

## Reference states

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

$$a_1 + a_2(T_0 + t) + a_3 S_A + a_4(T_0 + t) S_A . \quad (2.6.2)$$

This is equivalent to saying that both enthalpy  $h$  and entropy  $\eta$  are unknown and unknowable up to linear functions of Absolute Salinity; enthalpy is unknown up to  $a_1 + a_3 S_A$  and entropy is unknown up to  $-a_2 - a_4 S_A$ .

There are no known or conceivable experiments that could possibly constrain these four arbitrary numbers. By the same token, there can be no conceivable consequences to any arbitrary choice that is made for these four numbers.

## Now we can play

So we've spent ~20 pages of lecture notes deriving the Fundamental Thermodynamic Relation and the First Law of Thermodynamics. Now it's time to play. Here is a revision of our underlying equations.

The Continuity Equation is

$$\rho_t + \nabla \cdot (\rho \mathbf{u}) = 0. \quad (\text{A.21.2})$$

The Fundamental Thermodynamic Relation is

$$du + (p + P_0)dv = dh - v dP = (T_0 + t)d\eta + \mu dS_A. \quad (\text{A.7.1})$$

The First Law of Thermodynamics is

$$\rho \left( \frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left( (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon. \quad (\text{B.19})$$

The conservation equation of Absolute Salinity is

$$(\rho S_A)_t + \nabla \cdot (\rho \mathbf{u} S_A) = \rho \frac{dS_A}{dt} = -\nabla \cdot \mathbf{F}^S, \quad \text{approximate (A.21.8a)}$$

The definition of the Gibbs function

$$g(S_A, T, P) = g \equiv h - T\eta \equiv u + Pv - T\eta. \quad (\text{definition\_of\_g})$$

We will concentrate on the parts of these equations that involve enthalpy  $h$  (rather than internal energy  $u$ ), that is, we will concentrate on the **red parts** of the equations.

The above equations have several variables appearing in more than one equation (especially when you realize that  $\rho = v^{-1}$ ), but the Gibbs function appears in just the last equation, so why bother with it? The answer is that it is the Gibbs function that defines the fluid. That is, we have an internationally defined and accepted algorithm for  $g(S_A, t, p)$ , and all the other thermodynamic variables are actually not separate quantities but are actually various derivatives of the Gibbs function.

## Enthalpy is “isobaric conservative”

There is an important consequence of the First Law that is really easy to derive, and it's too beautiful to delay discussing, so we will do so right away. The First Law of Thermodynamics can be put in divergence form by invoking the continuity equation, giving

$$(\rho h)_t + \nabla \cdot (\rho \mathbf{u} h) - \frac{dP}{dt} = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon. \quad (\text{A.13.2})$$

An important consequence of Eqn. (A.13.2) is that when two finite sized parcels of seawater are mixed at constant pressure and under ideal conditions, the total amount of enthalpy is conserved. To see this, integrate over the volume that encompasses both fluid parcels while assuming there to be no radiative, boundary or molecular fluxes across the boundary of this control volume. This control volume may change with time as the fluid moves (at constant pressure), mixes and contracts. The dissipation of kinetic energy by viscous friction  $\rho \epsilon$  is commonly ignored during such mixing processes but in fact the dissipation term does cause a small increase in the enthalpy of the mixture with respect to that of the two original parcels, and is easy to include if needs be. Apart from this non-

conservative source term,  $\rho \varepsilon$ , under these assumptions Eqn. (A.13.2) reduces to the statement that the volume integrated amount of  $\rho h$  is the same for the two initial fluid parcels as for the final mixed parcel, that is, the total amount of enthalpy is unchanged.

This result of non-equilibrium thermodynamics (it is non-equilibrium because of the finite size of the parcels and the finite property differences) has been known since the days of Gibbs in the nineteenth century, and it is of the utmost importance in oceanography. The fact that enthalpy is conserved when fluid parcels mix at constant pressure is the central result upon which all of our understanding of “heat fluxes” and of “heat content” in the ocean rests. As important as this result is, it does not follow that enthalpy is the best variable to represent “heat content” in the ocean. Enthalpy is a very poor representation of “heat content” in the ocean because it does not possess the “potential” property. It will be seen that potential enthalpy  $h^0$  (referenced to zero sea pressure) is the best thermodynamic variable to represent “heat content” in the ocean.

## Review of Therm0\_Lecture02\_23April2013

The left-hand side of the First Law of Thermodynamics is identical to one of the three parts of the Fundamental Thermodynamic Relation,

$$\rho \left( \frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left( (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right), \quad (\text{B.6})$$

but the right-hand side of the First Law of Thermodynamics contains the physical processes that affect the “heat-like” variables  $u$ ,  $h$  and  $\eta$  that appear on the left-hand side. These physical processes are minus the divergences of the fluxes of heat by radiation and by molecular diffusion plus the dissipation of kinetic energy into “heat”.

We learnt that the way to derive the First Law of Thermodynamics is a bit torturous. One must first develop the conservation equation for Total Energy  $\mathcal{E} = u + \frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi$  and then one subtracts off the evolution equation for  $\frac{1}{2} \mathbf{u} \cdot \mathbf{u} + \Phi$ . What is left is the First Law of Thermodynamics. This is the only way of deriving the First Law of Thermodynamics even for a pure substance (like freshwater) and it is especially obvious that this is the only viable route when the fluid is not a pure substance (e.g. seawater which is pure water plus sea-salt in solution).

We then looked at the form of the molecular fluxes of salt and heat

$$\begin{bmatrix} \mathbf{F}^S \\ \mathbf{F}^Q \end{bmatrix} = \begin{bmatrix} A & B \\ B & C \end{bmatrix} \begin{bmatrix} \nabla(-\mu/T) \\ \nabla(1/T) \end{bmatrix}, \quad (\text{B.21, B.22})$$

and examined the constraints on  $A$ ,  $B$  and  $C$  required to ensure that entropy is never destroyed.

We then looked at the First Law of Thermodynamics, namely

$$\rho \left( \frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left( (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right). \quad (\text{B.19})$$

$$= -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \epsilon$$

and were able to show that when turbulent mixing occurs between two fluid parcels, enthalpy is conserved (apart from the heating caused by any dissipation of kinetic energy  $\rho \epsilon$ ). This is true because for fluid parcels to mix they have to be at the same physical location and therefore at the same pressure. This “isobaric conservative” nature of enthalpy is the most important consequence of the First Law of Thermodynamics for a turbulent fluid such as the atmosphere and ocean. However enthalpy has another drawback that makes it an undesirable variable; it varies with pressure, even for an adiabatic and isohaline change in pressure. We will find that a new variable that is based on enthalpy, namely potential enthalpy, is a much better variable for representing the “heat content” per unit mass of seawater.



## “adiabatic”, “isohaline” and “isentropic”; reversible and irreversible processes

The adjective “isohaline” means “at constant salinity” and describes a process in which the Absolute Salinity of a fluid parcel is constant because  $-\nabla \cdot \mathbf{F}^S$  is zero. The adjective “adiabatic” is traditionally taken to mean a process during which there is no exchange of heat between the environment and the fluid parcel one is considering. However, with this definition of “adiabatic” it is still possible for the entropy  $\eta$ , of a fluid parcel to change during an isohaline and adiabatic process (see Eqn. (B.19)). This is because the dissipation of mechanical energy  $\varepsilon$  causes an increase in  $\eta$ .

$$\rho \left( \frac{dh}{dt} - v \frac{dP}{dt} \right) = \rho \left( \frac{du}{dt} + (p + P_0) \frac{dv}{dt} \right) = \rho \left( (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_\Delta}{dt} \right) \quad (\text{B.19})$$

$$= -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon$$

While the dissipation of mechanical energy is a small term whose influence is routinely neglected in the First Law of Thermodynamics in oceanography, it seems advisable to modify the meaning of the word “adiabatic” in oceanography so that our use of the word more accurately reflects the properties we normally associate with an adiabatic process. Accordingly the word “adiabatic” in oceanography is taken to describe a process occurring without exchange of heat and also without the internal dissipation of mechanical energy. With this definition of “adiabatic”, a process that is both isohaline and adiabatic *does* imply that the entropy  $\eta$  is constant, that is, it is an “isentropic” process.

With this definition of “adiabatic”, an “adiabatic and isohaline” process, is identical to an “isentropic and isohaline” process. Often such a process is simply described as being simply “isentropic” as one could have an isentropic process in which there are changes in both temperature and in Absolute Salinity in just the right proportion to achieve no change in entropy. Hence one needs to say “adiabatic and isohaline” or “isentropic and isohaline”; two constancies are required, not one.

A reversible thermodynamic process must entail no change in entropy or salinity during the process, and no dissipation of mechanical energy. That is, a reversible thermodynamic process must have  $\mathbf{F}^S = \mathbf{F}^R = \mathbf{F}^Q = \varepsilon = 0$ . A slow change in the pressure of a fluid parcel may occur during a reversible process while  $\mathbf{F}^S = \mathbf{F}^R = \mathbf{F}^Q = \varepsilon = 0$ . If any of  $\mathbf{F}^S$ ,  $\mathbf{F}^R$ ,  $\mathbf{F}^Q$  or  $\varepsilon$  are non-zero, the processes is irreversible. The most common reversible processes is an adiabatic and isohaline change of pressure such as occurs during the vertical heaving motion of an internal gravity wave. During such motion both the entropy and the Absolute Salinity of the parcel are constant.

## potential temperature of seawater

Potential temperature  $\theta$  is the temperature that a fluid parcel would have if its pressure were changed to a fixed reference pressure  $p_r$  in an isentropic and isohaline (and reversible) manner. For a fluid parcel  $(S_A, t, p)$  at pressure  $p$  the following thought experiment is conducted. You wrap the fluid parcel in an insulating plastic bag and then you slowly move it to a different location where the pressure is  $p_r$ . The parcel experiences the changing pressure during this movement. When the parcel arrives at  $p_r$  you put a thermometer into the parcel and measure its *in situ* temperature at  $p_r$ . This temperature is called the parcel's potential temperature.

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

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

where  $\Gamma = \partial t / \partial P|_{S_A, \eta}$  is the rate at which *in situ* temperature changes with pressure at fixed entropy and salinity.

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

$$\eta(S_A, \theta, p_r) = \eta(S_A, t, p), \quad (3.1.2)$$

or, in terms of the Gibbs function,  $g$ ,

$$-g_T(S_A, \theta, p_r) = -g_T(S_A, t, p). \quad (3.1.3)$$

This relation is formally equivalent to Eqn. (3.1.1).

In equating the specific entropies of the seawater parcel at the two different pressures in Eqn. (3.1.2) we are exploiting the fact that in the thought experiment the slow change in pressure is done isentropically.

Consider now two seawater parcels with the same Absolute Salinities but at different *in situ* temperatures and different pressures. If these two seawater parcels have the same value of specific entropy then the two seawater parcels must also have the same value of potential temperature  $\theta$  at  $p_r$  (see Eqn. (3.1.2) where the right-hand side is the same for the two parcels).

## potential temperature of a perfect gas

An ideal gas obeys

$$Pv = RT \quad (\text{Perfect\_Gas\_A})$$

where  $R$  is the universal gas constant  $R = 287 \text{ J kg}^{-1} \text{ K}^{-1}$ . For an adiabatic change in pressure (this also being an isentropic processes) the Fundamental Thermodynamic Relation tells us that  $dh = v dP$ . For an ideal gas, specific enthalpy is equal to  $c_p T$  where  $c_p = \frac{7}{2} R$  for a diatomic gas. Hence for a perfect gas we have

$$c_p dT = \frac{RT}{P} dP \quad \text{or} \quad d(\ln T) = \frac{2}{7} d(\ln P). \quad (\text{Perfect\_Gas\_B})$$

Performing the adiabatic change in pressure from  $P$  to  $P_0$  gives

$$\int_P^{P_0} d(\ln T)' = \frac{2}{7} \int_P^{P_0} d(\ln P)' \quad \text{or} \quad \frac{T_0 + \theta}{T_0 + t} = \left( \frac{P_0}{P} \right)^{\frac{2}{7}} \quad (\text{Perfect\_Gas\_C})$$

Now consider a more general situation where the parcel of perfect gas does exchange heat with its surroundings, then the Fundamental Thermodynamic Relation shows that

$$\begin{aligned} d\eta &= c_p \frac{dT}{T_0 + t} - R \frac{dP}{P} = c_p d(\ln[T_0 + t]) - \frac{2}{7} c_p d(\ln P) \\ &= c_p d(\ln[T_0 + \theta]). \end{aligned} \quad (\text{Perfect\_Gas\_D})$$

Hence for a perfect gas, specific entropy is simply proportional to the natural logarithm of potential temperature (absolute potential temperature),

$$\eta = c_p \ln[T_0 + \theta] + \text{constant}. \quad (\text{Perfect\_Gas\_E})$$

## potential enthalpy

Potential enthalpy  $h^0$  is the enthalpy that a fluid parcel would have if its pressure were changed to a fixed reference pressure  $p_r$  in an isentropic and isohaline manner. Because heat fluxes into and out of the ocean occur mostly near the sea surface, the reference pressure for potential enthalpy is almost always taken to be  $p_r = 0$  dbar (that is, at zero sea pressure). The thought process involved with potential enthalpy is the same as for potential temperature, namely the parcel is enclosed in an insulating plastic bag and its pressure is slowly change to  $p_r$ . At this new pressure the parcel's enthalpy is calculated, and this is called potential enthalpy.

