

A 2-Lecture Overview of Seawater Thermodynamics

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These notes contain material presented over 2×1.5 hour lectures, following from material (reviewed in Appendix A) developing the equations used in oceanic geophysical fluid dynamics (GFD) theory, near the beginning of a 1-term graduate-level introductory GFD course. I like to use the blackboard.

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Introduction - the Need for Thermodynamics

In developing the equations for ocean dynamics¹, it is necessary to introduce an equation relating density ρ to pressure P , temperature T , and salinity S (eqn. A.6):

$$\rho = \rho(P, T, S) \quad (1)$$

This relationship is purely empirical, as it arises from the physico-chemical properties of the particular fluid. For seawater it depends on the properties of water and the constituents of salt². For air we have a similar equation, except that in place of the salinity we use a variable representing the water content (or humidity) of the air.

However, this results in the introduction of a new variable - temperature. We know how to write equations that conserve mass (of water and of salt) in seawater. Thus, we also need to write a conservation equation that governs temperature, or, more generally, “heat”.

But what is “heat”? It is not temperature, although clearly it is related to temperature³. We know that temperature cannot measure heat directly for several reasons, based on measurements of the actual properties of seawater. One is that the temperature increases with pressure. Thus it cannot be a conserved property of an isolated water parcel in the same way that salt content is conserved. We can remove this effect by considering a pressure-corrected variable called potential temperature (about which we shall say more later), but even the potential temperature cannot measure “heat” properly, because the heat capacity of seawater - the amount of energy it takes to change the temperature by 1 K - is not a constant, but varies with temperature and salinity. Thus when mixing parcels of seawater, the temperature of the mixture is not the average of the original temperatures.

Instead our understanding of “heat” must be related to energy in some way. Energy can come in different forms. For example, an equation for the mechanical energy in fluids which involves kinetic and gravitational potential energy can be derived from the momentum equation. Now we are also interested in the energy it takes to heat and cool seawater, change its volume, and perhaps its composition.

Heat and heat energy changes will involve an internal storage of energy (and hence, the *INTERNAL ENERGY*⁴). Investigations into the nature of internal energy conservation lead us into the field of THERMODYNAMICS.

The general approach used in the ocean (“quasi-equilibrium thermodynamics”) assumes that small parcels of water are effectively in a thermodynamic equilibrium at all times (i.e. we are

¹see Appendix A for a short review.

²For more technical information about temperature, salinity, and their relationship to density, see the article “[Key Physical Variables in the Ocean: Temperature, Salinity, and Density](#)”, *Nature Education Knowledge* 4(4):13.

³indeed, what exactly is “temperature”? Read the article referenced in the last footnote!

⁴This can be thought of as energy involved in the vibration and rotation of molecules as well as energy in chemical bonds and electrostatic charges.

dealing with time scales longer than any local disequilibrium in response to sudden changes in, for example, pressure), but that the ocean as a whole is not in equilibrium, so that we can track changes in heat and salt content from place to place using hydrodynamic equations.

So, the first step (described in Part 1 next) is to define the equilibrium thermodynamics of a parcel of water. This turns out to have an important consequence, namely that we can more properly define an equation of state. The next step (described in Part 2) is then to embed this understanding in a hydrodynamic system.

Part 1: Equilibrium Thermodynamics - The Equation of State

First, we consider the equilibrium behavior of a parcel of water. We begin with a postulate:

Postulate: The Internal Energy of a system in equilibrium is a function of its *EXTENSIVE* properties.

Extensive properties are ones that are proportional to the amount of material present. These properties include *VOLUME*, *MASS*, and something related to the arrangement and state of particles within the material, which we call *ENTROPY*. The actual functional relationship between internal energy and the extensive properties would then completely define the possible states of a particular system.

Entropy: is not usually considered to be as intuitive a concept as volume or salinity, nor can it be easily measured. Entropy is sometimes described as a measure of disorder, or a measure of the energy *not* available to do work.

