta \) and \( \theta \), respectively,

\[ -\varepsilon \frac{\mathbf{z}}{h_\Theta} - \varepsilon \frac{\mathbf{z}}{\hat{\theta}}. \quad (B30) \]

By definition, \( \varepsilon, \hat{h}_\Theta \), and \( \hat{h}_\Theta \) are positive throughout the ocean. Using a value of \( \Gamma = 0.2 \) (Osborn 1980), it can be seen that these terms contribute to the evolution equations of \( \Theta \) and \( \theta \) a negative value about \( 1/5 \) of the size of the last term in equations (B10) and (B11). These terms in Eq. (B30), while properly being in the laminar equations (B10) and (B11), should not appear in the turbulent forms of those equations (when the laminar diffusive fluxes \( F^\Theta, F^S \), and \( F^S \) are (arbitrarily) replaced by turbulent fluxes of \( \Theta, \theta \), and \( S_A \)). We conclude that the substitution of turbulent fluxes into the laminar diffusive fluxes is inappropriate at leading order.

We return to a discussion of Eq. (B12) and ask whether the sum of the second and third terms on the right-hand side is always guaranteed to be positive if these fluxes are simply changed form being the molecular fluxes (which contain the Dufour, Soret, and barodiffusion terms) to being turbulent fluxes directed down their respective gradients of the mean properties. Consider the case where the turbulent flux of entropy is zero [see Eq. (B9)], but there is a turbulent salt flux. Part of the third term on the right of Eq. (B12) is \( -\mu_p F^S \cdot \mathbf{S} \) and this changes sign with the sign of the salt flux, so that the second law of thermodynamics is not guaranteed to be obeyed (note that the Gibbs relations show that \( \mu_p = v S_A \), which is \( -v \) times the saline contraction coefficient). By contrast, it has been shown in section A.16 of IOC et al. (2010) that the turbulent mixing process as advocated in the present paper (namely the conservation of enthalpy when turbulent mixing occurs at constant pressure) does always produce entropy and hence does obey the second law of thermodynamics.

**APPENDIX C**

**The Mixing of Two Seawater Parcels at Constant Pressure**

When two parcels of seawater are mixed at fixed pressure and under thermodynamic equilibrium, the properties
that are conserved are mass, salt, and enthalpy. The conservation of mass and salt follows from conservation of material substances, and the conservation of enthalpy can be seen by considering the first law of thermodynamics in the following form (see IOC et al. 2010):

\[
\frac{p D h}{D t} = (\rho h)_{i} + \mathbf{v} \cdot (\rho \mathbf{u} h) = \frac{D p}{D t} - \mathbf{v} \cdot \mathbf{F}^R - \mathbf{v} \cdot \mathbf{F}^Q + \rho e + \rho h S A \Delta S . \tag{C1}
\]

Mixing is assumed to occur at fixed pressure, hence \(D p/D t = 0\). Although there will be dissipation of kinetic energy due to viscosity, the contribution is small and so the term \(\rho e\) will be ignored in this discussion. The rate of increase of enthalpy due to the interior source term of Absolute Salinity caused by remineralization is also small, so it too will be ignored. The system is assumed to be closed, that is, there are no radiative or boundary heat fluxes (\(\mathbf{F}^R = \mathbf{F}^Q\)). Then, the volume integral of the right hand side of Eq. (C1) is equal to zero, implying that the volume integrated amount of \(\rho h\) is constant during mixing at fixed pressure. This is a very important result in oceanography. The fact that enthalpy is conserved during mixing at fixed pressure forms the basis for understanding the flux of heat and “heat content” in the oceans. However, it does not follow that enthalpy can adequately represent heat content because it is only conserved during mixing at fixed pressure and it does not have the “potential” property.