Now considering specific enthalpy to be a function of entropy (rather than of temperature  $t$ ), that is, taking  $h = \hat{h}(S_A, \eta, p)$ , the Fundamental Thermodynamic Relation (FTR, Eqn. (A.7.1)) becomes

$$\hat{h}_\eta d\eta + \hat{h}_{S_A} dS_A = (T_0 + t)d\eta + \mu dS_A \quad \text{while} \quad \left. \partial \hat{h} / \partial P \right|_{S_A, \eta} = v, \quad (\text{A.11.4})$$

Also, from the previous section we know that if  $S_A$  and  $\eta$  are constant, then so is potential temperature  $\theta$ . Hence we also know that (recall that  $g_p = v$ )

$$\left. \partial h / \partial P \right|_{S_A, \theta} = v. \quad (\text{A.11.6})$$

Potential enthalpy  $h^0$  can the be expressed as the pressure integral of specific volume as

$$\begin{aligned} h^0(S_A, t, p) &= h(S_A, \theta, 0) = \tilde{h}^0(S_A, \theta) = h(S_A, t, p) - \int_{P_0}^P v(S_A, \theta(S_A, t, p, p'), p') dP' \\ &= h(S_A, t, p) - \int_{P_0}^P \hat{v}(S_A, \eta, p') dP' \\ &= h(S_A, t, p) - \int_{P_0}^P \tilde{v}(S_A, \theta, p') dP' \\ &= h(S_A, t, p) - \int_{P_0}^P \hat{v}(S_A, \Theta, p') dP', \end{aligned} \quad (3.2.1)$$

and we emphasize that the pressure integrals here must be done with respect to pressure expressed in Pa rather than dbar. In this equation we have introduced the over-tilde, over-hat etc. which we will use to indicate the functional dependence of a variable; see the list of Nomenclature that has been distributed. Note that in the first line of the above equation, specific volume  $v$  is a function of  $(S_A, t, p)$  while  $\theta(S_A, t, p, p')$  (see Eqn. (3.1.1)) is the potential temperature of parcel  $(S_A, t, p)$  with respect to the reference pressure  $p'$ .

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

$$h^0(S_A, t, p) = h(S_A, \theta, 0) = g(S_A, \theta, 0) - (T_0 + \theta)g_T(S_A, \theta, 0). \quad (3.2.2)$$

## Conservative Temperature

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

$$\Theta(S_A, t, p) = \tilde{\Theta}(S_A, \theta) = h^0(S_A, t, p)/c_p^0 = \tilde{h}^0(S_A, \theta)/c_p^0 \quad (3.3.1)$$

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

$$\frac{[h(S_{SO}, 25^\circ\text{C}, 0) - h(S_{SO}, 0^\circ\text{C}, 0)]}{(25\text{ K})} \approx 3991.867\,957\,119\,63\text{ J kg}^{-1}\text{ K}^{-1}, \quad (3.3.2)$$

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

$$c_p^0 \equiv 3991.867\,957\,119\,63\text{ J kg}^{-1}\text{ K}^{-1}. \quad (3.3.3)$$

The value of  $c_p^0$  in Eqn. (3.3.3) is very close to the average value of the specific heat capacity  $c_p$  at the sea surface of today's global ocean. This value of  $c_p^0$  also causes the average value of  $\theta - \Theta$  at the sea surface to be very close to zero. Since  $c_p^0$  is simply a constant of proportionality between potential enthalpy and Conservative Temperature, it is actually totally arbitrary and there was no need to choose a value with so many significant figures.

## The “conservative” and “isobaric conservative” properties

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

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

where the flux  $\mathbf{F}^C$  is a diffusive flux of property  $C$ . For such a “conservative” property,  $C$ , in the absence of fluxes  $\mathbf{F}^C$  at the boundary of a control volume, the total amount of  $C$ -substance is constant inside the control volume. In the special case when the material derivative of a property is zero (that is, the middle part of Eqn. (A.8.1) is zero) the property is said to be “materially conserved”.

Conservative Temperature  $\Theta$  (or equivalently, potential enthalpy  $h^0$ ) is not completely conservative, but we will find that the error in assuming it to be conservative is negligible. Because we are ignoring the non-conservative source term of Absolute Salinity in this course, we may also take Absolute Salinity to be conservative (as we have done in going from Eqn. (B.20) to Eqn. (B.20a) above).

Other variables such as potential temperature  $\theta$ , enthalpy  $h$ , internal energy  $u$ , entropy  $\eta$ , density  $\rho$ , potential density  $\rho^\theta$ , specific volume  $v$ , the total energy  $\mathcal{E} = u + 0.5\mathbf{u} \cdot \mathbf{u} + \Phi$  (see Eqn. (B.15)), and the Bernoulli function  $\mathcal{B} = h + 0.5\mathbf{u} \cdot \mathbf{u} + \Phi$  (see Eqn. (B.17)) are not conservative variables.

A different form of “conservation” attribute, namely “isobaric conservation” occurs when the total amount of the quantity is conserved when two fluid parcels are mixed at constant pressure without external input of heat or matter. This “isobaric conservative” property is a very valuable attribute for an oceanographic variable. Any “conservative” variable is also “isobaric conservative”, thus the conservative variables listed above, namely mass and Preformed Salinity  $S_*$  are exactly “isobaric conservative” variables, while Conservative Temperature  $\Theta$  and Absolute Salinity  $S_A$  are almost (but not exactly) “isobaric conservative”.

In addition, the Bernoulli function  $\mathcal{B}$  and specific enthalpy  $h$  are also almost exactly “isobaric conservative”. The issue with the Bernoulli function in this regard is the presence of the unsteady term  $P_t$ , while the issue with enthalpy not being totally 100% “isobaric conservative” is the presence of the dissipation of mechanical energy term  $\rho\epsilon$ . We will find that this is also the largest of several terms that cause Conservative Temperature to not be 100% “conservative” or “isobaric conservative”. Note that while  $h$  is almost exactly “isobaric conservative”, it is not a “conservative” variable.

Some variables that are not “isobaric conservative” include potential temperature  $\theta$ , internal energy  $u$ , entropy  $\eta$ , density  $\rho$ , potential density  $\rho^\theta$ , and specific volume  $v$ .

## The “potential” property

Any thermodynamic property of seawater that remains constant when a parcel of seawater is moved from one pressure to another adiabatically, without exchange of mass and without interior conversion between its turbulent kinetic and internal energies, is said to possess the “potential” property, or in other words, to be a “potential” variable. Prime examples of “potential” variables are entropy  $\eta$ , potential temperature  $\theta$  and potential density  $\rho_\theta$ . Recall that the constancy of entropy  $\eta$  can be seen from the First Law of Thermodynamics in Eqn. (B.19) below; with the right-hand side of Eqn. (B.19) being zero, and with no change in Absolute Salinity, it follows that entropy is also constant. Any thermodynamic property that is a function of only Absolute Salinity and entropy also remains unchanged by this procedure and is said to possess the “potential” property.

Recall that in oceanography we now define the word “adiabatic” to describe a process occurring without exchange of heat and also without the internal dissipation of kinetic energy. With this definition of “adiabatic”, a process that is both isohaline and adiabatic *does* imply that the entropy  $\eta$ , potential temperature  $\theta$  and Conservative Temperature  $\Theta$  are all constant.

Thermodynamic properties that posses the “potential” attribute include potential temperature  $\theta$ , potential enthalpy  $h^0$ , Conservative Temperature  $\Theta$  and potential density  $\rho^\theta$  (no matter what fixed reference pressure is chosen). Some thermodynamic properties that do not posses the potential property are temperature  $t$ , enthalpy  $h$ , internal energy  $u$ , specific volume  $v$ , density  $\rho$ , specific volume anomaly  $\delta$ , total energy  $\mathcal{E}$  and the Bernoulli function  $\mathcal{B}$ . From Eqn. (B.17) we notice that in the absence of molecular fluxes the Bernoulli function  $\mathcal{B}$  is constant following the fluid flow only if the pressure field is steady; in general this is not the case. The non-potential nature of  $\mathcal{E}$  is explained in the discussion following Eqn. (B.17).

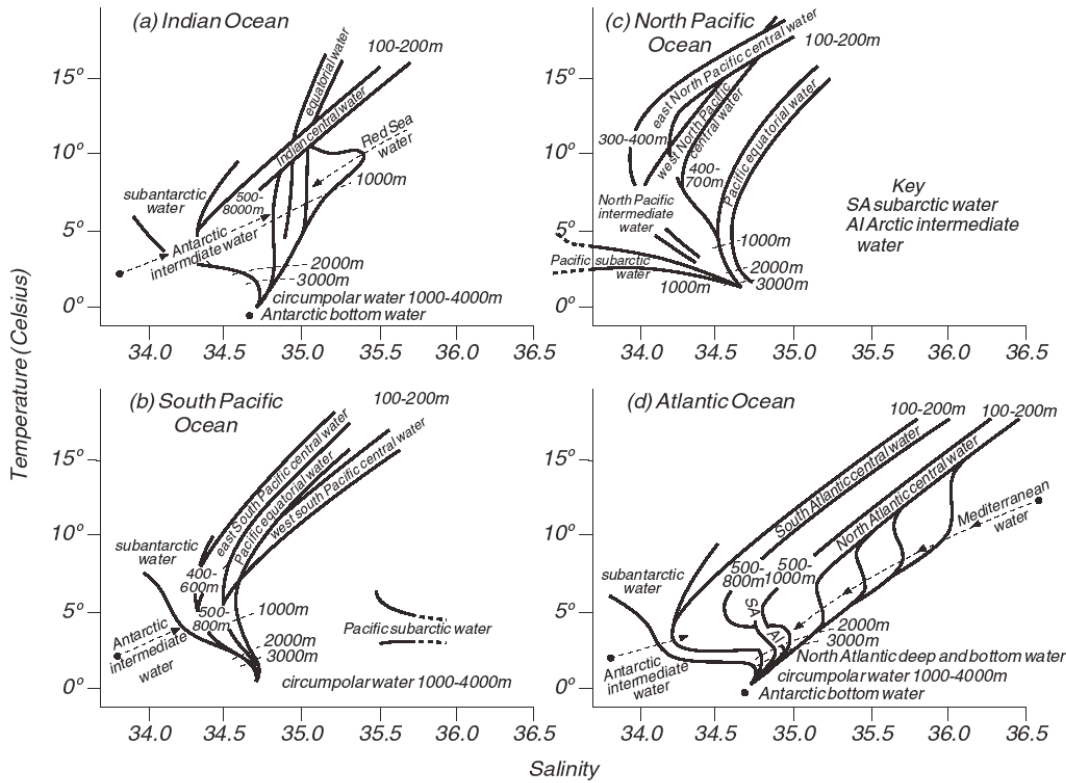


Figure 13.11  $T-S$  plots of water in the various ocean basins. After Tolmazin (1985: 138).

Oceanographers analyze “water-masses” on this  $S_A - \Theta$  diagram. The salinity and temperature variables on these axes should be both “potential” properties, and “conservative” properties so that turbulent mixing processes can be accurately visualized on such a diagram.

A “water mass” is defined to be a line (not necessarily a straight line) on this  $S_A - \Theta$  diagram.

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

Variable	“potential”?	“conservative”?	“isobaric conservative”?	function of $(S_A, t, p)$ ?
$S_*$	✓	✓	✓	✗
$S_A$	✓	✗ <sup>1</sup>	✗ <sup>1</sup>	✓
$t$	✗	✗	✗	✓
$\theta$	✓	✗	✗	✓
$\eta$	✓	✗	✗	✓
$h$	✗	✗	✓ <sup>2</sup>	✓
$\Theta, h^0$	✓	✓ <sup>3</sup>	✓ <sup>3</sup>	✓
$u$	✗	✗	✗	✓
$\mathcal{B}$	✗	✗	✓ <sup>4</sup>	✗
$\mathcal{E}$	✗	✗	✗	✗
$\rho, v$	✗	✗	✗	✓
$\rho^\theta$	✓	✗	✗	✓
$\delta$	✗	✗	✗	✓
$\gamma^n$	✗	✗	✗	✗

<sup>1</sup> The remineralization of organic matter changes  $S_A$ .

<sup>2</sup> Taking  $\varepsilon$  and the effects of remineralization to be negligible.

<sup>3</sup> Taking  $\varepsilon$  and other terms of similar size to be negligible (see the discussion following Eqn. (A.21.13)).

<sup>4</sup> Taking the effects of remineralization to be negligible.