An alternative interpretation is that the entropy is proportional to a value of the Shannon Measure of Information (SMI), a concept defined in information theory, once the SMI is maximized over all possible particle distributions in the system with fixed total energy and mass⁵.

Entropy is sometimes considered to be a measure of “heat content”, and has the particular advantage that, like potential temperature, it is not affected by changes in pressure alone. However, entropy is always produced, never destroyed, by mixing, so it is not “isobaric conservative” (i.e. entropy is not conserved when two water parcels are mixed together).

For fluids, it is more convenient to think of all these properties “per unit mass”. Such properties are called “specific” or *INTENSIVE*. Then, for any particular fluid we can equivalently postulate a relationship between the specific internal energy u of a parcel and intensive variables:

⁵Read about it in A. Ben-Naim, “Entropy and the Second Law”, (263pp., World Scientific Publishing Company, 2012)

$$u = u(\nu, \eta, S) \quad (2)$$

where

- u is the specific internal energy (units of J/kg),
- ν is the specific volume ($= 1/\rho$, where ρ is the density) with units of m^3/kg ,
- η is the specific entropy, with units of J/kg/K, and
- S specifies the composition of the system. S is the salinity in seawater (e.g., the g/kg of solute in seawater, as measured by Absolute Salinity S_A on the TEOS-10 Reference Composition Salinity Scale), or the relative humidity in air (i.e., the fraction of water).

Since u tells us about the thermodynamic state of a system it is called a *THERMODYNAMIC POTENTIAL*. If we can determine a particular functional form for this relationship then that functional form would provide a *FUNDAMENTAL EQUATION OF STATE* for the fluid.

The intensive variables used in eqn. (2) are somewhat arbitrary, but turn out to be “natural” for internal energy. That is, they are most convenient for many theoretical purposes (as we see below). Unfortunately, they are mostly not as useful for practical investigations. Entropy is unmeasurable. Specific volumes are easy to understand, but are difficult to measure to the accuracy required for ocean circulation studies outside of a specially equipped laboratory.

Ignoring these practical issues for now, this first postulate implies that changes in the volume, salinity, or entropy of a fluid can result in changes in internal energy. Alternatively, changes in the internal energy would have to be balanced by changes in the volume, composition, or entropy of the fluid. These changes could be caused by outside forces. This leads us to a second postulate, also known as the *FIRST LAW OF THERMODYNAMICS*:

Postulate (First Law of Thermodynamics): The Internal Energy of a system changes because of heat input, because of work done by or on it, or because of a change in composition.

In mathematical terms:

$$du = \delta Q - \delta W + \delta C \quad (3)$$

where

- du is a differential change in the internal energy
- δQ is an infinitesimal input of heat
- δW is an infinitesimal amount of work done, and
- δC is the internal energy change caused by an infinitesimal composition change.

The distinction between d and δ arises because the d are functions of the state of a body but the δ changes are not. Only very small changes are allowed in this expression in order that the system stays in equilibrium at all times.

Now, we can further parameterize each of terms on the right hand side:

1. δQ : The Heat Input. Heat and entropy are related through temperature.

Now we need to define temperature more precisely. The *ZEROTH LAW OF THERMODYNAMICS* states that heat fluxes arise from temperature gradients, or equivalently that objects in thermal equilibrium, without a heat flux passing between them, are at the same temperature - or even, rather flippantly, that temperature is something measured by thermometers!

Then we postulate a relationship (the *SECOND LAW OF THERMODYNAMICS*):

$$\boxed{\frac{\delta Q}{T} \leq d\eta} \quad (4)$$

where

- T is the absolute temperature (K), and
- $d\eta$ is a differential change in entropy.

That is, an input of heat results in an entropy change, but the magnitude of this change also depends on the temperature. In a *REVERSIBLE* system, which we will assume is the case here, the \leq is strictly $=$, so that

$$\delta Q = Td\eta \quad (5)$$

2. δW : The Work Done. Work is force times distance, or in this case the ambient pressure P times the (differential) change in volume:

$$\delta W = Pd\nu \quad (6)$$

3. δC : Composition changes. We will write this as

$$\delta C = \mu dS \quad (7)$$

where a known change in salinity (or humidity in air) is proportional to the change in internal energy through a proportionality factor μ which is called the *CHEMICAL POTENTIAL*.

