

The First Law of Thermodynamics in a Salty Ocean

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Abstract. The First Law of Thermodynamics is developed from fundamentals for open, non-equilibrium systems of seawater in motion, exchanging salt and freshwater internally and with their surroundings, and varying continuously in temperature, pressure, and salinity. The aim is clarity and consistency of concepts — and precision in the accompanying vocabulary. Particular attention is given to the way in which salinity variation plays out in the logical structures. The arbitrary constants in the thermodynamic potentials and the various First Law equations are highlighted, in order to remove them, and to recover the physically meaningful content. When this is done, it is seen that salinity variations have little consequence in application of the First Law to the ocean, apart from affecting values of coefficients.

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1. INTRODUCTION

Thermodynamics is about energy exchanges within systems and between systems and their surroundings. It is a structure of macroscopic concepts and general principles relating observables, rather than a microscopic model of matter and processes. Because of its generality, Einstein (1949, p. 33) declared, "It is the only physical theory of universal content concerning which I am convinced that, within the framework of applicability of its basic concepts, it will never be overthrown. . . ." For the same reason it is indispensable to oceanic physics, because there is no satisfactory kinetic theory of the liquid state, or model of pure water, or model of a moderately concentrated electrolytic solution like seawater.

The subject need not be difficult or obscure, and its mathematics, while idiosyncratic, even less so; but it is fussy. It needs consistent operational definitions of concepts to escape obfuscation, and careful distinction between what is physically significant and what is conventional tabulation to be sure what one is talking about. Unfortunately, it is easy to muddle concepts. In a fair amount of the oceanographic literature, "heat" is regarded, essentially, as some sort of eighteenth-century caloric fluid. Or the term may be applied to temperature changes not brought about by heating. The important text by de Groot and Mazur (1962, p. 17) defines internal energy, in effect, as total energy minus kinetic and potential energy; without an independent, operational definition of "total energy," this proposition is empty and useless. (On p. 18 they give a similarly circular definition of "heat flow".) The fact that thermodynamic potentials (e.g., internal energy, entropy) are determined only as changes in values between different states of a system (like the gravitational potential) is sometimes overlooked in oceanographic papers, and values of these potentials are mistakenly supposed to be physically meaningful, rather than specified by arbitrary choices of constants. Textbooks usually gloss over the place of salinity variation in the First Law of Thermodynamics (apart from parameter dependence), perhaps in the hope (well founded, as it turns out) that it is unimportant. However, I have not yet seen a satisfying treatment of salinity variation. [Davis (1994, Appendix A) gives a valuable summary of equations, but he doesn't explain where they all come from.] Nor have I found a proper derivation of the contribution (albeit small) of the freshwater cycle to the oceanic energy budget.

The aim of this essay is to develop the First Law of Thermodynamics rigorously in application to the ocean, with operational definitions of concepts insofar as possible, clarity as to

what is physically meaningful and what is not, care for getting the details right, and special attention to the consequences of salinity variation. The emphasis is on definition and meaning of concepts and on their logical connections (because I think that is wanting in the oceanographic literature), rather than on quantitative review of oceanic processes [because numerical calculations and global maps of the pertinent energy quantities are well presented in the literature, notably by Peixoto and Oort (1992) and by Oort et al. (1994)]. The essay breaks no new ground in thermodynamic fundamentals or physical chemistry, but it brings together material from several different sources into an organized and rigorous development in a physical-oceanographic context; it also offers original derivations of several relations that one would think must be in the literature somewhere, but which I have failed to discover. For these reasons it may be found useful.

Physical chemists thrive on luxuriant notation (multiple pre-, post-, sub-, and superscripts), and it seems necessary to the subject, but it can be bewildering, even dismaying, to non-practitioners (e.g., me), so I have limited my appeal to that division of thermodynamics to what seemed essential for my purpose. I have said nothing about entropy generation, or generalized forces and fluxes, because, pace Gregg (1984), I haven't found their calculation for the ocean to be very rewarding (that is a personal failing, I suppose). Nor do I think it is necessary for oceanographers, like physicists (e.g., Baierlein, 1999), to count energy eigenstates of matter.

The plan is to proceed in four stages. First is a discussion of a closed, homogeneous system at rest, mainly to define the fundamental concepts of internal energy and heat. Most of this material can be found in any good thermodynamics text (e.g., Zemansky and Dittman, 1997), but for the sake of an orderly development it seems desirable to lay out the basics at the start. This is then extended to an open homogeneous system at rest in order to show what exchanges of salt and freshwater mass do, to define the chemical potential, and to establish the Gibbs equation. Next is a lengthy digression on the structure of the thermodynamic potentials to show how salinity enters them, and to make explicit their measurable and arbitrary components; much of this section may be rudimentary to physical chemists, but perhaps not to physical oceanographers. Finally the concepts are applied to the oceanic case, the non-equilibrium system in motion in which temperature, pressure, and salinity vary spatially.

Seawater will be treated as a solution of a single solute, "sea salt," in pure water. Inadequacies in the approximation of lumping all the dissolved constituents into one aggregate

solute are described by Fofonoff (1985). The mean molecular weight of sea salt is 62.8, and, since the major solutes are all fully dissociated (except for boric acid), its mean ionic weight is 31.4 (Millero, 1974). Its concentration is expressed here as mass fraction, S , or "absolute salinity", which is slightly different from the "practical salinity" calculated from conductivity measurements. To dispense with the cumbersome factor of 1000, here S will mean mass fraction itself rather than g kg^{-1} .

Except where indicated otherwise, temperature throughout will be the physically defined absolute, thermodynamic, Kelvin temperature. (Of course for differences, as in derivatives, Celsius and Kelvin are the same.)

2. CLOSED HOMOGENEOUS SYSTEM

Thermodynamics describes the state of a system by the values of convenient thermodynamic coordinates: in the case of the ocean, pressure (p), temperature (T), salinity (S), and density (ρ) -- or its reciprocal, specific volume (α) -- as observationally accessible parameters. A system is in thermodynamic equilibrium when it is in mechanical equilibrium (no unbalanced forces), thermal equilibrium (uniform temperature equal to that of the surroundings), and chemical equilibrium (no spontaneous change of internal structure or transfer of matter from one part of the system to another). In such a condition there is no tendency for any change of state of the system or its surroundings, and the coordinates of the system are linked by an equation of state. A process occurring through a continuous succession of states all infinitesimally close to equilibrium is "quasistatic"; the equation of state holds throughout such a process. Reversible processes are both quasistatic and non-dissipative. Since all natural processes are dissipative, they are all irreversible, but, depending on the degree of disequilibrium and dissipation, reversibility can still be a useful idealization. A "closed" system exchanges no mass with its surroundings. An "adiabatically enclosed" system is a closed system whose coordinates are unaffected by changes in its surroundings, except insofar as the surroundings do work on the system; and an "adiabatic process" in a system is one for which the system is, at least effectively, adiabatically enclosed. A process that is not adiabatic, in which a system tends to approach thermal equilibrium with its surroundings, is "diathermic."