In Table A.9.1 various oceanographic variables are categorized according to whether they possess the “potential” property, whether they are “conservative” variables, whether they are “isobaric conservative”, and whether they are functions of only  $(S_A, t, p)$ . Note that  $\Theta$  is the only variable that achieves four “ticks” in this table, while Preformed Salinity  $S_*$  has ticks in the first three columns, but not in the last column since it is a function not only of  $(S_A, t, p)$  (since it also depends on the composition of seawater). Hence  $\Theta$  is the most “ideal” thermodynamic variable. If it were not for the non-conservation of Absolute Salinity, it too would be an “ideal” thermodynamic variable, but in this sense, Preformed Salinity is superior to Absolute Salinity. Conservative Temperature  $\Theta$  and Preformed Salinity  $S_*$  are the only two variables in this table to be both “potential” and “conservative”. The last three rows of Table A.9.1 are for potential density,  $\rho^\theta$ , specific volume anomaly,  $\delta$ , and Neutral Density  $\gamma^n$ . We will discuss these variables later in the course.

In this course we are assuming that Absolute Salinity is 100% conservative (hence the yellow highlighting in the table above). This is not strictly true. The important thing is that we use Absolute Salinity and not Practical or Reference Salinity in an ocean model and as the salinity argument to the expression for density. The non-conservative source term of Absolute Salinity is small on a timescale of less than a century.



### Proof that $\theta = \theta(S_A, \eta)$ and $\Theta = \Theta(S_A, \theta)$

When a pressure change occurs adiabatically and without exchange of salinity, both entropy  $\eta$  and Absolute Salinity  $S_A$  are unchanged. Potential temperature  $\theta$  and potential enthalpy are also unchanged during such an adiabatic and isohaline change in pressure, and since Conservative Temperature  $\Theta$  is proportional to potential enthalpy, it is also unchanged. Since potential enthalpy is a function of only Absolute Salinity and potential temperature (and not separately a function of pressure), it follows that  $\Theta = \tilde{\Theta}(S_A, \theta)$  and  $\theta = \hat{\theta}(S_A, \Theta)$ . Similarly, entropy is a function of only Absolute Salinity and potential temperature (and not separately a function of pressure), and so it follows that  $\theta = \hat{\theta}(S_A, \eta)$ ,  $\Theta = \tilde{\Theta}(S_A, \eta)$ ,  $\eta = \tilde{\eta}(S_A, \theta)$  and  $\eta = \hat{\eta}(S_A, \Theta)$ .

So we see that the four variables  $S_A$ ,  $\theta$ ,  $\eta$  and  $\Theta$  are all “potential” variables, they are all properties of a seawater parcel, they are all independent of pressure, and they are related to each other in the sense that if you know any two of them, you know the other two. Absolute Salinity  $S_A$  has a clear meaning and is different in character to the other three variables  $\theta$ ,  $\eta$  and  $\Theta$  which are very “temperature-like” variables.

### Various isobaric derivatives of specific enthalpy

We will not derive the following derivatives here, but here they are.

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

$$\partial \hat{h} / \partial S_A \big|_{\eta, p} = \mu. \quad (\text{A.11.5b})$$

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

$$\begin{aligned} \tilde{h}_{S_A} \big|_{\theta, p} &= \mu(S_A, t, p) - (T_0 + t) \mu_T(S_A, \theta, 0) \\ &= g_{S_A}(S_A, t, p) - (T_0 + t) g_{TS_A}(S_A, \theta, 0). \end{aligned} \quad (\text{A.11.11})$$

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

$$\begin{aligned} \hat{h}_{S_A} \big|_{\Theta, p} &= \mu(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} \mu(S_A, \theta, 0) \\ &= g_{S_A}(S_A, t, p) - \frac{(T_0 + t)}{(T_0 + \theta)} g_{S_A}(S_A, \theta, 0). \end{aligned} \quad (\text{A.11.18})$$

### Differential relationships between $\eta$ , $\theta$ , $\Theta$ and $S_A$

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

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

Similarly, considering specific enthalpy to be a function of Conservative Temperature (rather than of temperature  $t$ ), that is, taking  $h = \hat{h}(S_A, \Theta, p)$ , the fundamental thermodynamic relation (A.7.1) becomes

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

Using these forms of the Fundamental Thermodynamic Relation, together with the four boxed equations for the partial derivative of enthalpy (A.11.9), (A.11.11), (A.11.15) and (A.11.18), we find

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

The quantity  $\mu(p)dS_A$  is now subtracted from each of these three expressions and the whole equation is then multiplied by  $(T_0 + \theta)/(T_0 + t)$  obtaining

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

From this follows all the following partial derivatives between  $\eta$ ,  $\theta$ ,  $\Theta$  and  $S_A$ ,

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

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

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

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

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

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

## The First Law of Thermodynamics in terms of $\theta$ , $\eta$ and $\Theta$

Here we repeat the First Law of Thermodynamics

$$\boxed{\rho \left( \frac{dh}{dt} - v \frac{dp}{dt} \right) = \rho \left( \frac{du}{dt} + (p + p_0) \frac{dv}{dt} \right) = \rho \left( (T_0 + t) \frac{d\eta}{dt} + \mu \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon} \quad (\text{B.19})$$

We wish to interpret this statement as a conservation statement for a “potential” variable, since this is how ocean models treat their heat-like variable, which to date has been potential temperature  $\theta$ . None of enthalpy  $h$ , internal energy  $u$  or specific volume  $v$  are “potential” variables. Rather, these variables change simply due to a change in pressure even in the absence of heat or salt fluxes. The “heat-like” variables that are “potential” variables are entropy  $\eta$  potential temperature  $\theta$  and Conservative Temperature  $\Theta$ .

The First Law of Thermodynamics, Eqn. (A.13.1), can be written as an evolution equation for entropy as (by taking  $h = \hat{h}(S_A, \eta, p)$ )

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

The First Law of Thermodynamics can also be written in terms of potential temperature  $\theta$  (with respect to reference pressure  $p_r = 0$ ) by taking  $h = \hat{h}(S_A, \theta, p)$  and using Eqns. (A.11.9) and (A.11.11) as

$$\rho \left( \frac{(T_0 + t)}{(T_0 + \theta)} c_p(0) \frac{d\theta}{dt} + \left[ \mu(p) - (T_0 + t) \mu_T(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon, \quad (\text{A.13.4})$$

while in terms of Conservative Temperature  $\Theta$ , the First Law of Thermodynamics is (using  $h = \hat{h}(S_A, \Theta, p)$  and Eqns. (A.11.15) and (A.11.18))

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

A quick ranking of these three variables,  $\eta$ ,  $\theta$  and  $\Theta$ , from the viewpoint of the amount of their non-conservation, can be gleaned by examining the range of the **red** terms (at fixed pressure) that multiply the material derivatives on the left-hand sides of the above Eqns. (A.13.3), (A.13.4) and (A.13.5).

Why are we able to settle for examining the variation of these red terms only at constant pressure? The ocean circulation may be viewed as a series of adiabatic and isohaline movements of seawater parcels interrupted by a series of isolated turbulent mixing events. During any of the adiabatic and isohaline transport stages every “potential” property is constant, so each of the above variables, entropy, potential temperature and Conservative Temperature are 100% ideal during these adiabatic and isohaline advection stages. The turbulent mixing events occur at fixed pressure so the non-conservative production of say entropy depends on the extent to which the coefficients  $(T_0 + t)$  and  $\mu$  in Eqn. (A.13.3) vary at fixed pressure. Similarly the non-conservative production of potential temperature depends on the extent to which the coefficients  $c_p(0)(T_0 + t)/(T_0 + \theta)$  and  $[\mu(p) - (T_0 + t)\mu_T(0)]$  in Eqn. (A.13.4) vary at fixed pressure, while the non-conservative production of Conservative Temperature depends on the extent to which the coefficients  $(T_0 + t)/(T_0 + \theta)$  and  $[\mu(p) - \mu(0)(T_0 + t)/(T_0 + \theta)]$  in Eqn. (A.13.5) vary at fixed pressure.

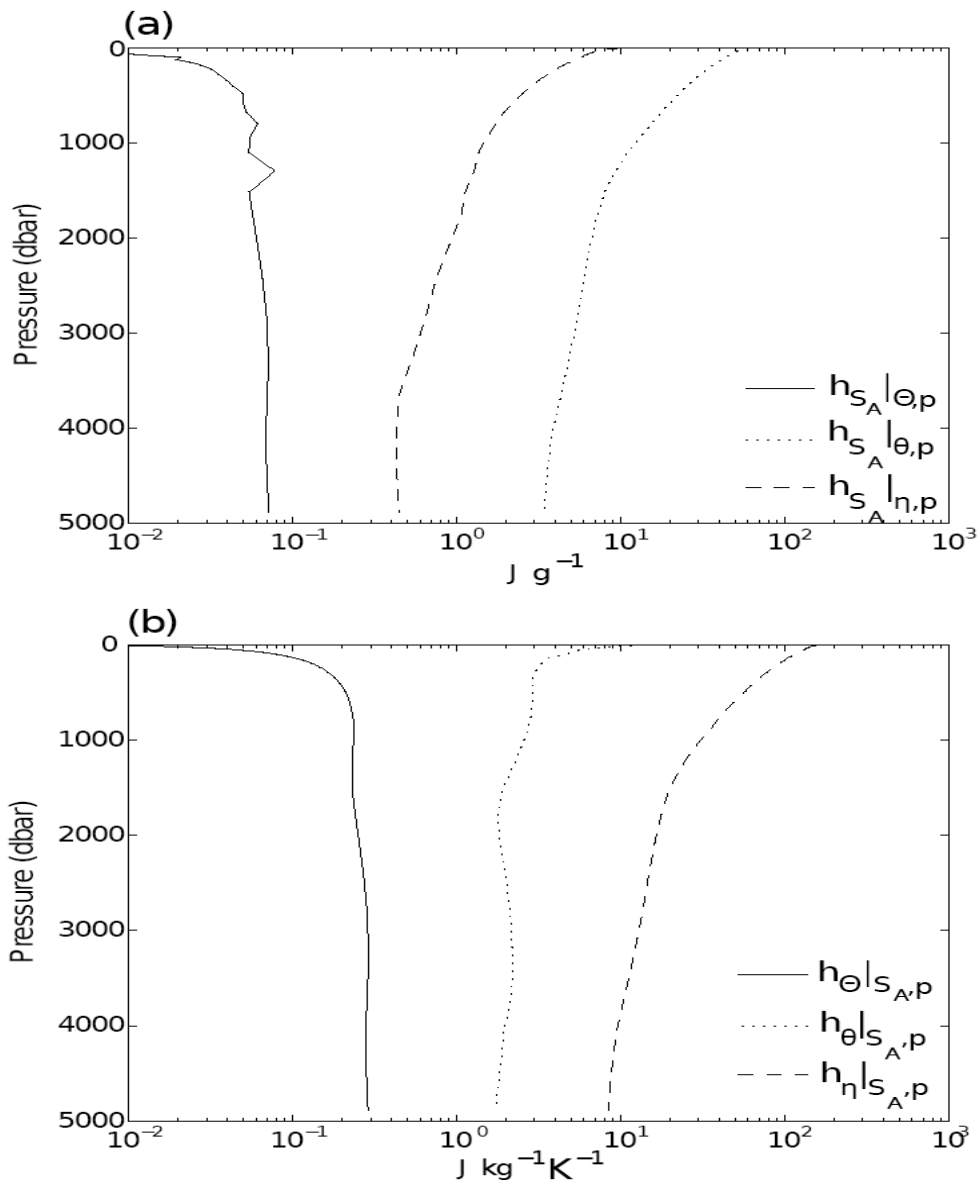
According to this way of looking at these equations we note that the material derivative of entropy appears in Eqn. (A.13.3) multiplied by the absolute temperature  $(T_0 + t)$  which varies by about 15% at the sea surface  $((273.15 + 40)/273.15 \approx 1.146)$ , the term that multiplies  $d\theta/dt$  in (A.13.4) is dominated by the variations in the isobaric specific heat  $c_p(S_A, t, p_r)$  which is

mainly a function of  $S_A$  and which varies by 5% at the sea surface (see [Figure 4](#) on page 1), while the material derivative of Conservative Temperature  $d\Theta/dt$  in Eqn. (A.13.5) is multiplied by the product of a constant “heat capacity”  $c_p^0$  and the factor  $(T_0 + t)/(T_0 + \theta)$  which varies very little in the ocean, especially when one realizes that it is only the variation of this ratio at each pressure level that is of concern. This factor is unity at the sea surface and is also very close to unity in the deep ocean.

More quantitatively, the r.m.s. variation of these six terms is shown in the following figure (from Graham and McDougall (2013), *Journal of Physical Oceanography*, *in press*). The variations of temperature in the ocean are about five times as large as the variations of Absolute Salinity (in g/kg) so if the horizontal axis of Fig (a) is divided by a factor of 5, the figures can be compared numerically.

This figure shows that both the red terms in the potential temperature version of the First Law contribute to non-conservation about equally (we will find out why shortly). The non-constancy of the terms that multiply  $dS_A/dt$  in both the entropy and Conservative Temperature cases are very small compared to the variation of the terms multiplying  $d\eta/dt$  and  $d\Theta/dt$  respectively.