Substituting these definitions into eqn. (3) results in the *FUNDAMENTAL THERMODYNAMIC RELATION*⁶:

$$\boxed{du = Td\eta - Pd\nu + \mu dS} \quad (8)$$

⁶It is the addition of the last term involving chemical potential that makes this definition different from ones found in standard approaches to thermodynamics.

Now, since $u = u(\eta, \nu, S)$ we have by the chain rule:

$$du = \left. \frac{\partial u}{\partial \eta} \right|_{\nu, S} d\eta + \left. \frac{\partial u}{\partial \nu} \right|_{\eta, S} d\nu + \left. \frac{\partial u}{\partial S} \right|_{\eta, \nu} dS \quad (9)$$

and so by comparing equations (8) and (9) we can identify

$$T = \left. \frac{\partial u}{\partial \eta} \right|_{\nu, S}, \quad P = - \left. \frac{\partial u}{\partial \nu} \right|_{\eta, S}, \quad \mu = \left. \frac{\partial u}{\partial S} \right|_{\eta, \nu} \quad (10)$$

which can therefore be regarded as definitions of these variables. Again though, these definitions are not very useful in practical terms since we don't know how to measure η and measuring ν is possible but usually only under controlled laboratory conditions.

However, here is a trick:

Let us DEFINE a different potential function g , called the *GIBBS FUNCTION* (or specific Gibbs free energy, units of J/kg), in terms of the internal energy and a few other factors:

$$g \equiv u + P\nu - T\eta \quad (11)$$

The Gibbs function can also be thought of as the internal energy required to create a mass, plus the pressure work needed to “make room” for it by pushing away the atmosphere surrounding it, minus the amount of heat energy that would be obtained from its surroundings (at temperature T) during this process.

The Gibbs function is useful in the study of chemical reactions at constant temperature and pressure, since reactions under those conditions will proceed spontaneously to a state with minimum Gibbs energy. However, the Gibbs function is useful here for another reason, which we now demonstrate: taking differentials on both sides of eqn. (11), and using eqn. (8) to replace du , we get

$$dg = \mu dS - \eta dT + \nu dP \quad (12)$$

which suggests that the “natural” coordinates for g are S, T , and P . That is, there can be a functional dependence for g :

$$g = g(S, T, P) \quad (13)$$

which is useful in practice for describing the state of seawater because S, T , and P are variables that we can measure (relatively) easily, even in the field.

If so, then it follows that (via the chain rule):

$$dg = \left. \frac{\partial g}{\partial S} \right|_{T, P} dS + \left. \frac{\partial g}{\partial T} \right|_{S, P} dT + \left. \frac{\partial g}{\partial P} \right|_{T, S} dP \quad (14)$$

and by comparing eqns. (14) and (12) we can now find the entropy, density, and chemical potential in terms of the Gibbs function:

$$\eta = -\left.\frac{\partial g}{\partial T}\right|_{S,P} \quad (15)$$

$$\rho = \nu^{-1} = \left(\left.\frac{\partial g}{\partial P}\right|_{T,S}\right)^{-1} \quad (16)$$

and

$$\mu = \left.\frac{\partial g}{\partial S}\right|_{T,P} \quad (17)$$

In addition, we can determine all other thermodynamic properties in terms of other equations involving g and its derivatives. For example, we can calculate the internal energy itself:

$$u = g + T\eta - P\nu \quad (18)$$

$$= g - T\left.\frac{\partial g}{\partial T}\right|_{S,P} - P\left.\frac{\partial g}{\partial P}\right|_{T,S} \quad (19)$$

Another useful measure of “heat content” is the specific enthalpy h :

$$h \equiv u + P\nu \quad (20)$$

$$= g + T\eta \quad (21)$$

$$= g - T\left.\frac{\partial g}{\partial T}\right|_{S,P} \quad (22)$$

The ENTHALPY is another thermodynamic potential⁷. It can be thought of as representing the internal energy required to “create” a mass, plus the pressure work needed to “make space” for it.