The First Law for a closed, finite system that is homogeneous in composition, uniform in coordinates, and at rest comes in three parts (Zemansky and Dittman, 1997, pp. 78-80). First, it

infers by extrapolation from observation that when work is performed adiabatically to change the state of such a system, the amount of work required depends only on the initial and final states of the system, not on the means or procedure by which the work was done. This fact defines, and tells how to measure, the differences in a function of the coordinates of the system, the internal energy. Only differences in internal energy are thus defined by classical thermodynamics (just as mechanics defines only differences in potential energies); particular values of internal energy are necessarily specified relative to an arbitrary reference state, and are, in themselves, physically meaningless. The establishment of the internal-energy function, or potential, is the central empirical content of the First Law.

Second, it asserts the Law of Conservation of Energy for closed systems. This is a curious principle because "energy" is not defined generically, only particular, operationally defined energies whose grand sum is stated to be constant. The principle has been disparaged as a convention, on the ground that, if physicists found it to fail, they would invent a new kind of energy to make the bookkeeping come out right [see, for instance, Poincaré (1906, Chap. 8), who said, among other things, that the principle of conservation of energy, in its full generality, reduces merely to the statement, "There is something which remains constant."] But if that were to happen, replied Bridgman (1941, p. 80), "when we had invented it we would demand that it be a function of an extended set of parameters of state, and that the law would continue to hold for all the infinite variety of combinations into which the new parameters might be made to enter. Whether conservation would continue to hold under such extended conditions could be determined only by experiment. The energy concept is very far from being merely a convention."

So the power and utility of the law are not vitiated, even though the idea of "energy-in-itself" is elusive, somewhat like that of "time" in St. Augustine's complaint (Confessions, Book XI): "What then is time? I know well enough what it is, provided that nobody asks me; but if I am asked what it is and try to explain, I am baffled . . . I do indeed measure it, but I do not know what I measure." (He skirts, but misses, the notion of an operational definition: that the meaning of a physical concept is to be found in the physical operations one carries out to apply it.) Probably the best one can do is to say, perhaps wryly, perhaps not, that energy qua energy is what is conserved by the Law of Conservation of Energy.

Third, by invoking the conservation principle for closed systems at rest that are not adiabatically enclosed, the First Law defines "heat" as the difference between internal-energy change and work performed. Zemansky and Dittman (1997, p. 79) stated it carefully: "When a closed system whose surroundings are at a different temperature and on which diathermic work may be done undergoes a process, then the energy transferred by nonmechanical means, equal to the difference between the change of internal energy and the diathermic work is called heat." In other words [those of Chandrasekahr (1939, pp. 14-15)], while work and internal-energy change can be determined experimentally, the concept of heat is a derived quantity. "Heat" or "heating" is a mode of energy transfer like work, and not a substance or a property of a system. [Bohren and Albrecht (1998, pp. 24-28), are trenchantly and very readably outspoken on this point.]

Thus if ΔU is the internal-energy change of a closed system during some process, W the amount of work performed on it, and Q the amount of heat flowing into it, the First Law states that

$$\Delta U = Q + W . \quad (1)$$

Here Q and W individually depend on the process by which the change of state is effected, whereas their sum, ΔU , does not, and depends only on the coordinates of the initial and final states. The statement is true for both reversible and irreversible processes. For small increments

$$dU = \delta Q + \delta W , \quad (2)$$

where dU is an exact differential, and δQ and δW are inexact differentials, not differentials of functions of the coordinates.

In the ocean the work always includes compression work. If the process considered is quasistatic, the compression work is $-pdV$, where V is the volume of the system and p is the equilibrium pressure. Because of the equilibrium condition, it is reversible work. Then

$$\delta Q = dU + pdV - \delta W' \quad (3)$$

where $\delta W'$ is all other forms of work being performed (e.g., dissipation work). Moreover, the assumption of close proximity to thermal equilibrium requires that the temperature difference

between a system and its surroundings — to which is due the heating δQ — be kept infinitesimally small. So quasistatic processes necessarily take a very long time to effect noticeable changes in a system, and are inherently idealizations. If, furthermore, $\delta W' = 0$, the process is reversible, because the absence of dissipation and the maintenance of near-equilibrium mean that slight changes in coordinates can reverse the process and move the system back and forth between two states without additional energy requirements. Thus

$$\delta Q_r = dU + pdV, \quad (4a)$$

or, after dividing by the mass M of the system,

$$\delta q_r = du + pd\alpha, \quad (4b)$$

where u and α are the specific internal energy and volume, respectively, $\delta q \equiv \delta Q/M$, and subscript r signifies heating in a reversible process.

Internal energy itself comes in several interchangeable forms. Pressure-work done on a liquid increases both compressional internal energy and thermal internal energy. Chemical energy released in a chemical reaction may be manifested as an increase of thermal internal energy, as may nuclear energy released in radioactive decay. In such cases the concentrations of reactants, radionuclides, and their products need to be included as coordinates of the system. Similarly, the amounts of different phases of a substance are required as coordinates when a phase change draws on thermal internal energy to provide the "latent" energy needed for the change. It is misleading to talk of "internal heat sources" in a system when no change in its total internal energy occurs, only redistribution of its components.

The other independent potential that thermodynamics defines is the entropy, N . The Second Law states that, for flow of heat into a closed system in a reversible process,

$$\int \frac{\delta Q_r}{T} = \Delta N, \quad (5)$$

where N is another function of the coordinates, T is the thermodynamic temperature, and the integration is over the process between the initial and final states of the system. Thus, for small increments, $\delta Q_r = TdN$. The Second Law also states that for irreversible heat flow into the closed system $\delta Q < TdN$ (but the accompanying entropy change can still be determined by carrying out a reversible process between the same two states). As with the internal energy, classical thermodynamics defines only differences in entropy between states of a system, not particular values for particular states.

3. OPEN HOMOGENEOUS SYSTEM

Restrict attention now to a region of seawater, and specifically to a system within it of volume V and of total mass M , that is composed of a mass of freshwater, M_w , and a mass of dissolved salt, M_s , all at uniform T, p . Both the volume and the internal energy are to be treated as functions of these coordinates: $V=V(T, p, M_w, M_s)$, $U=U(T, p, M_w, M_s)$. Imagine the system as contained in some way, say by a flexible diathermic bag, in order to keep track of it. Imagine further a process in which infinitesimal, quasistatic compression work, $-pdV$, is performed on it, and infinitesimal, reversible heat flow, δQ_r , is admitted to it; and, holding temperature and pressure constant, let the system exchange seawater with its surroundings somehow, say through a set of semi-permeable membranes, resulting in net infinitesimal additions (or subtractions) of freshwater mass dM_w and dissolved-salt mass dM_s , each bearing increments of volume and internal energy.