So the ranking of the variables can be seen simply by looking at Fig (b), especially if we mentally move the dotted line (the line for  $\theta$ ) to the right by a factor of two.



## Review of Therm0\_Lecture03\_30April2013

We discussed potential temperature, both for a real liquid (like seawater) and for a perfect gas, where things are considerably simpler.

We then extended the “potential” concept to enthalpy, defining potential enthalpy, and writing down the relationship between enthalpy and potential enthalpy as a pressure integral of specific volume.

The “conservative” and “isobaric conservative” properties were defined, and many oceanographic variables were categorized according to whether they are “potential” properties, “conservative” properties, “isobaric conservative” properties, and according to whether they are thermodynamic variables (that is, variables that are a function of Absolute Salinity, temperature and pressure).

We proved that once you know the Absolute Salinity of a seawater parcel and one of entropy, potential temperature or Conservative Temperature, then you know the other two “temperature-like” variables.

We used the various partial derivatives of enthalpy to rewrite the First Law of Thermodynamics

$$\rho \left( \frac{dh}{dt} - v \frac{dP}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon \quad (\text{B.19})$$

as

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

$$\rho \left( \frac{(T_0 + t)}{(T_0 + \theta)} c_p(0) \frac{d\theta}{dt} + \left[ \mu(p) - (T_0 + t) \mu_T(0) \right] \frac{dS_A}{dt} \right) = -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho \varepsilon, \quad (\text{A.13.4})$$

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

We then estimated a rough ranking of entropy, potential temperature and Conservative Temperature, in terms of how “conservative” these variables are. We did this by simply seeing how much the partial derivative of enthalpy with respect to these variables varied at fixed pressure in the ocean.

## Non-conservative production of entropy

Here the non-conservative nature of entropy will be quantified by considering the mixing of a pair of seawater parcels at fixed pressure. The mixing is taken to be complete so that the end state is a seawater parcel that is homogeneous in Absolute Salinity and entropy. That is, we will be considering mixing to completion by a turbulent mixing process.

Consider the mixing of two fluid parcels (parcels 1 and 2) that have initially different temperatures and salinities. The mixing process occurs at pressure  $p$ . The mixing is assumed to happen to completion so that in the final state Absolute Salinity, entropy and all the other properties are uniform. Assuming that the mixing happens with a vanishingly small amount of dissipation of kinetic energy, the  $\varepsilon$  term can be dropped from the First Law of Thermodynamics, (A.13.1), this equation becoming

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

Note that this equation has the “conservative” form and so  $h$  is conserved during mixing at constant pressure, that is,  $h$  is “isobaric conservative”. In the case we are considering of mixing the two seawater parcels, the system is closed and there are no radiative, boundary or molecular heat fluxes coming through the outside boundary so the integral over space and time of the right-hand side of Eqn. (A.16.1) is zero. The surface integral of  $(\rho \mathbf{u} h)$  through the boundary is also zero. Hence it is apparent that the volume integral of  $\rho h$  is the same at the final state as it is at the initial state, that is, enthalpy is conserved. Hence during the mixing process the mass, salt content and enthalpy are conserved, that is

$$m_1 + m_2 = m, \quad (\text{A.16.2})$$

$$m_1 S_{A1} + m_2 S_{A2} = m S_A, \quad (\text{A.16.3})$$

$$m_1 h_1 + m_2 h_2 = m h, \quad (\text{A.16.4})$$

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

$$m_1 \eta_1 + m_2 \eta_2 + m \delta \eta = m \eta. \quad (\text{A.16.5})$$

Here  $S_A$ ,  $h$  and  $\eta$  are the values of Absolute Salinity, enthalpy and entropy of the final mixed fluid and  $\delta \eta$  is the production of entropy, that is, the amount by which entropy is not conserved during the mixing process. Entropy  $\eta$  is now regarded as the functional form  $\eta = \tilde{\eta}(S_A, h, p)$  and is expanded in a Taylor series of  $S_A$  and  $h$  about the values of  $S_A$  and  $h$  of the mixed fluid, retaining terms to second order in  $[S_{A2} - S_{A1}] = \Delta S_A$  and in  $[h_2 - h_1] = \Delta h$ . Then  $\eta_1$  and  $\eta_2$  are evaluated and (A.16.4) and (A.16.5) used to find

$$\delta \eta = -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \tilde{\eta}_{hh} (\Delta h)^2 + 2 \tilde{\eta}_{hS_A} \Delta h \Delta S_A + \tilde{\eta}_{S_A S_A} (\Delta S_A)^2 \right\}. \quad (\text{A.16.6})$$

Shortly we will explore the production (A.16.6) of entropy will be quantified, but for now we ask what constraints the Second Law of Thermodynamics might place on the form of the Gibbs function  $g(S_A, t, p)$  of seawater. The Second Law of Thermodynamics tells us that the entropy excess  $\delta \eta$  must not be negative for all possible combinations of the differences in enthalpy and salinity between the two fluid parcels. From (A.16.6) this requirement implies the following three inequalities,

$$\tilde{\eta}_{hh} < 0, \quad \tilde{\eta}_{S_A S_A} < 0, \quad (\text{A.16.8})$$

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

where the last requirement reflects the need for the discriminant of the quadratic in (A.16.6) to be negative. Since entropy is already a first derivative of the Gibbs function, these constraints would seem to be three different constraints on

various third derivatives of the Gibbs function. In fact, we will see that they amount to only two rather well-known constraints on second order derivatives of the Gibbs function.

From the fundamental thermodynamic relation (A.7.1) we find that (where  $T$  is the absolute temperature,  $T = T_0 + t$ )

$$\tilde{\eta}_h = \left. \frac{\partial \eta}{\partial h} \right|_{S_A, p} = \frac{1}{T} \quad (\text{A.16.10})$$

$$\tilde{\eta}_{S_A} = \left. \frac{\partial \eta}{\partial S_A} \right|_{h, p} = -\frac{\mu}{T}, \quad (\text{A.16.11})$$

and from these relations the following expressions for the second order derivatives of  $\tilde{\eta}$  can be found,

$$\tilde{\eta}_{hh} = \left. \frac{\partial^2 \eta}{\partial h^2} \right|_{S_A, p} = \left. \frac{\partial T^{-1}}{\partial h} \right|_{S_A, p} = \frac{-T^{-2}}{c_p}, \quad (\text{A.16.12})$$

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

$$\begin{aligned} \tilde{\eta}_{S_A S_A} &= \left. \frac{\partial^2 \eta}{\partial S_A^2} \right|_{h, p} = \left. \frac{\partial(-\mu/T)}{\partial S_A} \right|_{T, p} - \left. \frac{\partial(-\mu/T)}{\partial h} \right|_{S_A, p} \left. \frac{\partial h}{\partial S_A} \right|_{T, p} \\ &= -\frac{\mu_{S_A}}{T} - \frac{T^2}{c_p} \left[ \left( \frac{\mu}{T} \right)_T \right]^2. \end{aligned} \quad (\text{A.16.14})$$

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

The constraint (A.16.8) that  $\tilde{\eta}_{hh} < 0$  simply requires (from (A.16.12)) that the isobaric heat capacity  $c_p$  is positive, or that  $g_{TT} < 0$ . Physically this constraint simply means that when you apply heat to a fluid parcel it warms up, rather than cools down.

The constraint (A.16.8) that  $\tilde{\eta}_{S_A S_A} < 0$ , requires (from (A.16.14)) that

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

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

$$\frac{g_{S_A S_A}}{T^3 c_p} > 0, \quad (\text{A.16.16})$$

and since the isobaric heat capacity must be positive, this requirement is that  $g_{S_A S_A} > 0$ , and so is more demanding than (A.16.15).

We conclude that while there are the three requirements (A.16.8) to (A.16.9) on the functional form of entropy  $\eta = \tilde{\eta}(S_A, h, p)$  in order to satisfy the constraint of the Second Law of Thermodynamics that entropy be produced when water parcels mix, these three constraints are satisfied by the following two constraints on the form of the Gibbs function  $g(S_A, t, p)$ ,

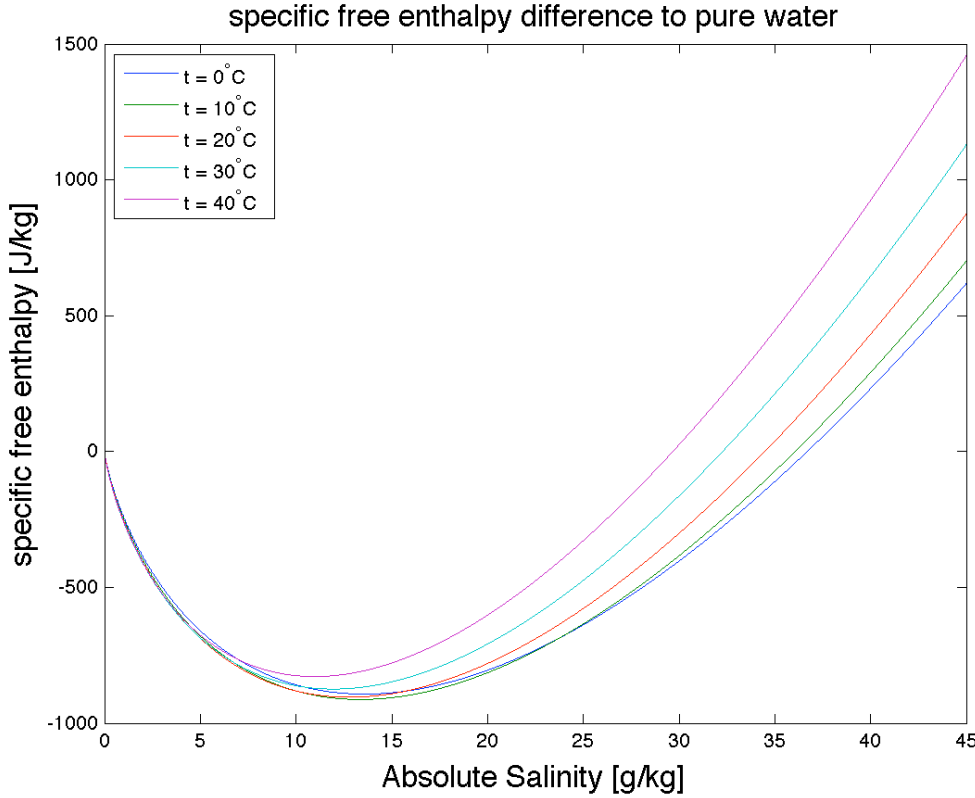
$$g_{TT} < 0 \quad (\text{A.16.17})$$

and

$$g_{S_A S_A} > 0. \quad (\text{A.16.18})$$

The Second Law of Thermodynamics does not impose any additional requirement on the cross derivatives  $g_{S_A T}$  nor on any third order derivatives of the Gibbs function! (In any case, recall that  $g_{S_A T}$  is completely arbitrary and unknowable.)

The constraint  $g_{S_A S_A} > 0$  can be understood by considering the molecular diffusion of salt, which, in an isothermal ocean, is known to be directed down the gradient of chemical potential  $\mu(S_A, t, p)$  (see Eqn. (B.21)). That is, the molecular flux of salt is proportional to  $-\nabla\mu$ . Expanding  $-\nabla\mu$  in terms of gradients of Absolute Salinity, of temperature, and of pressure, one finds that the first term is  $-\mu_{S_A} \nabla S_A$  and in order to avoid an unstable explosion of salt one must have  $\mu_{S_A} = g_{S_A S_A} > 0$ . Hence the constraint (A.16.18) amounts to the requirement that the molecular diffusivity of salt is positive. The following figure shows that, indeed,  $g_{S_A S_A} = \mu_{S_A} > 0$ .



The two constraints (A.16.17) and (A.16.18) on the Gibbs function are well known in the thermodynamics literature. Landau and Lifshitz (1959) derive them on the basis of the contribution of molecular fluxes of heat and salt to the production of entropy (their equations 58.9 and 58.13). It is pleasing to obtain the same constraints on the seawater Gibbs function from the above Non-Equilibrium Thermodynamics approach of mixing fluid parcels since this approach involves turbulent mixing which is the type of mixing that dominates in the ocean; molecular diffusion has the complementary role of dissipating tracer variance.