Enthalpy is very useful in the study of chemical reactions because changes in enthalpy are related to the energy required (or produced) by a reaction at constant pressure. As we show later, it is important in fluid dynamics because it is (almost completely) conserved under mixing at constant pressure (it is “isobaric conservative”, as long as the heating from viscous dissipation of kinetic energy is neglected). This importance will become more obvious when we consider heat in the ocean as a whole.

⁷Other potential functions can also be defined; the most common of these is the specific Helmholtz energy $f \equiv u - T\eta$ with natural coordinates of T , ν , and S . Best available estimates of the thermodynamic properties of pure water from 251 K to 1273 K at pressures of up to 1000 MPa can be found from a standard called IAPWS-95, which is in the form of a Helmholtz function $f = f(\rho, T)$.

A related property (which can be measured in the laboratory) is the isobaric heat capacity, which is the rate of change of enthalpy with temperature at constant salinity and pressure:

$$c_p \equiv \left. \frac{\partial h}{\partial T} \right|_{S,P} = -T \left. \frac{\partial^2 g}{\partial T^2} \right|_{S,P} \quad (23)$$

If we want to determine the effect of changes in pressure on the in-situ temperature when no heat is gained or lost from the parcel, we need the adiabatic lapse rate Γ :

$$\Gamma = \left. \frac{\partial T}{\partial P} \right|_{S,\eta} = -\frac{g_{TP}}{g_{TT}} \quad (24)$$

(where subscripts are used here to denote derivatives of the Gibbs function). Another important thermodynamic parameter is the sound speed, which can also be written in terms of the Gibbs function:

$$c = \sqrt{\left. \frac{\partial P}{\partial \rho} \right|_{S,\eta}} = g_P \sqrt{\frac{g_{TT}}{g_{TP}^2 - g_{TT}g_{PP}}} \quad (25)$$

Other parameters such as the osmotic coefficient of seawater which can be related to freezing point lowering and vapour-pressure lowering equations (with increases in salinity and pressure) can also be derived from g .

Note that it is also possible to go the other way - if we have measurements of density, sound speed, heat capacity, freezing-point lowering, and so on, then we can use all of this data together to fit an empirical function that represents the Gibbs function (eqn 13)⁸.

Currently the Thermodynamic Equation of Seawater 2010 (TEOS-10) defines a Gibbs function to describe the thermodynamic state of seawater, using temperature t on the ITS-90 scale, TEOS-10 Absolute Salinity S_A , and gauge pressure p (i.e. absolute pressure minus 101325 Pa) as its state variables:

$$g(S_A, t, p) = g^W(t, p) + g^S(S_A, t,) \quad (26)$$

where a pure water part g^W is given by a 41-term polynomial:

$$g^W(t, p) = g_u \sum_{j=0}^7 \sum_{k=0}^6 g_{jk} \left(\frac{t}{t_u} \right)^j \left(\frac{p}{p_u} \right)^k \quad (27)$$

⁸Actually, since only various derivatives of g are measurable, there are several integration constants in the complete expression for g that cannot be determined by any known experiment. However, this in turn implies that their values have no practical significance for any real property of seawater.

(with specified constants g_u, t_u, p_u , and $g_{jk}, j = 0, \dots, k = 0, \dots$), and the saline correction g^S is given by a 64-term equation that includes logarithmic and polynomial terms:

$$g^S(S_A, t, p) = g_u \sum_{j,k} \left\{ \hat{g}_{1jk} \left(\frac{S_A}{S_u} \right)^2 \ln \left(\frac{S_A}{S_u} \right) + \sum_{i>1} \hat{g}_{ijk} \left(\frac{S_A}{S_u} \right)^i \right\} \left(\frac{t}{t_u} \right)^j \left(\frac{p}{p_u} \right)^k \quad (28)$$

with additional specified constants S_u and $\hat{g}_{ijk}, i = 1, \dots, j = 0, \dots, k = 0, \dots$). Note that it is NOT recommended that you type in all these constants yourself; instead use software available from www.teos-10.org.