Eqn. (4a) cannot be applied directly to this complete process, because energy is conserved only in closed systems (as to be discussed at length, mass exchange entails inherent indeterminacy in energetics). Therefore the contributions to dU and dV due to the mass exchanges must first be subtracted to obtain the closed-system values to which energy-conservation applies. These "corrected" differentials are:

$$dU - \frac{\partial U}{\partial M_w} dM_w - \frac{\partial U}{\partial M_s} dM_s, \text{ and}$$

$$dV - \frac{\partial V}{\partial M_w} dM_w - \frac{\partial V}{\partial M_s} dM_s.$$

[The state variables here are T, p, M_w, M_s (or later, T, p, M, S); it is to be understood that where a derivative is taken with respect to one (e.g., M_w), the others (T, p, M_s) are held constant.]

Then the proper version of (4a) for this open system is

$$\delta Q_r = dU + pdV - \frac{\partial H}{\partial M_w} dM_w - \frac{\partial H}{\partial M_s} dM_s, \quad (6a)$$

or

$$\delta Q_r = dH - Vdp - \frac{\partial H}{\partial M_w} dM_w - \frac{\partial H}{\partial M_s} dM_s, \quad (6b)$$

where the enthalpy $H \equiv U + pV$. To relate δQ_r to the entropy change, following (5), it is similarly necessary to subtract that part of the entropy change due to the mass exchange:

$$\delta Q_r = TdN - T \frac{\partial N}{\partial M_w} dM_w - T \frac{\partial N}{\partial M_s} dM_s. \quad (7)$$

Combining (6) and (7) produces the Gibbs equation for the system,

$$TdN = dU + pdV - \frac{\partial G}{\partial M_w} dM_w - \frac{\partial G}{\partial M_s} dM_s, \quad (8a)$$

or

$$TdN = dH - Vdp - \frac{\partial G}{\partial M_w} dM_w - \frac{\partial G}{\partial M_s} dM_s, \quad (8b)$$

where the Gibbs energy $G \equiv H - TN$. [The function G has a variety of names in the literature: Gibbs function, Gibbs free energy, free energy, free enthalpy, thermodynamic potential. Here I follow the usage of Castellan (1983, p. 205), who in turn followed that of the International Union of Pure and Applied Chemistry.] The mass derivatives of G are defined as the chemical potentials of the system:

$$\mu_w \equiv \frac{\partial G}{\partial M_w}, \mu_s \equiv \frac{\partial G}{\partial M_s}.$$

Chemists generally take these derivatives with respect to mole number, and physicists with respect to number of molecules, but mass-derivatives are more natural to physical oceanography. Moreover, physicists often define the chemical potential not as change in Gibbs energy at constant temperature and pressure but as change in internal energy at constant volume and entropy. The values are the same, but it is very difficult to keep a liquid at constant volume during a process (tremendous pressures or tensions may be needed), and it is hard even to conceive what it means to change internal energy in a mass exchange while holding entropy constant. So while the concept is formally legitimate, it seems inaccessible in practice.

The quantities M_w , M_s , and G depend on the size of the system (halving it halves their values). The chemical potentials, being derivatives of these quantities, are necessarily independent of the size of the system, and so can depend on M_w and M_s only through their concentrations, or mass fractions (e.g., M_w/M and M_s/M). For a distribution of masses to be stationary in a system (i.e., for it to be in chemical equilibrium) the Second Law requires that the chemical potentials be uniform throughout the system [see, for instance, Castellan (1983, pp. 222–223)].

The Gibbs equation is a relation among functions of the coordinates of a system (it can be regarded, formally, as expressing the differential of $U(V, N, M_w, M_s)$ or $H(p, N, M_w, M_s)$, where U and H are equilibrium functions), so it is true for any quasistatic process; while it is a statement of the First Law only for reversible processes. But both (6) and (8) teem with arbitrary, physically meaningless constants, as will be shown in detail in Section 4.

It will be useful there to re-express the Gibbs energy in terms of the chemical potentials. Incorporating the Gibbs equation (8b) into the differential of G shows that

$$dG = Vdp - NdT + \mu_w dM_w + \mu_s dM_s . \quad (9)$$

Following a demonstration by Castellan (1983, pp. 223-224), consider a volume of seawater in thermodynamic equilibrium, so that T, p , and chemical composition are uniform throughout, and so, therefore, are μ_w and μ_s . Identify a sub-volume by some mathematical bounding surface, and assign it $G = G_o$. Enlarge the volume by expanding the mathematical surface to include additional masses ΔM_w and ΔM_s . Then by (9), G for the new volume is

$$G = G_o + \mu_w \Delta M_w + \mu_s \Delta M_s . \quad (10)$$

Since the initial volume was arbitrary, shrink it to zero, leaving

$$G = \mu_w M_w + \mu_s M_s \quad (11)$$

as the equilibrium value of G .

Of course oceanographers do not measure directly, or talk in terms of, M_w and M_s , but of total mass M and salinity S , where $M_s = MS$, and $M_w = (1-S)M$. In these variables (11) can be rewritten in two ways,

$$g = \mu_w + \mu S = \frac{\partial G}{\partial M} , \quad (12)$$

where the specific Gibbs energy $g \equiv G/M$, and the chemical-potential difference, or effective chemical potential, or pseudo-chemical potential, $\mu \equiv \mu_s - \mu_w$. The left-hand equality is the basis for the development to be undertaken in Section 4. It is to be underscored that the function

μ_w is not the potential of pure freshwater, but of the freshwater component of the solution, and so depends on T, p, S ; and μ_s is not the potential of pure dissolved salt (whatever that means), but of the salt in solution, and so also depends on T, p, S .

To discuss a system like the ocean with continuous spatial variation of properties (Section 5), it is necessary to state all the relations in specific form (i.e., with quantities depending on system size recast as amounts per unit mass). Thus, the specific form of (9) can be obtained by combining (9) with (12), to give the differential of g as:

$$dg = d\left(\frac{G}{M}\right) = \frac{1}{M}dG - \frac{g}{M}dM = \alpha dp - \eta dT + \mu dS, \quad (13)$$

where the specific entropy $\eta \equiv N/M$. Parallel use of (12) puts the Gibbs equations (8a, b) into specific form, as well,

$$Td\eta = du + pd\alpha - \mu dS, \quad (14a)$$

$$Td\eta = dh - \alpha dp - \mu dS, \quad (14b)$$

where the specific enthalpy $h \equiv H/M$.