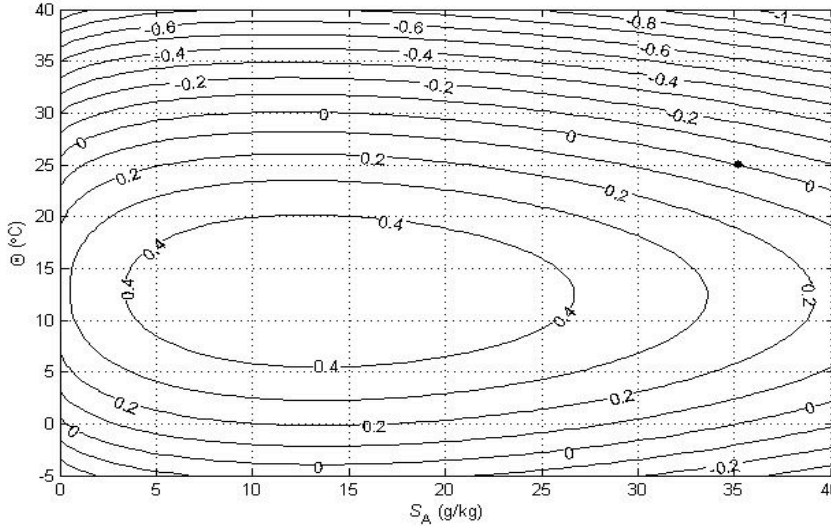
When the mixing process occurs at  $p = 0$ , the expression (A.16.6) for the production of entropy can be expressed in terms of Conservative Temperature  $\Theta$  (since  $\Theta$  is simply proportional to  $h$  at  $p = 0$ ) as follows (now entropy is taken to be the functional form  $\eta = \hat{\eta}(S_A, \Theta)$ )

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

The maximum production occurs when parcels of equal mass are mixed so that  $\frac{1}{2} m_1 m_2 m^{-2} = \frac{1}{8}$  and we adopt this value in what follows. To illustrate the magnitude of this non-conservation of entropy we first scale entropy by a dimensional constant so that the resulting variable ("entropic temperature") has the value 25 °C at  $(S_A, \Theta) = (S_{SO}, 25^\circ\text{C})$  and then  $\Theta$  is subtracted. The result is contoured in  $S_A - \Theta$  space in Figure A.16.1.



The fact that the variable in Figure A.16.1 is not zero over the whole  $S_A - \Theta$  plane is because entropy is not a conservative variable. The non-conservative production of entropy can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels and then reading off the production (in  $^\circ\text{C}$ ) of entropy from the figure. Taking the most extreme situation with one parcel at  $(S_A, \Theta) = (0 \text{ g kg}^{-1}, 0^\circ\text{C})$  and the other at the warmest and saltiest corner of the figure, the production of  $\eta$  on mixing parcels of equal mass is approximately  $0.9^\circ\text{C}$ .



**Figure A.16.1.** Contours (in  $^\circ\text{C}$ ) of a variable which illustrates the non-conservative production of entropy  $\eta$  in the ocean.

Since entropy can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature  $\eta = \hat{\eta}(S_A, \Theta)$ , and since at any pressure in the ocean both  $S_A$  and  $\Theta$  may quite accurately be considered conservative variables, it is clear that the non-conservative production given by (A.16.22) and illustrated in Figure A.16.1 is very nearly equivalent to the slightly more accurate expression (A.16.6) which applies at any pressure. The only discrepancy between the production of entropy calculated from (A.16.22) and that from (A.16.6) is due to the very small non-conservative production of  $\Theta$  at pressures other than zero (as well as the fact that both expressions contain only the second order terms in an infinite Taylor series).

### Non-conservative production of potential temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved during the mixing process are mass, Absolute Salinity and enthalpy. As in the case of entropy, we again consider two parcels being mixed without external input of heat or mass and the three equations that represent the conservation of these quantities are again Eqns. (A.16.2) – (A.16.4). The production of potential temperature during the mixing process is given by

$$m_1 \theta_1 + m_2 \theta_2 + m \delta\theta = m \theta. \quad (\text{A.17.1})$$

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

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

The maximum production occurs when parcels of equal mass are mixed so that  $\frac{1}{2}m_1m_2m^{-2} = \frac{1}{8}$ . The “heat capacity”  $\tilde{h}_\theta$  is not a strong function of  $\theta$  but is a stronger function of  $S_A$  so the first term in the curly brackets in Eqn. (A.17.2) is generally small compared with the second term. Also, the third term in Eqn. (A.17.2) which causes the so-called “dilution heating”, is usually small compared with the second term. A typical value of  $\tilde{h}_{\theta S_A}$  is approximately  $-5.4 \text{ J kg}^{-1} \text{ K}^{-1} (\text{g kg}^{-1})^{-1}$  (see the dependence of isobaric heat capacity on  $S_A$  in [Figure 4](#) on page 1) so that an approximate expression for the production of potential temperature  $\delta\theta$  is

$$\frac{\delta\theta}{\Delta\theta} \approx \frac{1}{4} \tilde{h}_{\theta S_A} \Delta S_A / \tilde{h}_\theta \approx -3.4 \times 10^{-4} (\Delta S_A / [\text{g kg}^{-1}]). \quad (\text{A.17.3})$$

The same form of the non-conservative production terms in Eqn. (A.17.2) also appears in the following turbulent evolution equation for potential temperature, in both the epineutral and vertical diffusion terms (Graham and McDougall, 2013). (See later for an explanation of the symbols that appear in this thickness-weighted averaged equation.)

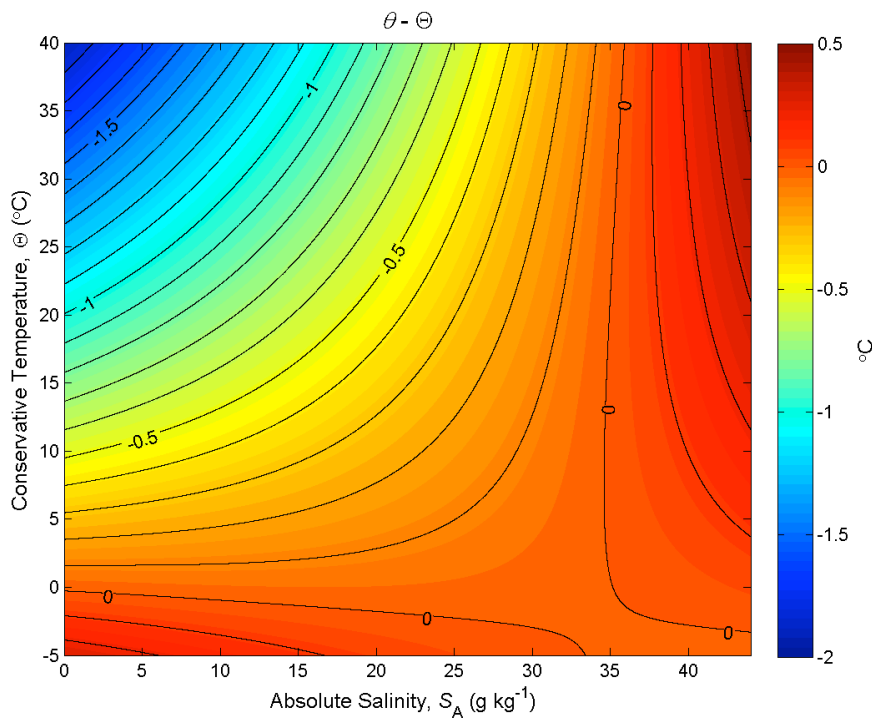
$$\begin{aligned} \frac{d\hat{\theta}}{dt} = \frac{\partial\hat{\theta}}{\partial t} \Big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\theta} + \tilde{\varepsilon} \frac{\partial\hat{\theta}}{\partial z} = \gamma_z \nabla_n \cdot (\gamma_z^{-1} K \nabla_n \hat{\theta}) + (D\hat{\theta}_z)_z + \varepsilon / \tilde{h}_\theta \\ + K \left( \frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta} \nabla_n \hat{\theta} \cdot \nabla_n \hat{\theta} + 2 \frac{\tilde{h}_{\theta S_A}}{\tilde{h}_\theta} \nabla_n \hat{\theta} \cdot \nabla_n \hat{S}_A + \frac{\tilde{h}_{S_A S_A}}{\tilde{h}_\theta} \nabla_n \hat{S}_A \cdot \nabla_n \hat{S}_A \right) \\ + D \left( \frac{\tilde{h}_{\theta\theta}}{\tilde{h}_\theta} \hat{\theta}_z^2 + 2 \frac{\tilde{h}_{\theta S_A}}{\tilde{h}_\theta} \hat{\theta}_z \hat{S}_{Az} + \frac{\tilde{h}_{S_A S_A}}{\tilde{h}_\theta} (\hat{S}_{Az})^2 \right). \end{aligned} \quad (\text{A.17.4})$$

Since potential temperature  $\theta = \hat{\theta}(S_A, \Theta)$  can be expressed independently of pressure as a function of only Absolute Salinity and Conservative Temperature, and since during turbulent mixing both  $S_A$  and  $\Theta$  may be considered approximately conservative variables (see section A.18 below), it is clear that the non-conservative production given by (A.17.2) can be approximated by the corresponding production of potential temperature that would occur if the mixing had occurred at  $p = 0$ , namely

$$\delta\theta \approx \frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \frac{\tilde{\Theta}_{\theta\theta}}{\tilde{\Theta}_\theta} (\Delta\theta)^2 + 2 \frac{\tilde{\Theta}_{\theta S_A}}{\tilde{\Theta}_\theta} \Delta\theta \Delta S_A + \frac{\tilde{\Theta}_{S_A S_A}}{\tilde{\Theta}_\theta} (\Delta S_A)^2 \right\}, \quad (\text{A.17.5})$$

where the exact proportionality between potential enthalpy and Conservative Temperature  $h^0 \equiv c_p^0 \Theta$  has been exploited. The maximum production occurs when parcels of equal mass are mixed so that  $\frac{1}{2}m_1m_2m^{-2} = \frac{1}{8}$  and we adopt this value in what follows.

Equations (A.17.2) or (A.17.5) may be used to evaluate the non-conservative production of potential temperature due to mixing a pair of fluid parcels across a front at which there are known differences in salinity and temperature. The temperature difference  $\theta - \Theta$  is contoured in [Figure A.17.1](#) and can be used to illustrate Eqn. (A.17.5).  $\delta\theta$  can be read off this figure by selecting two seawater samples and mixing along the straight line between these parcels (along which both Absolute Salinity and Conservative Temperature are conserved) and then calculating the production (in  $^\circ\text{C}$ ) of  $\theta$  from the contoured values of  $\theta - \Theta$ . Taking the most extreme situation with one parcel at  $(S_A, \Theta) = (0 \text{ g kg}^{-1}, 0^\circ\text{C})$  and the other at the warmest and saltiest corner of [Figure A.17.1](#), the non-conservative production of  $\theta$  on mixing parcels of equal mass is approximately  $-0.55^\circ\text{C}$ . This is to be compared with the corresponding maximum production of entropy, as discussed above in connection with [Figure A.16.1](#), of approximately  $0.9^\circ\text{C}$ .



**Figure A.17.1.** Contours (in  $^{\circ}\text{C}$ ) of the difference between potential temperature and Conservative Temperature  $\theta - \Theta$ . This plot illustrates the non-conservative production of potential temperature  $\theta$  in the ocean.

### *How NOT to quantify the error involved in using potential temperature*

If **Figure A.17.1** were to be used to quantify the errors in oceanographic practice incurred by assuming that  $\theta$  is a conservative variable, one might select property contrasts that were typical of a prominent oceanic front and decide that because  $\delta\theta$  is small at this one front, that the issue can be ignored. But the observed properties in the ocean result from a large and indeterminate number of such prior mixing events and the non-conservative production of  $\theta$  accumulates during each of these mixing events, often in a sign-definite fashion. How can we possibly estimate the error that is made by treating potential temperature as a conservative variable during all of these unknowably many past individual mixing events?

### *How to quantify the error involved in using potential temperature*

This seemingly difficult issue is partially resolved by considering what is actually done in ocean models today. These models carry a temperature conservation equation that does not have non-conservative source terms, so that the model's temperature variable is best interpreted as being  $\Theta$ . If an ocean model is written with potential temperature  $\theta$  as the prognostic temperature variable rather than Conservative Temperature  $\Theta$ , and is run with the same constant value of the isobaric specific heat capacity  $c_p^0$ , the neglect of the non-conservative source terms that should appear in the prognostic equation for  $\theta$  means that such an ocean model incurs errors in the model output. These errors will depend on the nature of the surface boundary condition; for flux boundary conditions the errors are as shown in **Figure A.17.1**, because in this case the model's temperature variable is actually Conservative Temperature  $\Theta$  but has been interpreted and initialized incorrectly as potential temperature  $\theta$ .

The contoured values of temperature difference in [Figure A.17.1](#) encapsulate the accumulated non-conservative production that has occurred during all the many mixing processes that have lead to the ocean's present state. The maximum such error for  $\eta$  is approximately  $-1.0\text{ }^{\circ}\text{C}$  (from [Figure A.16.1](#)) while for  $\theta$  the maximum error is approximately  $-1.8\text{ }^{\circ}\text{C}$  (from [Figure A.17.1](#)). From the curvature of the isolines on [Figure A.17.1](#) it is clear that the non-conservative production of  $\theta$  takes both positive and negative signs.

Here is an enlarged view of  $\theta - \Theta$  on the  $S_A - \Theta$  diagram, and also of the error involved with using another previous suggestion for the "heat content" of seawater,  $\theta c_p(S_A, \theta, p)/c_p^0$ .