The TEOS-10 Gibbs function is created by a fitting procedure that incorporates experimental data on density, heat capacity, vapour pressure, freezing and boiling points, sound speed, compressibility, and enthalpy changes, and also has a theoretically correct pure-water limit as $S_A \rightarrow 0$.

Other Gibbs functions are available for humid air and ice, so the combination can also be used to examine mixtures of the different fluids. The TEOS-10 Gibbs functions and their derivatives then replace a whole suite of independently-derived correlations for thermodynamic properties, including the EOS-80 density equations, a variety of sound speed equations, and more, with a thermodynamically consistent and complete set of specified mathematical functions.

In summary, specifying an equation of state for seawater in terms of a Gibbs function is USEFUL, because

1. All thermodynamics properties can be derived in a consistent way from the Gibbs function (by taking appropriate derivatives in terms of easily measured variables), and
2. The Gibbs function itself depends on easily measured variables S, T , and P , and
3. We can come up with an empirical parametric equation for the Gibbs function, by regressing onto sets of observational data of relatively easily measured properties.

Now we include this small-scale equilibrium framework into a set of equations for large scale motions of an ocean which (over these large scales) is *not* in equilibrium.

Part 2: Non-equilibrium Thermodynamics - An Energy Conservation Equation

There are 3 steps to forming an heat energy conservation equation suitable for describing seawater dynamics. First, assuming that the fundamental relation (8) applies to each seawater parcel, we can track its properties as the parcel moves through the ocean at longer time scales:

$$\rho \frac{Du}{Dt} = \rho T \frac{D\eta}{Dt} - \frac{P}{\nu} \frac{D\nu}{Dt} + \rho \mu \frac{DS}{Dt} \quad (29)$$

which, using eqn. (20), we can rewrite in terms of the enthalpy:

$$\boxed{\rho \frac{Dh}{Dt} - \frac{DP}{Dt} = \rho T \frac{D\eta}{Dt} + \rho \mu \frac{DS}{Dt} = \rho \frac{Du}{Dt} + \frac{P}{\nu} \frac{D\nu}{Dt}} \quad (30)$$

to get the *FUNDAMENTAL THERMODYNAMIC RELATIONSHIP FOR FLUIDS*.

The second step is a little more complex. It turns out that we cannot just write down an equation for internal energy conservation the same way that we can write down an equation for momentum conservation starting with $F = m\vec{a}$ and defining a set of forces. This is because the “heating rate” which we denoted δQ in our equilibrium dynamics becomes difficult to specify properly in cases where heat and mass diffuse through gradients in the system.

Instead we begin by defining the total energy per unit mass E as the sum of internal, kinetic, and potential energies:

$$E \equiv u + \frac{|\vec{v}|^2}{2} + \Phi \quad (31)$$

where \vec{v} is the velocity and Φ the geopotential (recall $\nabla\Phi = \vec{g}$, the gravitational acceleration). Next, we *construct* a conservation equation for E :

$$\rho \frac{DE}{Dt} = -\nabla \cdot (P\vec{v}) - \nabla \cdot F^R + \nabla \cdot (\rho c_p \kappa \nabla T) + \nabla \cdot (\rho \nu^{\text{visc}} \nabla \frac{|\vec{v}|^2}{2}) \quad (32)$$

where we *a priori* postulate that the total energy of a parcel changes because of divergences in:

- $P\vec{v}$: the pressure work done in compressing the system,
- F^R : the effects of radiative fluxes (e.g., light),
- $\rho c_p \kappa \nabla T$: the molecular diffusion of heat, which occurs along T gradients⁹, and
- $\rho \nu^{\text{visc}} \nabla |\vec{v}|^2/2$: the viscous diffusion of kinetic energy.