To make a similar transformation of the First Law equations (6a,b) and Second Law equation (7), first decompose G to turn (11) into

$$H - \frac{\partial H}{\partial M_w} M_w - \frac{\partial H}{\partial M_s} M_s = T \left[N - \frac{\partial N}{\partial M_w} M_w - \frac{\partial N}{\partial M_s} M_s \right]. \quad (15)$$

Since H and N are independent functions of (T, p, M_w, M_s) , the left-hand and right-hand sides of (15) must each be zero. So, corresponding to the right-hand equality in (12),

$$h = \frac{\partial H}{\partial M} \quad \text{and} \quad \eta = \frac{\partial N}{\partial M}.$$

In the coordinates (M, S) ,

$$\frac{\partial H}{\partial M_w} dM_w + \frac{\partial H}{\partial M_s} dM_s = \frac{\partial H}{\partial M} dM + \frac{\partial H}{\partial S} dS, \quad (16)$$

and similarly for N , whereby (6a, b) and (7) take the specific forms,

$$\delta q_r = du + pda - \frac{\partial h}{\partial S} dS, \quad (17a)$$

$$\delta q_r = dh - \alpha dp - \frac{\partial h}{\partial S} dS, \quad (17b)$$

$$\delta q_r = Td\eta - T \frac{\partial \eta}{\partial S} dS, \quad (17c)$$

where $\delta q_r = \delta Q_r / M$. Thus, the First Law is stated in (17a,b) for reversible processes in an open, homogeneous, seawater system in the natural oceanographic coordinates (T,p,S) . In its restriction to systems at rest experiencing no other work but compression, this version of the law is the analogue to (4b) for the closed homogeneous system.

4. THE STRUCTURE OF THE POTENTIALS

It has been adumbrated several times that the potentials $(u, h, \eta, \mu_w, \mu_s, \mu, g)$ are composed jointly of operationally defined, measurable parts and of arbitrary, reference-state values. The latter are necessary to generate formulas (or tables) for the potentials from which the physically relevant differences and derivatives may be obtained, but they make values of the potentials themselves physically meaningless. To explicate the logical character of the potentials -- so where they are useful and where they are not -- it is desirable to show exactly where measurement and arbitrary choice come into their specification.

An efficient strategy is to calculate the specific Gibbs energy from (12) because everything follows from it: according to (13),

$$\mu = \frac{\partial g}{\partial S}, \eta = -\frac{\partial g}{\partial T}, h = g - T \frac{\partial g}{\partial T} = -T^2 \frac{\partial}{\partial T} \left(\frac{g}{T} \right), \text{ and } u = h - p\alpha .$$

The following exposition is long and somewhat tedious, but it is, at least, rigorous. ["The justification for a rigorous treatment is pedagogical: it makes the subject simpler." (Castellan, 1983, p. vii)].

First, calculate the chemical potentials, since g can then be obtained from them through (12). Raoult's Law considers a solution composed of a liquid solvent and an involatile solute; it states that for low concentrations of solute the equilibrium vapor pressure of the solvent over the solution equals the mole fraction of solvent in the solution times the vapor pressure for pure solvent. An "ideal solution" is one which follows Raoult's Law over the full range of solute concentration, zero to one. Chemical equilibrium requires that for such a solution the chemical potentials of solvent and solute vary as the logarithms of their respective mole fractions.

Real solutions depart from ideality, however, so, keeping the physically motivated logarithmic structure, physical chemists introduce experimentally determined "activities", which depend on temperature, pressure, and (for seawater) salinity, and which approach one as the respective mole fractions approach one; for an ideal solution the activities are just the mole fractions. Then, in the "rational activity system," for the present context,

$$\mu_w(T, p, S) = \mu_{wo}(T, p) + \frac{RT}{m_w} \ln a_w(T, p, S), \quad (18)$$

$$\mu_s(T, p, S) = \mu'_{so}(T, p) + \frac{RT}{m_s} \ln a'_s(T, p, S), \quad (19)$$

where R is the universal gas constant, and m_w and m_s are the molecular weights of water (18.0) and sea salt (62.8), respectively. The activities are constructed so that a_w and a'_s approach one as S approaches zero and one, respectively; and μ_{wo} and μ'_{so} are the values of μ_w and μ_s in these respective limits. [It would be too long and peripheral a digression to develop (rather than sketch and assert) this structure here; see, for example, Castellan (1983, pp. 277-281), except that his potentials are per unit mole, rather than unit mass, and his composition variables are mole fractions of solute and solvent, rather than salinity. He makes it clear why the gas constant should appear in expressions for a liquid solvent and an involatile solute.]

In this formulation the sea-salt activity is referenced to the chemical potential of pure sea salt in its dissolved (liquid) state of aggregation. That is not a comfortable basis for discussion because pure liquid sea salt does not exist in oceanic conditions, and talk about the potential of an unknowable substance would be occult or metaphysical. For example, NaCl is a solid at temperatures below 800°C, and the mass fraction of dissolved NaCl in a water solution cannot exceed about 0.26.

It is easy, however, to change the reference substance for μ_s to a solution that *is* physically realizable. Consider a standard seawater of salinity S_R , of activity $a'_s(T, p, S_R)$ with the above formal referencing. Then,

$$\begin{aligned}\mu_s &= \mu'_{so} + \frac{RT}{m_s} \ln \frac{a'_s(T, p, S) a'_s(T, p, S_R)}{a'_s(T, p, S_R)} = \mu'_{so} + \frac{RT}{m_s} \ln a'_s(T, p, S_R) + \frac{RT}{m_s} \ln \frac{a'_s(T, p, S)}{a'_s(T, p, S_R)} \\ &= \mu_{so}(T, p) + \frac{RT}{m_s} \ln a_s(T, p, S),\end{aligned}\quad (20)$$

where $a_s(T, p, S) \equiv \frac{a'_s(T, p, S)}{a'_s(T, p, S_R)}$, so $a_s = 1$ at $S = S_R$; $\mu_{so} \equiv \mu'_{so} + \frac{RT}{m_s} \ln a'_s(T, p, S_R)$, a function only of (T, p) , and is the chemical potential for a physically possible reference solution of salinity S_R . An adequate consideration of chemical potentials in seawater requires treating it as a

moderately strong electrolyte (Millero, 1974), but that is intricate, and it seems unnecessary for the purposes to which the Gibbs energy is put here.

By (12), and the definition of the Gibbs energy,

$$\mu_{wo}(T, p) = \mu_w(T, p, 0) \equiv g(T, p, 0) = h(T, p, 0) - T\eta(T, p, 0). \quad (21)$$

Since enthalpy and entropy are defined (and measurable) only as differences between values at a given state and some reference state,

$$h(T, p, 0) = h_r(0) + h_D(T, p, 0) \quad (22)$$

$$\eta(T, p, 0) = \eta_r(0) + \eta_D(T, p, 0) \quad (23)$$

where $h_r(0)$ and $\eta_r(0)$ are the indeterminate values for pure water at the reference-state values, T_0 and p_0 , and $h_D(T, p, 0)$ and $\eta_D(T, p, 0)$ are the thermodynamically defined, measurable differences from these values.