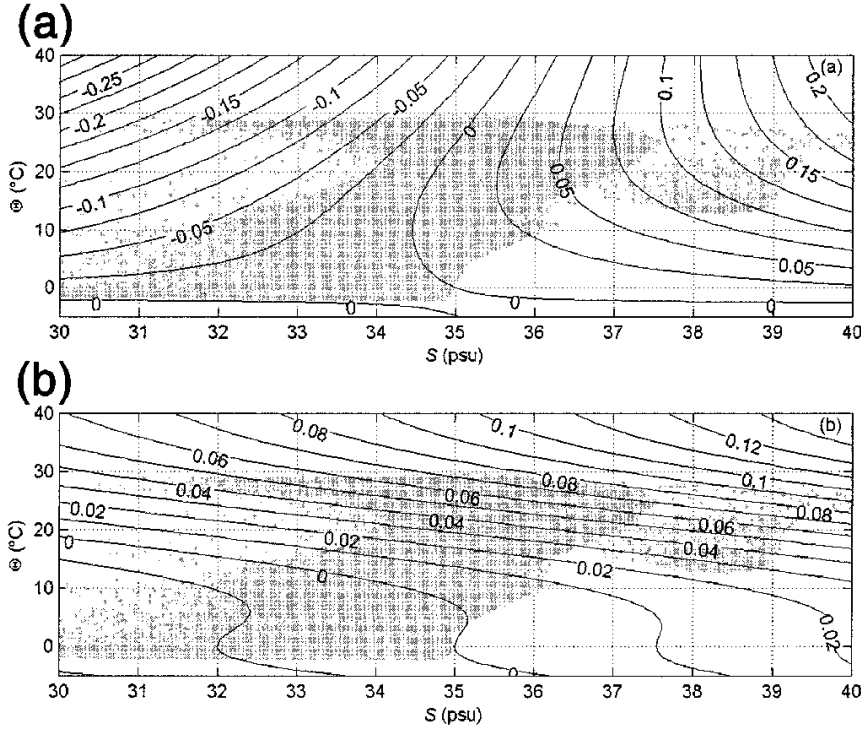
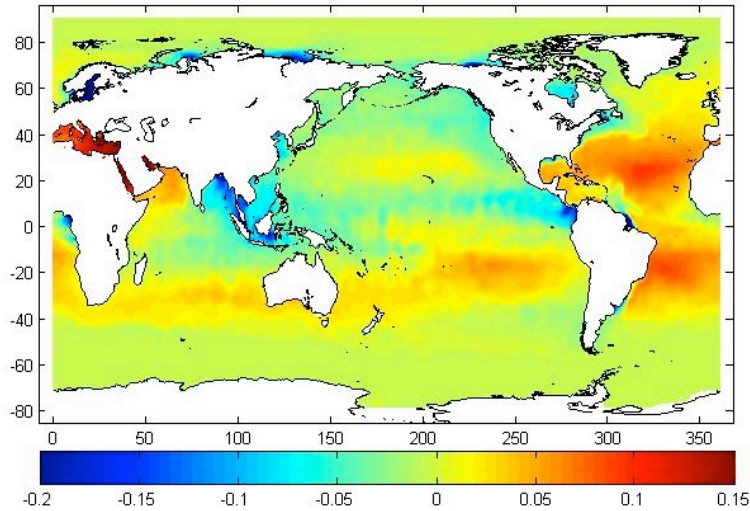
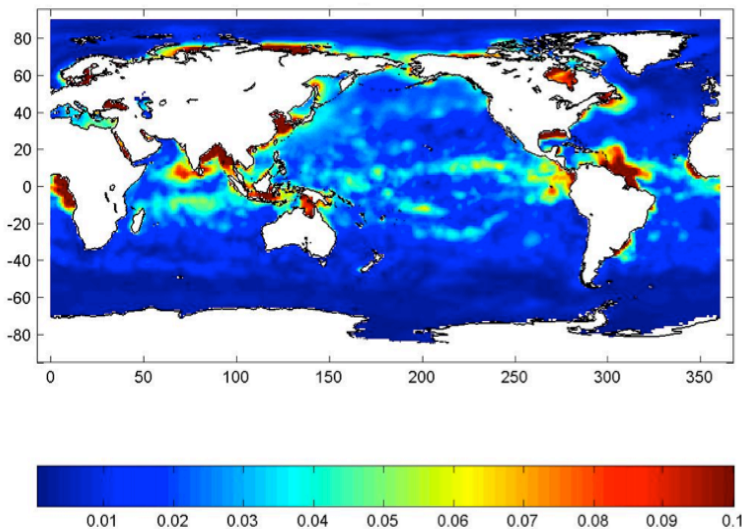


FIG. 3. Contours of (a)  $\theta - \Theta$  and of (b)  $C_p(S, \theta, 0)\theta/C_p^0 - \Theta$  in a smaller range of salinity than in Figs. 1 and 4. Panel (a) illustrates the error in regarding  $C_p^0\theta$  as heat content; panel (b) illustrates the error in regarding  $C_p(S, \theta, 0)\theta$  as heat content, in both cases measured in temperature units. The background cloud of points illustrate where there is data from somewhere in the World Ocean.

One percent of the data at the sea surface of the world ocean have values of  $\theta - \Theta$  that lie outside a range that is  $0.25\text{ }^{\circ}\text{C}$  wide (see [Figure A.13.1](#)), implying that this is the magnitude of the error incurred by ocean models when they treat  $\theta$  as a conservative quantity. To put a temperature difference of  $0.25\text{ }^{\circ}\text{C}$  in context, this is the typical difference between *in situ* and potential temperatures for a pressure difference of 2500 dbar, and it is approximately 100 times as large as the typical differences between  $t_{90}$  and  $t_{68}$  in the ocean.



**Figure A.13.1.** The difference  $\theta - \Theta$  (in  $^{\circ}\text{C}$ ) between potential temperature  $\theta$  and Conservative Temperature  $\Theta$  at the sea surface of the annually-averaged atlas of Gouretski and Koltermann (2004).



The maximum value of the seasonal variation in  $|\theta - \Theta|$  (in  $^{\circ}\text{C}$ ) at the sea surface throughout the annual cycle of the hydrographic atlas of Gouretski and Koltermann (2004).



## Review of Therm0\_Lecture04\_02May2013

We examined the process of turbulent mixing and showed that in order for the Second Law of Thermodynamics to be obeyed (and entropy to be always produced), there are only two constraints on the form of the Gibbs function, namely

$$g_{TT} < 0 \quad (\text{A.16.17})$$

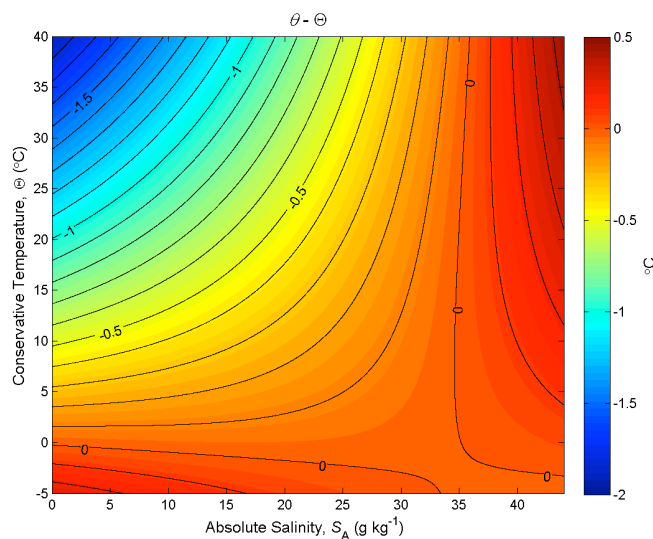
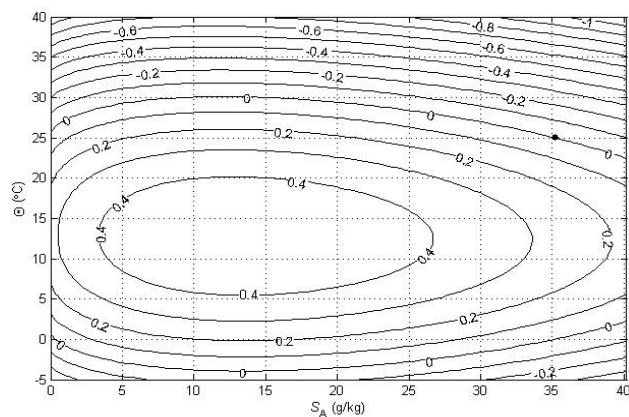
and

$$g_{S_A S_A} > 0. \quad (\text{A.16.18})$$

These constraints mean that (i) the fluid must increase its temperature when it is heated, and (ii) the solute should not spontaneously “unmix”. These constraints on the Gibbs function are well known from considerations of molecular fluxes. It is encouraging that they emerge also from the turbulent mixing process, which happens quite independently of the form of the molecular fluxes.

We considered the turbulent mixing of pairs of seawater parcels that had finite amplitude differences of Absolute Salinity and of temperature. By employing a Taylor series analysis, we were able to get an expression for the non-conservative production of entropy and of potential temperature when the parcels are mixed to uniformity.

We were able to illustrate the non-conservative production of entropy and of potential temperature, when mixing occurs between pairs of fluid parcels, on the following carefully-constructed diagrams.



We then showed that these diagrams are the measure of the error involved with assuming that entropy or potential temperature is conserved in the ocean. Because of the unknowably many mixing events in the life-history of a seawater parcel, these diagrams illustrate the sum of these non-conservative sources in the past, over many different mixing events over the past 1000 years.

## Non-conservative production of Conservative Temperature

When fluid parcels undergo irreversible and complete mixing at constant pressure, the thermodynamic quantities that are conserved are mass, Absolute Salinity and enthalpy. As above we consider two parcels being mixed without external input of heat or mass, and the three equations that represent the conservation of these quantities are Eqns. (A.16.2) – (A.16.4). Neither potential enthalpy  $h^0$  nor Conservative Temperature  $\Theta$  are exactly conserved during the mixing process and the production of  $\Theta$  is given by

$$m_1 \Theta_1 + m_2 \Theta_2 + m \delta\Theta = m \Theta. \quad (\text{A.18.1})$$

Enthalpy in the functional form  $h = \hat{h}(S_A, \Theta, p)$  is expanded in a Taylor series of  $S_A$  and  $\Theta$  about the values  $S_A$  and  $\Theta$  of the mixed fluid, retaining terms to second order in  $[S_{A2} - S_{A1}] = \Delta S_A$  and in  $[\Theta_2 - \Theta_1] = \Delta\Theta$ . Then  $h_1$  and  $h_2$  are evaluated and Eqns. (A.16.4) and (A.18.1) are used to find

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

Graham and McDougall (2013) have shown that the same form of the non-conservative production terms in Eqn. (A.18.2) also appears in the following turbulent evolution equation for Conservative Temperature, in both the epineutral and vertical diffusion terms (see appendix A.21 for an explanation of the symbols that appear in this thickness-weighted averaged equation),

$$\begin{aligned} \frac{d\hat{\Theta}}{dt} = \frac{\partial \hat{\Theta}}{\partial t} \Big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} + \hat{z} \frac{\partial \hat{\Theta}}{\partial z} = & \gamma_z \nabla_n \cdot (\gamma_z^{-1} K \nabla_n \hat{\Theta}) + (D\hat{\Theta}_z)_z + \varepsilon / \hat{h}_{\Theta} \\ & + K \left( \frac{\hat{h}_{\Theta\Theta}}{\hat{h}_{\Theta}} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_{\Theta}} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{S}_A + \frac{\hat{h}_{S_A S_A}}{\hat{h}_{\Theta}} \nabla_n \hat{S}_A \cdot \nabla_n \hat{S}_A \right) \\ & + D \left( \frac{\hat{h}_{\Theta\Theta}}{\hat{h}_{\Theta}} \hat{\Theta}_z^2 + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_{\Theta}} \hat{\Theta}_z \hat{S}_{Az} + \frac{\hat{h}_{S_A S_A}}{\hat{h}_{\Theta}} (\hat{S}_{Az})^2 \right). \end{aligned} \quad (\text{A.18.3})$$

In order to evaluate the partial derivatives in Eqns. (A.18.2) and (A.18.3), first write enthalpy in terms of potential enthalpy ( $c_p^0 \Theta$ ) using Eqn. (3.2.1), as

$$h = \hat{h}(S_A, \Theta, p) = c_p^0 \Theta + \int_{p_0}^P \hat{v}(S_A, \Theta, p') dp'. \quad (\text{A.18.4})$$

This is differentiated with respect to  $\Theta$  giving

$$h_{\Theta}|_{S_A, p} = \hat{h}_{\Theta} = c_p^0 + \int_{p_0}^P \alpha^{\Theta} / \rho dp'. \quad (\text{A.18.5})$$

The right-hand side of Eqn. (A.18.5) scales as  $c_p^0 + \rho^{-1} (P - P_0) \alpha^{\Theta}$ , which is more than  $c_p^0$  by only about  $0.0015 c_p^0$  for  $(P - P_0)$  of  $4 \times 10^7$  Pa (4,000 dbar). Hence, to a very good approximation,  $\hat{h}_{\Theta}$  in Eqns. (A.18.2) and (A.18.3) may be taken to be simply  $c_p^0$ . It is interesting to examine why this approximation is so accurate when the difference between enthalpy,  $h$ , and potential enthalpy,  $h^0$ , as given by Eqns. (3.2.1) and (A.18.4), scales as  $\rho^{-1} P$  which is as large as typical values of potential enthalpy. The reason is that the integral in Eqns. (3.2.1) or (A.18.4) is dominated by the integral of the mean value of  $\rho^{-1}$ , so causing a significant offset between  $h$  and  $h^0$  as a function of pressure but not affecting the partial derivative  $\hat{h}_{\Theta}$  which is taken at fixed pressure. Even the dependence of density on pressure alone does not affect  $\hat{h}_{\Theta}$ .