Note that since the right hand side terms are all written as the divergence of fluxes, the total energy E is “conservative” (that is, the amount of E in a water parcel remains constant in the absence of fluxes across the boundary of the parcel) and hence is also “isobaric conservative” under mixing processes (i.e. it is not created or destroyed by mixing). However, it is affected by pressure changes (via the first term on the RHS).

In reality there should be a small additional non-conservative term on the right hand side arising from the production and remineralization of organic material in the ocean. Particulate is formed by removing inorganic material that is part of the “salt” of seawater and hence there is an associated energy loss; in turn remineralization adds dissolved material and hence there is an associated increase in the total energy. However, the consequences of these sources and sinks for overall energy budgets are not yet clear.

⁹a complete development also includes a heat flux arising from salt diffusion, the so-called “Dufour Effect”, but this is not important in the ocean.

Now, it is a little awkward for the analysis of heat that our energy equation involves velocities and the geopotential. So, the third step is to remove these by subtracting a conservation equation for mechanical energy. Such an equation is easily formed by taking the dot product of \vec{v} with the usual equation for conservation of momentum (recall eqns. A.3 and A.4):

$$\vec{v} \cdot \left(\rho \frac{D\vec{v}}{Dt} + 2\Omega \times \rho\vec{v} \right) = \vec{v} \cdot \left(-\nabla P - \nabla\Phi + \nabla \cdot (\rho\nu^{\text{visc}}\nabla\vec{v}) \right) \quad (33)$$

which can be written more conventionally as

$$\rho \frac{D}{Dt} \left(\frac{|\vec{v}|^2}{2} + P\nu + \Phi \right) = \frac{\partial P}{\partial t} + \nabla \cdot (\rho\nu^{\text{visc}}\nabla \frac{|\vec{v}|^2}{2}) - \rho\varepsilon \quad (34)$$

where $\varepsilon = \nu^{\text{visc}}|(\nabla\vec{v})|^2 \geq 0$ is the nonnegative dissipation rate of mechanical energy.

Finally, after performing the subtraction, simplifying with the aid of mass conservation (eqn. A.1)

$$\frac{D\rho}{Dt} + \rho\nabla \cdot \vec{v} = 0 \quad (35)$$

and using the fundamental relation (30) to replace u with h , we find:

$$\boxed{\rho \frac{Dh}{Dt} - \frac{DP}{Dt} = -\nabla \cdot F^R + \nabla \cdot (\rho c_p \kappa \nabla T) + \rho\varepsilon} \quad (36)$$

This is an equation that governs “heat” in the ocean. and as such is an expression of the *FIRST LAW OF THERMODYNAMICS IN A NON-EQUILIBRIUM FLUID*.

The dissipation rate term (which links the conversion of kinetic energy into heat at very small spatial scales) is small and can be neglected for most purposes, so the right hand side can be written as the divergence of a set of fluxes, in the same way as the other scalar balance equations.

A Practical “Heat” Conservation Equation

With the development of eqn. (36) we have achieved our goal. However, the P term on the left hand side of the equation is awkward. It implies that the enthalpy of a water parcel will change as the parcel moves vertically, even if the motion is adiabatic and no salt is gained or lost. On the other hand, at least at constant P it implies that h is conserved (e.g., under mixing), which is a useful property.

Unfortunately, although we can easily replace the left hand side of eqn. (36) with other expressions for either internal energy u or entropy η using the fundamental thermodynamic relationship (30) these other forms also have awkward additional terms. An internal energy equation would also involve pressure and changes in density. The entropy equation is more promising, since

entropy is conserved under horizontal and vertical motions, in the absence of boundary fluxes as long as no salt is gained or lost, but it is unwieldy to have to consider salt evolution and the chemical potential in a heat equation.

There is therefore no perfect way to create a conservative heat tracer. Instead, we can try to derive approximate equations, which have different levels of “error”. These approximate equations often use *POTENTIAL* variables. Variables with the potential property do not change with changes in pressure. Entropy and salinity have this property, as does potential temperature, which has traditionally been used as a measure of heat in the ocean. Traditionally, so-called potential temperature has been used as an approximately conservative heat tracer, but doing so cannot be rigorously justified. As we shall show, the best solution currently known is to consider the potential enthalpy.