Similarly, from (12),

$$\begin{aligned} g(T, p, S_R) &= \mu_{w0} + \frac{RT}{m_w} \ln a_w(T, p, S_R) + S_R \left[\mu_{so}(T, p) - \mu_{w0} - \frac{RT}{m_w} \ln a_w(T, p, S_R) \right] \\ &= h(T, p, S_R) - T\eta(T, p, S_R), \end{aligned} \quad (24)$$

where, as above for the solution of zero salinity, now for the solution of salinity S_R ,

$$h(T, p, S_R) = h_r(S_R) + h_D(T, p, S_R), \quad (25)$$

$$\eta(T, p, S_R) = \eta_R(S_R) + \eta_D(T, p, S_R). \quad (26)$$

These terms serve to specify $\mu_{so}(T, p)$.

Working through the algebra produces the desired, though ungainly, expression for g :

$$\begin{aligned} g = & h_R(0) + h_D(T, p, 0) - T\eta_R(0) - T\eta_D(T, p, 0) + (1-S)\frac{RT}{m_w} \ln a_w(T, p, S) \\ & + \frac{S}{S_R} \left\{ h_R(S_R) + h_D(T, p, S_R) - T\eta_R(S_R) - T\eta_D(T, p, S_R) - h_R(0) - h_D(T, p, 0) \right. \\ & \left. + T\eta_R(0) + T\eta_D(T, p, 0) - \frac{RT}{m_w} (1-S_R) \ln a_w(T, p, S_R) \right\} + S \frac{RT}{m_s} \ln a_s(T, p, S). \end{aligned} \quad (27)$$

It may be summarized as:

$$g = A + BT + CS + DTS + f_1(T, p) + Sf_2(T, p) + f_3(T, p, S), \quad (28)$$

where the four constants,

$A = h_R(0)$, $B = -\eta_R(0)$, $C = [h_R(S_R) - h_R(0)]/S_R$, and $D = [\eta_R(0) - \eta_R(S_R)]/S_R$ have no physical significance, although arbitrary values must be assigned to them in any tabulation of $g(T, p, S)$.

The function f_1 is the determinate part of g for pure water, f_2 is the difference between the determinate parts of g for pure water and standard water of $S = S_R$, and f_3 comprises the activities of the solution.

It follows that h , u , and η must each include an arbitrary linear function of salinity, $A+CS$ for h and u , and $B+DS$ for η , and μ an arbitrary linear function of temperature, $C+DT$. In particular $\partial h / \partial S$ includes the arbitrary constant C . So, for example, the two tables of enthalpy given by Feistel (1993) and by Feistel and Hagen (1995) differ not just by a constant, but by the rates of change with salinity, owing to their differing assignments of values to the constants A , B , C , D . Feistel and Hagen (1995) chose them by setting the reference temperature and pressure to 0°C and 1013mb (mean atmospheric pressure at sea level), $S_R=0.035000$, $h_R(0)=h_R(S_R)=0$, and

$\eta_R(0) = \eta_R(S_R) = 0$, which choice removes all appearance of the arbitrary salinity function from the enthalpy -- but its ghost haunts it nonetheless (as they acknowledged).

The full expression for the enthalpy is:

$$\begin{aligned}
 h = -T^2 \frac{\partial}{\partial T} \left(\frac{g}{T} \right) = & A + h_D(T, p, 0) - (1-S) \frac{RT^2}{m_w} \frac{\partial}{\partial T} \ln a_w(T, p, S) + CS \\
 & + \frac{S}{S_R} \left\{ h_D(T, p, S_R) - h_D(T, p, 0) + (1-S_R) \frac{RT^2}{m_w} \frac{\partial}{\partial T} \ln a_w(T, p, S_R) \right\} \\
 & - \frac{SRT^2}{m_s} \frac{\partial}{\partial T} \ln a_s(T, p, S), \tag{29}
 \end{aligned}$$

where the T -derivatives are taken at constant p and S ; u is just $h - p\alpha$. In the ideal solution the activities are simply the mole fractions, so their temperature derivatives are zero, and, according to (29), the enthalpy of the solution is just the salinity-weighted linear combination of the enthalpies for $S = 0$ and S_R . That seawater is *not* an ideal solution is shown by the non-zero values of Feistel and Hagen (1995) for h (0°C, 1013mb, S) at $S \neq 0, 0.035$ (although the maximum departure from linear mixing is only around 120 J kg⁻¹ -- equivalent merely to a 12m depth change, or 0.03°C temperature change).

The arbitrary constant in $\partial h / \partial S$ and arbitrary linear function of T in μ might seem to make (13), (14), and (17) physically meaningless. They do not, because the indeterminacy in the coefficients of dS is matched by hidden indeterminacies elsewhere. For example, if $dh(T, p, S)$ is expanded in (17b), the resulting two salinity differentials cancel each other, and one is left with

$$\delta q_r = C_p dT + \left[\frac{\partial h}{\partial p} - \alpha \right] dp, \tag{30}$$

or

$$\delta q_r = C_p dT - T \frac{\partial \alpha}{\partial T} dp, \tag{31}$$

where (31) is proved by exploiting the exact-differential properties of h and η . The relations are exactly as for a closed system, as are the corresponding versions of (13), (14), and (17a).

If so desired, one could remove the pressure differential by changing coordinates from (T,p,S) to (θ,p,S) where θ is the potential temperature (see historical note in Appendix), defined

so that $\left(\frac{\partial T}{\partial p}\right)_{\theta,S} = \frac{T}{C_p} \left(\frac{\partial \alpha}{\partial T}\right)_{p,S}$ (which is the adiabatic temperature gradient), and $\theta = T$ at

$p=p_a=1013$ mb; T is now the dependent variable $T(\theta,p,S)$. Then (31) becomes

$$\delta q_r = C_p \left[\left(\frac{\partial T}{\partial \theta}\right)_{p,S} d\theta + \left(\frac{\partial T}{\partial S}\right)_{\theta,p} dS \right]. \quad (32)$$

One can show (e.g., McDougall, 2003) that $\left(\frac{\partial T}{\partial \theta}\right)_{p,S} = \frac{TC_p(\theta, p_a, S)}{\theta C_p(T, p, S)}$ which for the normal

range of coordinates for seawater is within three percent of one.

Eliminating the pressure differential carries the cost of generating a salinity-differential term, but that is equivalent at most to a few millidegrees even for a salinity change of 0.001 (Feistel, 1993, Appendix B, Table 3). The error in taking $\delta q_r = C_p d\theta$ is thus little worse than in treating C_p as a constant. (Conversely, if one does make that approximation to (32), there is no justification for treating C_p as other than a constant.) Eqns. (30), (31), and (32) are equivalent companions to (17a,b) as statements of the First Law for reversible processes in an open, homogenous seawater system at rest that experiences no other work but compression.