Recall from Eqn. (A.11.15), namely

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

and combining this with (A.18.5) we see that

$$\frac{(t - \theta)}{(T_0 + \theta)} c_p^0 = \int_{P_0}^P \alpha^\Theta / \rho \, dP' = \int_{P_0}^P \hat{v}_\Theta(S_A, \Theta, p') \, dP' \quad (\text{A.18.5a})$$

which is an interesting relationship between a temperature difference on the left-hand side (which is related directly to the entropy function) and a pressure integral of essentially the thermal expansion coefficient on the right-hand side.

The second order derivatives of  $\hat{h}$  are needed in Eqns. (A.18.2) and (A.18.3), and these can be estimated by differentiating Eqn. (A.18.4) or (A.18.5), so that, for example,

$$\hat{h}_{\Theta\Theta} = \int_{P_0}^P \hat{v}_{\Theta\Theta} \, dP' = \int_{P_0}^P (\alpha^\Theta / \rho)_\Theta \, dP', \quad (\text{A.18.6})$$

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

$$\delta\Theta \approx \frac{(P - P_0)}{8c_p^0} \left\{ \hat{v}_{\Theta\Theta} (\Delta\Theta)^2 + 2\hat{v}_{S_A\Theta} \Delta\Theta \Delta S_A + \hat{v}_{S_A S_A} (\Delta S_A)^2 \right\}. \quad (\text{A.18.7})$$

This equation is approximate because the variation of  $\hat{v}_{\Theta\Theta}$ ,  $\hat{v}_{\Theta S_A}$  and  $\hat{v}_{S_A S_A}$  with pressure has been ignored. The dominant term in Eqn. (A.18.7) is usually the term in  $\hat{v}_{\Theta\Theta}$  and from Eqn. (A.19.2) below we see that  $\delta\Theta$  is approximately proportional to the non-conservative destruction of specific volume at fixed pressure caused by the “cabbeling” non-linearities in the equation of state (McDougall, 1987b), so that

$$\delta\Theta \approx \frac{(P - P_0)}{8c_p^0} \hat{v}_{\Theta\Theta} (\Delta\Theta)^2 \approx -\frac{(P - P_0)}{c_p^0} \delta v. \quad (\text{A.18.8})$$

The production of  $\Theta$  causes an increase in Conservative Temperature and a consequent decrease in density of  $-\rho\alpha^\Theta\delta\Theta$ . The ratio of this change in density (using Eqn. (A.18.7)) to that caused by cabbeling (from Eqn. (A.19.2) and using  $\delta\rho \approx -\rho^2\delta v$ ) is  $-(P - P_0)\alpha^\Theta / \rho c_p^0$  which is about 0.0015 for a value of  $(P - P_0)$  of 40 MPa. Hence it is clear that cabbeling has a much larger effect on density than does the non-conservation of  $\Theta$ . Nevertheless, it is interesting to note from Eqn. (A.18.7) that the non-conservative production of  $\Theta$  is approximately proportional to the product of sea pressure and the strength of cabbeling.

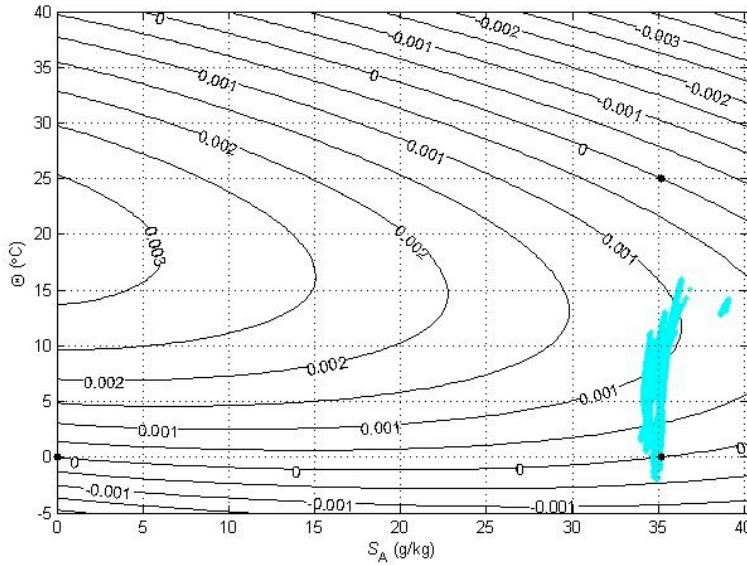
The first term in the bracket in Eqn. (A.18.7) is usually about a factor of ten larger than the other two terms, so the production of Conservative Temperature  $\delta\Theta$  as a ratio of the contrast in Conservative Temperature  $\Delta\Theta = \Theta_2 - \Theta_1$  may be approximated as (since  $\hat{v}_{\Theta\Theta} \approx -\rho^{-2}\hat{\rho}_{\Theta\Theta} \approx \rho^{-1}\alpha_\Theta^\Theta$ )

$$\frac{\delta\Theta}{\Delta\Theta} \approx \frac{(P - P_0)\alpha_\Theta^\Theta \Delta\Theta}{8\rho c_p^0} \approx 3.3 \times 10^{-9} (p/\text{dbar})(\Delta\Theta/\text{K}). \quad (\text{A.18.9})$$

where  $\alpha_\Theta^\Theta$  has been taken to be  $1.1 \times 10^{-5} \text{ K}^{-2}$ .

At the sea surface Conservative Temperature  $\Theta$  is totally conserved ( $\delta\Theta = 0$ ). The expression for the non-conservative production of Conservative Temperature,  $\delta\Theta$ , increases almost linearly with pressure (see Eqn. (A.18.7)) but at larger pressure the range of temperature and salinity in the ocean decreases, and from the above equations it is clear that the magnitude of  $\delta\Theta$  is proportional to the square of the temperature and salinity contrasts. McDougall (2003) concluded that the production  $\delta\Theta$  between extreme seawater parcels at each pressure is largest at 600 dbar. The magnitude of the non-conservative production of Conservative Temperature,  $\delta\Theta$ , is illustrated in [Figure A.18.1](#) for data at this pressure.





**Figure A.18.1.** Contours (in °C) of a variable that is used to illustrate the non-conservative production of Conservative Temperature  $\Theta$  at  $p = 600$  dbar. The cloud of points show where most of the oceanic data reside at  $p = 600$  dbar. The three points that are forced to be zero are shown with black dots.

The quantity contoured on this figure is the difference between  $\Theta$  and the following totally conservative quantity at  $p = 600$  dbar. This conservative quantity was constructed by taking the conservative property enthalpy  $h$  at this pressure and adding the linear function of  $S_A$  which makes the result equal to zero at  $(S_A=0, \Theta=0^\circ\text{C})$  and at  $(S_A=35.16504\text{ g kg}^{-1}, \Theta=0^\circ\text{C})$ . This quantity is then scaled so that it becomes  $25^\circ\text{C}$  at  $(S_A=35.16504\text{ g kg}^{-1}, \Theta=25^\circ\text{C})$ . In this manner the quantity that is contoured in Figure A.18.1 has units of  $^\circ\text{C}$  and represents the amount by which Conservative Temperature  $\Theta$  is not a totally conservative variable at a pressure of 600 dbar. The maximum amount of production by mixing seawater parcels at the boundaries of Figure A.18.1 is about  $4 \times 10^{-3}^\circ\text{C}$  although the range of values encountered in the real ocean at this pressure is actually quite small, as indicated in Figure A.18.1.

From the curvature of the isolines on Figure A.18.1 it is clear that the non-conservative production of Conservative Temperature at  $p = 600$  dbar is positive, so that an ocean model that ignores this production of Conservative Temperature will slightly underestimate  $\Theta$ . From Eqn. (A.18.2) one sees the non-conservative production of Conservative Temperature is always positive if  $\hat{h}_{\Theta\Theta} > 0$ ,  $\hat{h}_{S_A S_A} > 0$  and  $(\hat{h}_{\Theta S_A})^2 < \hat{h}_{\Theta\Theta} \hat{h}_{S_A S_A}$ , and Graham and McDougall (2013) have shown that these requirements are met everywhere in the full TEOS-10 ranges of salinity, temperature and pressure for both the full TEOS-10 Gibbs function and for the 48-term approximate expression for specific enthalpy of Appendix A.30.

From Eqns. (A.18.9) and (A.17.3) we can write the ratio of the production of Conservative Temperature to the production of potential temperature when two seawater parcels mix as the approximate expression

$$\frac{\partial\Theta}{\partial\theta} \approx -10^{-5} (p/\text{dbar})(\Delta\Theta/\text{K})(\Delta S_A / [\text{g kg}^{-1}])^{-1}. \quad (\text{A.18.10})$$

Taking a typical ratio of temperature differences to salinity differences in the deep ocean to be  $5\text{ K} / [\text{g kg}^{-1}]$ , Eqn. (A.18.10) becomes  $\partial\Theta/\partial\theta \approx -5 \times 10^{-5} (p/\text{dbar})$ . At a pressure of 4000 dbar this ratio is  $\partial\Theta/\partial\theta \approx -0.2$  implying that Conservative Temperature is a factor of five more conservative than potential temperature at these great depths. Note also that the temperature and salinity contrasts in the deep ocean are small, so the non-

conservation of both types of temperature amount to very small temperature increments of both  $\delta\theta$  and  $\delta\Theta$ . The largest non-conservative increment of Conservative Temperature  $\delta\Theta$  seems to occur at a pressure of about 600 dbar (McDougall (2003)) and this value of  $\delta\Theta$  is approximately two orders of magnitude less than the maximum value of  $\delta\theta$  which occurs at the sea surface.

### Non-conservative production of specific volume

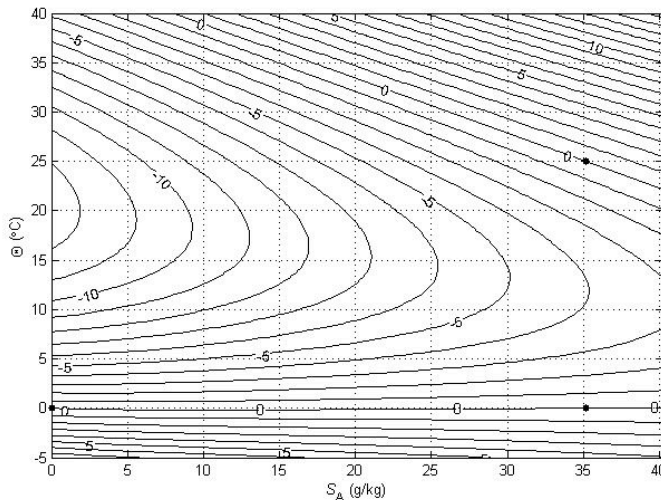
Specific volume is expressed as a function of Absolute Salinity  $S_A$ , specific enthalpy  $h$  and pressure as  $v = \tilde{v}(S_A, h, p)$  and the same mixing process between two fluid parcels is considered as in the previous appendices. Mass, salt and enthalpy are conserved during the turbulent mixing process (Eqns. (A.16.2) - (A.16.4)) while the non-conservative nature of specific volume means that it obeys the equation,

$$m_1 v_1 + m_2 v_2 + m \delta v = m v. \quad (\text{A.19.1})$$

Specific volume is expanded in a Taylor series of  $S_A$  and  $\Theta$  about the values of  $S_A$  and  $\Theta$  of the mixed fluid at pressure  $p$ , retaining terms to second order in  $[S_{A2} - S_{A1}] = \Delta S_A$  and in  $[h_2 - h_1] = \Delta h$ . Then  $v_1$  and  $v_2$  are evaluated and (A.19.1) is used to find

$$\begin{aligned} \delta v &= -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \tilde{v}_{hh} (\Delta h)^2 + 2 \tilde{v}_{hS_A} \Delta h \Delta S_A + \tilde{v}_{S_A S_A} (\Delta S_A)^2 \right\} \\ &\approx -\frac{1}{2} \frac{m_1 m_2}{m^2} \left\{ \hat{v}_{\Theta\Theta} (\Delta\Theta)^2 + 2 \hat{v}_{\Theta S_A} \Delta\Theta \Delta S_A + \hat{v}_{S_A S_A} (\Delta S_A)^2 \right\}. \end{aligned} \quad (\text{A.19.2})$$

The non-conservative destruction of specific volume of Eqn. (A.19.2) is illustrated in **Figure A.19.1** for mixing at  $p = 0$  dbar. The quantity contoured on this figure is formed as follows. First the linear function of  $S_A$  is found that is equal to specific volume at  $(S_A=0, \Theta=0^\circ\text{C})$  and at  $(S_A=35.16504\text{ g kg}^{-1}, \Theta=0^\circ\text{C})$ . This linear function of  $S_A$  is subtracted from  $v$  and the result is scaled to equal  $25^\circ\text{C}$  at  $(S_A=35.16504\text{ g kg}^{-1}, \Theta=25^\circ\text{C})$ . The variable that is contoured in Figure A.19.1 is the difference between this scaled linear combination of  $v$  and  $S_A$ , and Conservative Temperature. This figure allows the non-conservative nature of specific volume to be understood in temperature units. The mixing of extreme fluid parcels on Figure A.19.1 causes the same decrease in specific volume as a cooling of approximately  $10^\circ\text{C}$ , which is approximately 4000 times larger than the corresponding non-conservative production of  $\Theta$  at 600dbar (from Figure A.18.1).