The potential temperature θ is the temperature that a fluid parcel would have, if it was moved in an adiabatic (actually isentropic) and isohaline way from its in-situ pressure P to a reference pressure P_{ref} (usually taken to be at the surface). This can be written explicitly in terms of the adiabatic lapse rate Γ as:

$$\theta(S, T, P, P_{\text{ref}}) = T + \int_P^{P_{\text{ref}}} \Gamma(S, \theta, P') dP' \quad (37)$$

Alternatively, we can define $\theta(S, T, P, P_{\text{ref}})$ using an implicit definition, in terms of the entropy, which can easily be implemented by iteration using the Gibbs function (eqn. 15):

$$\eta(S, \theta, P_{\text{ref}}) = \eta(S, T, P) \quad (38)$$

However, potential temperature is not conserved under isobaric mixing! Attempting to replace h with θ in eqn. (36) results in all kinds of additional terms on the right hand side of the resulting equation; these result in the “production” of temperature when parcels are mixed. These extra terms have traditionally been ignored, but their effect is in fact noticeable (i.e., lead to predictions that are not matched by observations) when considering ocean processes.

Another variable with the potential property is the potential enthalpy h^0 . This is the enthalpy that a fluid parcel would have, if it was moved in an isentropic and isohaline way to a reference pressure. That is

$$h^0(S, T, P) \equiv h(S, \theta, P_{\text{ref}}) \quad (39)$$

Although potential enthalpy is not perfectly conservative, it has been shown that the approximate “heat” equation:

$$\rho \frac{Dh^0}{Dt} \approx -\nabla \cdot F^R + \nabla \cdot (\rho c_p \kappa \nabla T) + \rho \varepsilon \quad (40)$$

has errors in the ocean that are two orders of magnitude smaller than those arising from a similar equation for θ , and that these errors are smaller than the errors that result from the neglect of ε

(i.e., the heating due to viscous dissipation which is around 6 mW m^{-2}), or from the neglect of the geothermal heat flux (averaging 86 mW m^{-2}). Thus h^0 is *effectively* conservative.

Since the potential enthalpy is a somewhat unusual parameter for oceanographers (and for anyone else!), under TEOS-10 a temperature-like variable called the Conservative Temperature (denoted Θ , or sometimes CT) has been defined by scaling h^0 by a nominal heat capacity $c_p^0 \equiv 3991.86795711963 \text{ J/kg/K}$ ¹⁰:

$$\Theta = \frac{h^0}{c_p^0} \quad (41)$$

This definition for c_p^0 is close to the average value of the specific heat capacity at the ocean surface, so that the average value of $\theta - \Theta$ at the ocean surface is close to zero¹¹.

Then a suitable heat equation is:

$$\rho c_p^0 \frac{D\Theta}{Dt} = -\nabla \cdot F^R + \nabla \cdot (\rho c_p \kappa \nabla T) \quad (42)$$

Note that T still appears in the term for diffusive heat fluxes. In many cases this will not be a problem because turbulent diffusion (which will appear when these equations are averaged over suitable eddy length scales) is more important than molecular diffusion, so a more realistic equation might be

$$\boxed{\rho \frac{D\Theta}{Dt} = -\nabla \cdot \frac{F^R}{c_p^0} + \nabla \cdot (\rho \kappa_{\text{eddy}} \nabla \Theta)} \quad (43)$$

where $\kappa_{\text{eddy}} \gg \kappa$ is an eddy-diffusivity. This is of the same form as the salinity conservation equation (A.2).

For numerical modelling purposes, it is then useful to have a state equation for density in the form

$$\rho = \rho(S_A, \Theta, p) \quad (44)$$

and a computationally efficient 75-term polynomial is available for this purpose.