5. THE OCEAN

The previous three sections have discussed the thermodynamic equilibrium state, and quasistatic, reversible changes in systems (time changes, in effect). Temperature, pressure, and salinity vary continuously in the ocean, however, so in general it is in neither thermal, nor mechanical, nor chemical equilibrium. (Of course pressure variation need not of itself imply mechanical disequilibrium, since a pressure gradient may be in place to balance some other force, like gravity.) Moreover, mechanical energy is dissipated in the ocean, and heat flows

across finite temperature differences, so processes are not reversible. Nevertheless, in the non-equilibrium approach one assumes that the system is sufficiently close to equilibrium that (a) the equilibrium equation of state relates the coordinates, and (b) the thermodynamic potentials are the same functions of the (now continuously varying) coordinates as in the equilibrium state. The latter assumption is far-reaching, because it supposes that the relationships derived among time changes of properties in finite homogeneous systems, like the Gibbs equation, also connect the spatial changes within systems having non-uniform properties. There are limits to these assumptions of course: one would not try to apply the equation of state to the spume from a breaking wave.

The aim of the present section is to expand the statement of energy conservation (1) on this basis to comprise the specifics of the ocean. Since the ocean is usually moving, the statement has to include changes of kinetic energy as well as of internal energy. The work done by shearing stresses and gravity must be added to the pressure work of the previous sections, and it is assumed that the mechanical pressure in the moving fluid is the same as the thermodynamic pressure in the equilibrium equation of state (Batchelor, 1967, pp. 153-156).

As in Section 3, consider an arbitrary finite volume in the ocean of volume V and mass M , delimited in some way to keep track of its identity (at least in the short term), but still free to exchange (through diffusion) salt and freshwater mass with its surroundings. The system, however, is in relative motion, and T , p , and S are not uniform within it. Furthermore, not as in Section 3, require that the diffusive salt and freshwater exchanges compensate to keep the mass of the system constant, so that it makes sense to write energy and momentum equations for the bulk volume. Conservation of energy then states that (1) the time rate of change of the energy of the system equals (2) the rate at which work is done on it, plus (3) the rate at which it is heated, minus (4) the rate at which diffusion adds enthalpy to the system. Each of these terms will be specified in sequence.

5.1. Rate of Energy Change

The energies are internal and kinetic, so the volume integrals are

$$\frac{d}{dt} \int_V \rho \left(u + \frac{1}{2} v^2 \right) dV = \int_V \rho \frac{d}{dt} \left(u + \frac{1}{2} v^2 \right) dV \quad (33)$$

since the total mass of the volume is constant; v is the magnitude of the fluid velocity \mathbf{V} (see section 5.4).

5.2. Work performed

The pressure and shearing-stress forces are surface forces so the work they perform must be integrated over the surface A of the volume (e.g., Batchelor, 1967, p. 152):

$$\int_A (-p \mathbf{V} \cdot \mathbf{n} + v_i \tau_{ij} n_j) dA = \int_V (-\nabla \cdot p \mathbf{V} + \frac{\partial}{\partial x_j} v_i \tau_{ij}) dV, \quad (34)$$

where \mathbf{n} is the unit outward vector normal to the surface, with components n_j , v_i are the components of \mathbf{V} , and τ_{ij} is the shearing-stress component acting in the i -direction along the surface element perpendicular to the j -direction ($i \neq j$). In the expansion,

$$\frac{\partial}{\partial x_j} (v_i \tau_{ij}) = v_i \frac{\partial}{\partial x_j} \tau_{ij} + \tau_{ij} \frac{\partial v_i}{\partial x_j}, \quad (35)$$

the first term on the right is the work done on the center of mass of a parcel by the shearing-stress force, and the second is the deformation work done on the parcel; the latter is identified (e.g., Batchelor, 1967, p. 153) as the rate of dissipation of mechanical energy.

Gravity is a body force, proportional to the volume considered; the work it performs, γ , is

$$\gamma = - \int_V \rho \mathbf{V} \cdot \nabla \phi dV, \quad (36)$$

where φ is the gravity potential, including both the earth's gravitation and its centripetal acceleration; $\varphi = \varphi_0 + \int_0^z g dz$, where φ_0 is the arbitrary value at the reference geopotential (the geoid), g is the local value of the gravity acceleration, z is the plumb-line elevation above the geoid, and $z=0$ at the geoid. Since g increases by only 0.1% from the sea surface down to 5000 m, $\varphi - \varphi_0$ is well approximated as gz .

5.3. Heating

Heat flows into (or out of) the volume across its boundary, so the rate of heating \dot{Q} (not a time-derivative), is represented as

$$\dot{Q} = -\int_A \mathbf{q} \cdot \mathbf{n} dA = -\int_V \nabla \cdot \mathbf{q} dV, \quad (37)$$

where the heat-flux vector \mathbf{q} is the directed rate of heat flow per unit area. The vector is a construction, and if the connection between \dot{Q} and $\nabla \cdot \mathbf{q}$ is not to be merely definitional, it must be constructed as a point function varying continuously in some specified way with the geometric coordinates of the system. However, it is not derivable from the basic thermodynamic concepts; it is to be calculated from a model of the substance (not feasible for seawater), or from the properties of electromagnetic radiation, or developed from experimentation subject to the condition that the $\nabla \cdot \mathbf{q}$ then deduced match measured values of \dot{Q} (or something equivalent in some equivalent situation), which is the only "heating" that can be measured.

But \mathbf{q} is still not uniquely determined by \dot{Q} because any nondivergent vector could be added to it without affecting \dot{Q} . For example, one could hypothesize a spatially uniform heat flow through an adiabatically enclosed system without any consequence for the state of the system; specifying $\mathbf{q} = 0$, say, as the boundary condition on it is a matter of convenience. This is not a pedantic quibble, because a system transparent to electromagnetic radiation allows a radiative heat flux to pass through it unchanged; the appropriate boundary condition there is still \mathbf{q} constant, but non-zero.

The ocean is not transparent to radiation, however, and nearly all the incident solar radiation is absorbed in the upper 100 m (Morel and Antoine, 1994). Hence depth-dependent radiative heat-flux vectors have to be constructed from observations in varying regional and seasonal conditions in order to reproduce this near-surface contribution to \dot{Q} . And the proper sea-surface boundary condition on \mathbf{q} has to be determined from theory and measurement.

A useful generalization from experiment (Fourier's law) prescribes \mathbf{q} in liquids at rest (and hidden from radiation) as $-k_T \nabla T$, where the molecular conductivity k_T is a function of T, p, S . For ideal gases a similar formula can be derived from kinetic theory (e.g. Castellan, 1983, pp. 746-752), which success provides a motivation in addition to economy (Ockham's razor) for not adding any nondivergent vector to the empirical Fourier formula. One assumes, moreover, that the motion field is not so violent as to derange this relationship.

In mixtures of gases with spatially varying concentrations it is observed that where the concentration gradient of a component increases with distance the temperature may increase or decrease with time, depending on the component, and where the gradient decreases with distance, the opposite temperature change occurs. This is the "diffusion thermo-effect" (Jost, 1960, pp. 520-521) or "Dufour effect" (de Groot and Mazur, 1962, pp. 273-284). It may be interpreted (roughly) in terms of the transfer of kinetic energy in elastic collisions among recoiling molecules of initially equal kinetic energy ("temperature") but different masses. It is thus due to internal redistribution of internal energy, rather than the "heating" due to a temperature difference defined in Section 2 for homogeneous systems. The effect is cited, however, as the experimental basis for the concept of a heat flux component proportional to concentration gradient, which is a logical extension to inhomogeneous systems of "heating" as internal energy change minus work performed. But it is said to be difficult to detect in liquids (de Groot and Mazur, 1962, p. 279), and it is estimated to be unmeasurably small in the ocean (Gregg, 1984); so it is disregarded.