Following Fofonoff (1962) and IOC et al. (2010), we consider the mixing of two adjacent parcels of seawater (parcels 1 and 2) at fixed pressure, which have different temperatures and salinities. Mixing is assumed to occur to completion so that in the final state, the temperature, Absolute Salinity, entropy, and enthalpy are uniform. Now, since mass, salt content, and enthalpy are conserved during mixing at fixed pressure, the following equations must hold

\[
m_1 + m_2 = m, \tag{C2}
\]

\[
m_1 S_{A_1} + m_2 S_{A_2} = m S_A, \tag{C3}
\]

\[
m_1 h_1 + m_2 h_2 = m h, \tag{C4}
\]

where the right-hand sides of the above equations denote the mass, salt, and enthalpy of the mixed parcel. Because Conservative Temperature, potential temperature, entropy, and specific volume are not “isobaric conservative” variables, then they obey the following equations, respectively:

\[
m_1 \Theta_1 + m_2 \Theta_2 + m \delta \Theta = m \Theta, \tag{C5}
\]

\[
m_1 \theta_1 + m_2 \theta_2 + m \delta \theta = m \theta, \tag{C6}
\]

\[
m_1 \eta_1 + m_2 \eta_2 + m \delta \eta = m \eta, \tag{C7}
\]

\[
m_1 v_1 + m_2 v_2 + m \delta v = m v, \tag{C8}
\]

Here \(\delta C\) denotes the nonconservative production of scalar \(C\) during mixing at fixed pressure.

### a. The nonconservative production of \(\Theta\)

An expression for \(\delta \Theta\) under mixing at fixed pressure is derived by considering enthalpy in the functional form \(h = \hat{h}(S_A, \Theta, p)\). Let \(h_1 = \hat{h}(S_{A_1}, \Theta_1, p^m)\) and \(h_2 = \hat{h}(S_{A_2}, \Theta_2, p^m)\), where \(p = p^m\) dbar denotes the fixed pressure at which the mixing occurs. Then \(h_1\) and \(h_2\) are expanded in a Taylor series about the values \(S_A\) and \(\Theta\) of the mixed parcel, \(S_A\) and \(\Theta\), respectively, noting that the enthalpy of the mixed parcel is given by \(h^m = \hat{h}(S_A, \Theta, p^m)\), and terms to second order are retained. Then equations (C2)–(C5) are used to derive the following expression for the production of Conservative Temperature when two parcels are mixed

\[
\delta \Theta = \frac{m_1 m_2}{2 m^2} \left[ \frac{\hat{h}_{\Theta \Theta}}{\hat{h}_{\Theta}} (\Delta \Theta)^2 + 2 \frac{\hat{h}_{\Theta S}}{\hat{h}_{\Theta}} \Delta \Theta \Delta S_A + \frac{\hat{h}_{S S}}{\hat{h}_{\Theta}} (\Delta S_A)^2 \right], \tag{C9}
\]

where all the partial derivatives are evaluated at \(p = p^m\).

It is clear from the above equation and from the definition of potential enthalpy, namely \(h^0 = h - p^0 \nu dp^t\) (IOC et al. 2010), that \(\Theta\) is conservative at the sea surface. Now, rearranging equation (C9) yields

\[
\delta \Theta = \frac{m_1 m_2}{2 m^2} \left[ \frac{\hat{h}_{\Theta \Theta}}{\hat{h}_{\Theta}} (\Delta \Theta)^2 \right] + 2 \frac{\hat{h}_{\Theta S}}{\hat{h}_{\Theta}} \frac{(\Delta \Theta)}{\Delta S_A} + \frac{\hat{h}_{S S}}{\hat{h}_{\Theta}} (\Delta S_A)^2 , \tag{C10}
\]

and since \(\hat{h}_{\Theta}\) is always positive, it becomes apparent that \(\delta \Theta\) is positive definite if the following three inequalities are satisfied:

\[
\hat{h}_{\Theta \Theta} > 0, \quad \hat{h}_{S S_A} > 0, \quad \hat{h}_{\Theta S_A} < \hat{h}_{\Theta \Theta} \hat{h}_{S S_A} . \tag{C11}
\]