¹⁰defined to all 15 digits

¹¹for 99% of the ocean surface the difference is less than 0.25°C

References

The derivation of eqn. (8) is more rigorously explained in Warren, “The first law of thermodynamics in a salty ocean” (*Progress in Oceanography* 70, 149–167, 2006). The derivation for quasi-equilibrium heat conservation is a paraphrase of material in Appendix A of the TEOS-10 manual (IOC, SCOR and IAPSO, 2010: *The international thermodynamic equation of seawater 2010: Calculation and use of thermodynamic properties*. Intergovernmental Oceanographic Commission, Manuals and Guides No. 56, UNESCO (English), 196 pp), see also Trevor McDougall’s “Lecture Notes on Thermodynamics” (both available at www.teos-10.org), and material in Griffies’ “Fundamentals of Ocean Climate Models” (528 pp., Princeton University Press, 2004).

Entropy is a tricky concept. If you are interested in learning more, A. Ben-Naim, “Entropy and the Second Law”, (263pp., World Scientific Publishing Company, Singapore, 2012) is an interesting and readable attempt to argue for a link between entropy and information theory.

Technical information about TEOS-10 can be found in the TEOS-10 Manual; a brief introduction is in the “TEOS-10 Primer” (both at www.teos-10.org). A practical overview of temperature, salinity, and density in the ocean can be found in Pawlowicz, “Key Variables in the Ocean: Temperature, Salinity, and Density” (*Nature Education Knowledge* 4(4):13), easiest to find online by searching on “Pawlowicz Key Variables”).

Appendix A: Review - the Standard Equations

In developing the governing equations for a geophysical fluid (e.g., the ocean), we have

1. Conservation of mass for the fluid:

$$\frac{D\rho}{Dt} + \rho \nabla \cdot \vec{v} = 0 \quad (\text{A.1})$$

where ρ is the density and $\vec{v} = (u, v, w)$ the fluid velocity,

2. Conservation of mass for dissolved solute in the fluid:

$$\rho \frac{DS}{Dt} = \nabla \cdot (\rho \kappa \nabla S) \quad (\text{A.2})$$

where S is the mass fraction of dissolved content (salt in the ocean, water content in the atmosphere) and κ is a diffusivity¹²,

3. Conservation of momentum (from $F = m\vec{a}$ in a rotating frame):

$$\rho \frac{D\vec{v}}{Dt} + 2\vec{\Omega} \times \rho \vec{v} = -\nabla P - \nabla \Phi + \nabla \cdot (\rho \nu^{\text{visc}} \nabla \vec{v}) \quad (\text{A.3})$$

where $\vec{\Omega}$ is the (constant) reference frame rotation vector, P is pressure, Φ is the geopotential, and ν^{visc} is the viscosity. Note that by taking the dot product of \vec{v} with both sides we can transform the 3-component momentum equation into a different (but not independent) equation for the conservation of mechanical energy:

$$\rho \frac{D}{Dt} \left(\frac{|\vec{v}|^2}{2} + P\nu + \Phi \right) = \frac{\partial P}{\partial t} + \nabla \cdot (\rho \nu^{\text{visc}} \nabla \frac{|\vec{v}|^2}{2}) - \rho \varepsilon \quad (\text{A.4})$$

where $\varepsilon = \nu^{\text{visc}} |\nabla \vec{v}|^2 \geq 0$ is the nonnegative dissipation rate of mechanical energy.

4. With 6 variables ρ, u, v, w, P, S we need one more equation to close this system, and this need can be satisfied if there is a known relationship (an “equation of state”):

$$\rho = \rho(S, P) \quad (\text{A.5})$$

However, we know that for seawater, density is additionally affected by temperature

$$\rho = \rho(S, T, P) \quad (\text{A.6})$$

and the introduction of another variable also means we need another equation involving temperature to close the system! Where will this come from?

¹²Although once we learn more about thermodynamics we will find that diffusive fluxes are more correctly written as being proportional to gradients in chemical potential, which takes into account the chemical activity of solute, and not to gradients of salinity itself, and that we can also have salt fluxes in response to temperature gradients, the so-called “Soret Effect”, and in response to pressure gradients, called barodiffusion.