5.4. Diffusion of Enthalpy

Decompose, conceptually, the mass flux in the ocean into a salt flux, $\rho_s \mathbf{V}_s$, and a freshwater flux, $\rho_w \mathbf{V}_w$, where ρ_s and ρ_w are the densities of salt and freshwater, respectively, and \mathbf{V}_s and \mathbf{V}_w are the overall velocities of these two components of a parcel of seawater. The total mass flux is $\rho \mathbf{V} = \rho_s \mathbf{V}_s + \rho_w \mathbf{V}_w$, where ρ is the density of a parcel of seawater, and \mathbf{V} its aggregate velocity. Relative to a surface moving with velocity \mathbf{V} , the (diffusive) flux of salt mass per unit area \mathbf{F}_s is then $\rho_s(\mathbf{V}_s - \mathbf{V})$, and that of fresh water, \mathbf{F}_w , is $\rho_w(\mathbf{V}_w - \mathbf{V})$; and $\mathbf{F}_s = -\mathbf{F}_w$.

For a volume whose bounding surface moves with the local velocity \mathbf{V} , the net diffusive mass flux into the volume is zero, but the enthalpy flux is not, because the sea salt and freshwater bear different enthalpies (Section 4); whereby the mass exchanges produce a net enthalpy flux. As for the uniform equilibrium system (Section 3), so for this mass-conserving, open system of internally varying coordinates, the contributions to internal-energy change and specific-volume change (combined as enthalpy change) that are due to mass exchange across its boundary have to be subtracted from the total energy change of the system, in order to calculate by energy conservation that due to heat flow and work.

To evaluate the rate of diffusive flux of enthalpy across a surface, per unit area of surface, \mathbf{F}_h , consider $\mathbf{F}_h \cdot \mathbf{n} \delta t \delta A = \delta H$, the incremental amount of enthalpy transferred isothermally and isobarically in the time interval δt through an element of surface area δA . The corresponding amount of salt mass δM_s transferred in this process of reciprocal exchange of salt and freshwater mass is $\mathbf{F}_s \cdot \mathbf{n} \delta t \delta A$. As in (6b), the enthalpy introduced to a system of mass M by the mass increments (temperature and pressure being held constant) is

$$\delta H = \frac{\partial H}{\partial M_w} \delta M_w + \frac{\partial H}{\partial M_s} \delta M_s.$$

If, as in (16), variables are changed from (M_w, M_s) to (M, S) , and it is required for the diffusive process that $\delta M_w = -\delta M_s$, then

$$\delta H = \frac{1}{M} \frac{\partial H}{\partial S} \delta M_s = \frac{\partial h}{\partial S} \delta M_s .$$

Thus $\mathbf{F}_h \cdot \mathbf{n} \delta t \delta A = \frac{\partial h}{\partial S} \mathbf{F}_s \cdot \mathbf{n} \delta t \delta A$, and therefore

$$\mathbf{F}_h = \frac{\partial h}{\partial S} \mathbf{F}_s \quad (38)$$

since \mathbf{n} is arbitrary.

The expression \mathbf{F}_h is often called “heat of transfer” and subsumed with \mathbf{q} into a “total heat transport”. As far as physical oceanography is concerned, this usage is obfuscatory and unphysical: obfuscatory, because it masks what is just a correction to the rate of enthalpy increase, so that the principle of conservation of energy can be applied to the remainder; and unphysical, because through the salinity derivative its divergence includes an indeterminate constant [C in (29)], unlike the real heat flux \mathbf{q} , whose divergence is operationally defined and measurable.

The surface integral of \mathbf{F}_h over the complete boundary of the volume being considered is

$$\int_{\mathbf{A}} \mathbf{F}_h \cdot \mathbf{n} dA = \int_{\mathbf{V}} \nabla \cdot \left(\frac{\partial h}{\partial S} \mathbf{F}_s \right) dV, \quad (39)$$

where the negative of the integrals is the diffusive influx of enthalpy to the volume.

The integrand

$$\nabla \cdot \left(\frac{\partial h}{\partial S} \mathbf{F}_s \right) = \mathbf{F}_s \cdot \nabla \frac{\partial h}{\partial S} - \rho \frac{\partial h}{\partial S} \frac{dS}{dt}, \quad (40)$$

since

$$\rho \frac{dS}{dt} = -\nabla \cdot \mathbf{F}_s . \quad (41)$$

The second term on the right is sullied by the arbitrary constant in $(\partial h / \partial S)$ but the expansion of du / dt in (33) in derivatives of T , p , and S includes exactly the same constant, and so ultimately they cancel each other, leaving no physical ambiguity in the energy equation. The first term

involves the temperature, pressure, and salinity derivatives of $\partial h / \partial S$, each multiplied by the gradient of the respective state variable. These second-derivatives of h include no arbitrary constants [see (29)].

However, the term is quantitatively insignificant in the ocean, as may be illustrated by a simple calculation for a motionless horizontal layer with temperature, salinity, and pressure fixed at the upper and lower boundaries, and differences ΔT , ΔS , and Δp imposed across the layer. There is thus a uniform Fickian salt flux, $-k_s \partial S / \partial z$, through the layer, and since $\partial h(T, p, S) / \partial S$ varies across the layer, the accompanying diffusive flux of enthalpy near the upper boundary differs from that near the lower boundary. The resulting build-up (or depletion) of enthalpy is manifested as a perturbation temperature $T^*(z)$, fixed at zero on the boundaries. In steady state the Fourier heat fluxes, $-k_T \partial T^* / \partial z$, across the boundaries compensate the diffusive enthalpy input, so the resulting magnitude of T^* measures the size of that input. The shape of $T^*(z)$ is parabolic, with maximum departure T_m^* from the imposed linear variation at mid-level, of magnitude

$$T_m^* = \frac{1}{8} \frac{k_s}{k_T} \left[\frac{\partial^2 h}{\partial T \partial S} \Delta T \Delta S + \frac{\partial^2 h}{\partial S^2} (\Delta S)^2 + \frac{\partial^2 h}{\partial p \partial S} \Delta S \Delta p \right]$$

where $\partial^2 h / (\partial T \partial S) = \partial C_p / \partial S$.