### b. The nonconservative production of \(\theta\)

Defining enthalpy in the functional form \(h = \hat{h}(S_A, \theta, p)\), an expression for the nonconservative production of \(\Theta\) is
derived. First, $h_1 = \tilde{h}(S_A, \theta_1, p^m)$ and $h_2 = \tilde{h}(S_A, \theta_2, p^m)$ are expanded separately in Taylor series about the values of $S_A$ and $\theta$ of the mixed fluid at fixed pressure $p^m$, retaining terms to second order. Then, equations (C2)–(C4) and (C6) are invoked, yielding

$$
\delta \theta = \frac{m_1 m_2}{2 m^2} \left[ \frac{\tilde{h}_{\theta \theta} (\Delta \theta)^2}{\tilde{h}_\theta} + 2 \frac{\tilde{h}_{S_A \theta} \Delta \theta \Delta S_A}{\tilde{h}_\theta} + \frac{\tilde{h}_{S_A S_A} (\Delta S_A)^2}{\tilde{h}_\theta} \right].
$$

(C12)

The first and middle terms are the dominant terms in this expression, and given that the middle term can be either positive or negative across the range of values of $\theta$ and $S_A$ in the ocean, $\delta \theta$ is not sign definite.

c. The nonconservative production of $\eta$

Proceeding as in the previous sections, the nonconservative source terms of entropy are derived. This time entropy is expressed as a function of $S_A$, $h$, and $p$, namely, $\eta = \eta(S_A, h, p)$. Then $\eta_1 = \eta(S_A, h_1, p^m)$ and $\eta_2 = \eta(S_A, h_2, p^m)$ are expanded separately in Taylor series about the values of $S_A$ and $h$ of the mixed fluid at fixed pressure $p^m$, retaining terms to second order. Equations (C2)–(C4) and (C7) are used to find

$$
\delta \eta = \frac{m_1 m_2}{2 m^2} \left[ \eta_{hh} (\Delta h)^2 + 2 \eta_{hS_A} \Delta h \Delta S_A + \eta_{S_A S_A} (\Delta S_A)^2 \right].
$$

(C13)

The second law of thermodynamics requires that $\eta$ be strictly produced during mixing. In their appendix A.16, IOC et al. (2010) derived three constraints on the functional form of entropy $\eta = \eta(S_A, h, p)$ to satisfy the second law of thermodynamics during turbulent mixing in the ocean. They further showed that these three constraints are satisfied by two conditions on the Gibbs function $g(S_A, t, p)$, namely,

$$
g_{TT} < 0, \quad g_{S_A S_A} > 0.
$$

(C14)

No requirements on the cross derivative $g_{S_A T}$ or on the third-order derivatives of the Gibbs function are imposed by the second law of thermodynamics.

d. The nonconservative production of $\nu$

Proceeding as in the previous sections, the nonconservative source terms of specific volume are derived. Specific volume is expressed as a function of $S_A$, $h$, and $p$, namely, $\nu = \nu(S_A, h, p)$. Then $\nu_1 = \nu(S_A, h_1, p^m)$ and $\nu_2 = \nu(S_A, h_2, p^m)$ are expanded separately in Taylor series about the values of $S_A$ and $h$ of the mixed fluid at fixed pressure $p^m$, retaining terms to second order. Equations (C2)–(C4) and (C8) are used to find

$$
\delta \nu = -\frac{m_1 m_2}{2 m^2} \left[ \nu_{hh} (\Delta h)^2 + 2 \nu_{hS_A} \Delta h \Delta S_A + \nu_{S_A S_A} (\Delta S_A)^2 \right].
$$

(C15)

It follows that the nonconservative source terms of specific volume are negative definite if the following inequalities are satisfied:

$$
\nu_{hh} > 0, \quad \nu_{S_A S_A} > 0, \quad \nu_{hS_A} \nu_{S_A S_A} < \nu_{hh} \nu_{S_A S_A}.
$$

(C16)

REFERENCES