**Figure A.19.1.** Contours (in  $^\circ\text{C}$ ) of a variable that is used to illustrate the non-conservative production of specific volume at  $p = 0$  dbar. The three points that are forced to be zero are shown with black dots.

From Eqn. (A.19.2) it follows that specific volume is always destroyed by turbulent mixing processes if  $\tilde{v}_{hh} > 0$ ,  $\tilde{v}_{s_A s_A} > 0$  and  $(\tilde{v}_{h s_A})^2 < \tilde{v}_{s_A s_A} \tilde{v}_{hh}$ , and Graham and McDougall (2013) have shown that these conditions are satisfied over the full TEOS-10 ranges of salinity, temperature and pressure by both the full TEOS-10 Gibbs function and by the 48-term expression for specific volume. Note that in contrast to the case of specific volume, the non-conservation of density is not sign-definite. That is, while turbulent mixing always destroys specific volume, it does not always produce density  $\rho = v^{-1}$ .

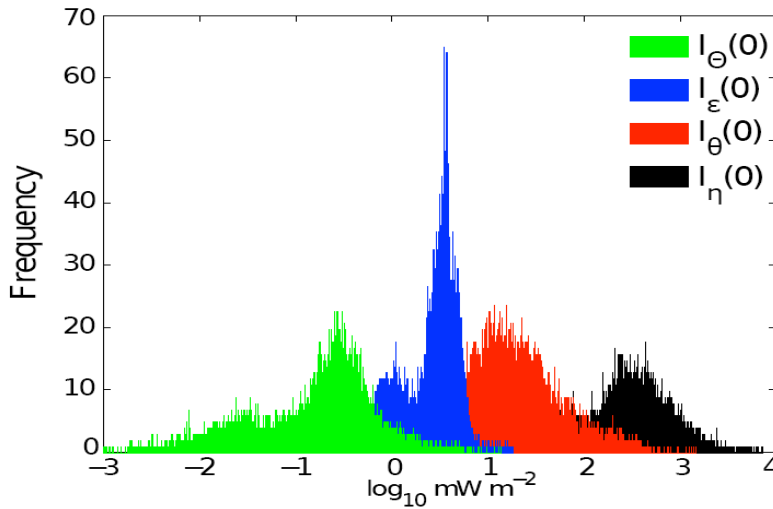
The fact that turbulent mixing at constant pressure always destroys specific volume also implies that internal energy is always produced by this turbulent mixing at constant pressure (see the First Law of Thermodynamics, Eqn. (B.19)).

### Depth-integrated measures of the non-conservation of $\theta$ , $\eta$ and $\Theta$

Graham and McDougall (2013) have derived the evolution equations for potential temperature, Conservative Temperature and specific entropy in a turbulent ocean, with the one for Conservative Temperature, Eqn. (A.18.3), being repeated here.

$$\begin{aligned} \frac{d\hat{\Theta}}{dt} = \frac{\partial \hat{\Theta}}{\partial t} \Big|_n + \hat{\mathbf{v}} \cdot \nabla_n \hat{\Theta} + \tilde{\varepsilon} \frac{\partial \hat{\Theta}}{\partial z} = \gamma_z \nabla_n \cdot (\gamma_z^{-1} K \nabla_n \hat{\Theta}) + (D\hat{\Theta}_z)_z + \varepsilon / \hat{h}_\Theta \\ + K \left( \frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{\Theta} + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \nabla_n \hat{\Theta} \cdot \nabla_n \hat{S}_A + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} \nabla_n \hat{S}_A \cdot \nabla_n \hat{S}_A \right) \\ + D \left( \frac{\hat{h}_{\Theta\Theta}}{\hat{h}_\Theta} \hat{\Theta}_z^2 + 2 \frac{\hat{h}_{\Theta S_A}}{\hat{h}_\Theta} \hat{\Theta}_z \hat{S}_{Az} + \frac{\hat{h}_{S_A S_A}}{\hat{h}_\Theta} (\hat{S}_{Az})^2 \right). \end{aligned} \quad (\text{A.18.3})$$

The red terms on the second and third lines of this equation are the non-conservative production terms and they can be evaluated in an ocean model. One way of quantifying how big they are is to vertically integrate these terms and to express this vertical integral as a vertical heat flux. Consider a vertical ocean water column that is the full depth of the ocean and is one square meter in area. The vertical integral of the red source terms is the equivalent extra air-sea or geothermal heat flux that is required to be equal to the effect of the neglected non-conservative terms. This is shown as a histogram for the whole world ocean in the figure below.



The 95 percentile largest values of these four error measures is shown below.

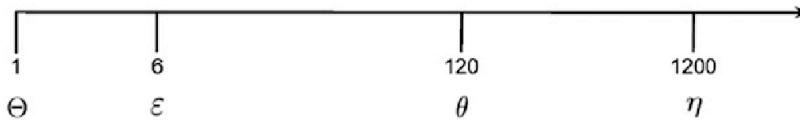


FIG. 10. The 95% error occurrences of the depth-integrated nonconservative source terms for  $\varepsilon$ ,  $\theta$ , and  $\eta$  to that of  $\Theta$  ( $10^{-3} \text{ W m}^{-2}$ ) on a logarithmic scale.

This demonstrates that the non-conservative source terms of potential temperature are two orders of magnitude larger than those for Conservative Temperature, and that the dissipation of kinetic energy is almost an order of magnitude larger than the non-conservative source terms in the evolution equation for Conservative Temperature.

To put this in perspective, the mean geothermal heat flux is  $\sim 86.4 \text{ mW m}^{-2}$ , and the extra surface heat flux that the planet is receiving now from global warming is  $\sim 1.5 \text{ W m}^{-2}$ .

## Advective and diffusive “heat” fluxes

The turbulent flux of a “potential” property can be thought of as the exchange of parcels of equal mass but contrasting values of the “potential” property, and the turbulent flux can be parameterized as being down the gradient of the “potential” property. The conservative form of Eqn. (A.21.15) implies that the turbulent flux of heat should be directed down the mean gradient of Conservative Temperature rather than down the mean gradient of potential temperature. Here we quantify the ratio of the mean gradients of potential temperature and Conservative Temperature along the neutral tangent plane; along a surface of constant “density” if you like.

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

$$\nabla_n \theta = \hat{\theta}_\Theta \nabla_n \Theta + \hat{\theta}_{S_A} \nabla_n S_A, \quad (\text{A.14.3})$$

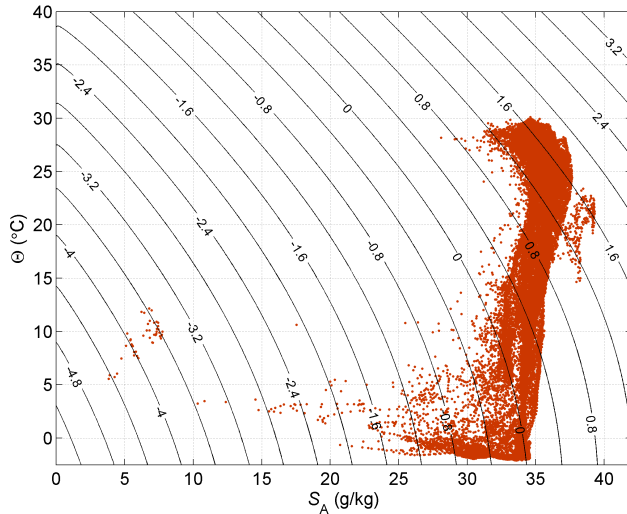
and using the neutral relationship  $\nabla_n S_A = (\alpha^\Theta / \beta^\Theta) \nabla_n \Theta$  we find

$$\nabla_n \theta = \left( \hat{\theta}_\Theta + \left[ \alpha^\Theta / \beta^\Theta \right] \hat{\theta}_{S_A} \right) \nabla_n \Theta, \quad (\text{A.14.4})$$

or

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

The ratio, Eqn. (A.14.5), of the epineutral gradients of  $\theta$  and  $\Theta$  is shown in Figure A.14.1 at  $p = 0$ , indicating that the epineutral gradient of potential temperature is sometimes more than 1% different to that of Conservative Temperature. This ratio  $|\nabla_n \theta| / |\nabla_n \Theta|$  is only a weak function of pressure.



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

## Keeping track of “heat” in the ocean; advection and diffusion of heat

We have shown that the First Law of Thermodynamics is practically equivalent to the conservation equation for Conservative Temperature  $\Theta$ . We have emphasized that this means that the advection of “heat” is very accurately given as the advection of  $c_p^0 \Theta$ . In this way  $c_p^0 \Theta$  can be regarded as the “heat content” per unit mass of seawater. The error involved with making this association is approximately 1% of the error in assuming that either  $c_p^0 \theta$  or  $c_p(S_A, \theta, 0 \text{ dbar}) \theta$  is the “heat content” per unit mass of seawater.

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

The First Law of Thermodynamics can be approximated as

$$\rho c_p^0 \frac{d\Theta}{dt} = c_p^0 (\rho\Theta)_t + c_p^0 \nabla \cdot (\rho\Theta \mathbf{u}) \approx -\nabla \cdot \mathbf{F}^R - \nabla \cdot \mathbf{F}^Q + \rho\epsilon, \quad (3.23.1)$$

with an error in  $\Theta$  that is approximately one percent of the error incurred by treating either  $c_p^0 \theta$  or  $c_p(S_A, \theta, 0) \theta$  as the “heat content” of seawater. Equation (3.23.1) is exact at 0 dbar.

Because the left-hand side of the First Law of Thermodynamics, Eqn. (3.23.1), can be written as density times the material derivative of  $c_p^0 \Theta$  it follows that  $\Theta$  can be treated as a conservative variable in the ocean and that  $c_p^0 \Theta$  is transported by advection and mixed by turbulent epineutral and dianeutral diffusion as though it is the “heat content” of seawater. For example, the advective meridional flux of “heat” is the area integral of  $\rho v h^0 = \rho v c_p^0 \Theta$  (here  $v$  is the northward velocity).

Some have argued that because enthalpy is unknown up to a linear function of salinity, it is only possible to talk of a flux of “heat” through an ocean section if the fluxes of mass and salt through the ocean section are both zero. This opinion seems to be widely held, but it is incorrect. The fact that  $c_p^0 \Theta$  is unknowable up to a linear function of  $S_A$  does not affect the usefulness of  $h^0$  or  $c_p^0 \Theta$  as measures of “heat content”:- the difference between the meridional fluxes of  $c_p^0 \Theta$  across two latitudes is equal to the area-integrated air-sea and geothermal heat fluxes between these latitudes (after allowing for any unsteady accumulation of  $c_p^0 \Theta$  in the volume), irrespective of whether there are non-zero fluxes of mass or salt across the sections. This powerful result follows directly from the fact that  $c_p^0 \Theta$  is taken to be a conservative variable, obeying the simple conservation statement Eqn. (3.23.1) (modulo the dissipation of kinetic energy,  $\rho\epsilon$ ). No one would doubt the sensibleness of calculating the meridional flux of a general passive tracer that obeyed such a conservation evolution equation, and the same applies to the flux of potential enthalpy.

### The intuitive explanation of why Conservative Temperature makes sense

These lectures have largely demonstrated the benefits of potential enthalpy and Conservative Temperature from the viewpoint of conservation equations, but the benefits can also be deduced by the following parcel-based argument.

1. First, the air-sea heat flux needs to be recognized as a flux of potential enthalpy which is exactly  $c_p^0$  times the flux of Conservative Temperature.
2. Second, the non-conservative production of Conservative Temperature at non-zero pressure needs to be calculated and shown to be much less than that for potential temperature.
3. Third, note that the ocean circulation can be regarded as a series of adiabatic and isohaline movements during which  $\Theta$  is absolutely unchanged (because of its “potential” nature) followed by a series of turbulent mixing events during which  $\Theta$  is almost totally conserved.

Hence it is clear that  $\Theta$  is the quantity that is advected and diffused in an almost conservative fashion and whose surface flux is exactly proportional to the air-sea heat flux.