In the ideal solution the activities depend only on mole fractions (i.e., salinity), so their temperature derivatives in (29) are zero. Then $\partial^2 h / \partial S^2 = 0$, and $\partial C_p / \partial S$ and $\partial^2 h / (\partial p \partial S)$ are just the temperature and pressure derivatives of $[h_D(T, p, S_R) - h_D(T, p, 0)]$, respectively,

independent of salinity. But seawater is not quite an ideal solution, so, from Feistel and Hagen (1995, Tables A.4 and A.10), the enthalpy derivatives near $S = 0.035$ are about:

$$\partial C_p / \partial S = -5 \times 10^3 \text{ J kg}^{-1} (\text{°C})^{-1}, \quad \partial^2 h / \partial S^2 = -0.7 \times 10^6 \text{ J kg}^{-1}, \quad \text{and}$$

$\partial^2 h / (\partial p \partial S) = -1.3 \times 10^{-3} \text{ J kg}^{-1} \text{ Pa}^{-1}$ where salinity is still specified as mass fraction rather than as per mille. (The ocean is not far from ideal, because the first and third values differ by less than 10% from those for the ideal solution.)

The molecular conductivity k_T of seawater is about $0.6 \text{ W m}^{-1} (\text{°C})^{-1}$ (Caldwell, 1974a). Measured values of the molecular diffusivity k_s / ρ in a NaCl solution of equivalent salinity 0.0285 had a mean value over the interval $0 - 30^\circ\text{C}$ that gives $k_s = 1.2 \times 10^{-6} \text{ kg m}^{-1}\text{s}^{-1}$ (Caldwell, 1974b). So a representative value of k_s / k_T for molecular processes in the ocean might be $2 \times 10^{-6} \text{ kg} (\text{°C})\text{J}^{-1}$.

A phenomenon in which these are likely to be controlling is thermocline staircases, for which cross-step differences are typically $\Delta T = 0.25 \text{ °C}$, $\Delta S = 0.044 \times 10^{-3}$, and $\Delta p = 1 \text{ db} = 10^4 \text{ Pa}$ (Tait and Howe, 1968). With these values inserted in (42), the magnitudes of the contributions of the three terms to T_m^* , are, from left to right, $1.4 \times 10^{-8} \text{ °C}$, $3.4 \times 10^{-10} \text{ °C}$, and $1.3 \times 10^{-10} \text{ °C}$.

A layer analogous to the main thermocline in the Sargasso Sea might have property differences across it of, say, $\Delta T = 10^\circ\text{C}$, $\Delta S = 1.0 \times 10^{-3}$, and $\Delta p = 500 \text{ db} = 5 \times 10^6 \text{ Pa}$. The contributions to T_m^* are then, respectively, $1.2 \times 10^{-5} \text{ °C}$, $2 \times 10^{-7} \text{ °C}$, and $3 \times 10^{-7} \text{ °C}$. Of course molecular processes are not thought to be dominant at this scale in the ocean, but even for small-scale turbulence, in which one expects the eddy diffusivities $k_T / (\rho C_p)$ and k_s / ρ to be approximately equal, the factor k_s / k_T would increase by only about one hundred, yielding values of T_m^* , barely approaching measurability.

These model calculations are not proposed as imitations of actual oceanic phenomena. Rather, they are intended as simple, concrete demonstrations of the size of effects that might be anticipated in a system like the ocean from the determinate part of the diffusion of enthalpy. Obviously, the effects are inconsequential.

5.5. Conservation of Energy

The principle of conservation of energy now equates the terms (33), (34), (36), (37), and (39). Since each term is an integral over a finite volume of mass that is itself arbitrary, the integrands themselves must sum up:

$$\rho \frac{d}{dt} \left(u + \frac{1}{2} v^2 \right) = -\nabla \cdot p \mathbf{V} + \frac{\partial}{\partial x_j} (v_i \tau_{ij}) - \rho \mathbf{V} \cdot \nabla \phi - \nabla \cdot \mathbf{q} - \nabla \cdot \left(\frac{\partial h}{\partial S} \mathbf{F}_s \right). \quad (42)$$

This is the full statement of the First Law for a parcel in the ocean. As stated before, when salinity varies du/dt is not itself physically meaningful in its entirety because of that arbitrary constant, but the indeterminacy is removed by the last term in (42).

Conservation of *mechanical* energy for a parcel is a trivial result of dotting the velocity into the momentum equation:

$$\rho \frac{d}{dt} \left(\frac{1}{2} v^2 \right) = -\mathbf{V} \cdot \nabla p + v_i \frac{\partial \tau_{ij}}{\partial x_j} - \rho \mathbf{V} \cdot \nabla \varphi. \quad (43)$$

[Some physics teachers (e.g., Arons, 1990, pp. 123-124) call center-of-mass work – that which appears in (43) – “pseudowork”, and reserve “real work” for the full calculation over the parcel, as in Section 5.2] . Subtraction of (43) from (42) yields the equation for the internal-energy change alone:

$$\rho \frac{du}{dt} = -\nabla \cdot \mathbf{q} - p \nabla \cdot \mathbf{V} + \tau_{ij} \frac{\partial v_i}{\partial x_j} - \nabla \cdot \left(\frac{\partial h}{\partial S} \mathbf{F}_s \right). \quad (44)$$

It is due to heat flow, deformation work, and salt diffusion. Body-force work contributes nothing, and, in particular, if friction had been represented as a body force, proportional to \mathbf{V} , say, it would have affected the kinetic energy but not the internal energy.

Using the continuity equation in the form

$$\frac{d\alpha}{dt} = \alpha \nabla \cdot \mathbf{V}, \quad (45)$$

one can shift from internal energy to enthalpy,

$$\frac{du}{dt} + \frac{p}{\rho} \nabla \cdot \mathbf{V} = \frac{dh}{dt} - \alpha \frac{dp}{dt},$$

and then expand $dh(T, p, S)/dt$ in the spirit of (30) and (31), using (41), to recast (44) as:

$$\rho C_p \frac{dT}{dt} - \rho T \left(\frac{\partial \alpha}{\partial T} \right)_{p,S} \frac{dp}{dt} = -\nabla \cdot \mathbf{q} + \tau_{ij} \frac{\partial v_i}{\partial x_j} - \mathbf{F}_s \cdot \nabla \frac{\partial h}{\partial S}. \quad (46)$$

In terms of potential temperature, as in (32),

$$\rho C_p \left[\left(\frac{\partial T}{\partial \theta} \right)_{p,S} \frac{d\theta}{dt} + \left(\frac{\partial T}{\partial S} \right)_{\theta,p} \frac{dS}{dt} \right] = -\nabla \cdot \mathbf{q} + \tau_{ij} \frac{\partial v_i}{\partial x_j} - \mathbf{F}_s \cdot \nabla \frac{\partial h}{\partial S}. \quad (47)$$

All indeterminacy has been removed from (46) and (47), and all terms are operationally defined and measurable. Given the magnitudes of the temperature derivatives (Section 4), $\rho C_p d\theta/dt$ alone is very close to the full left-hand side of (47), so that substitution turns (47) into a convenient approximation to the internal-energy equation (44).

The Gibbs equation (14a, b) is not an expression of the First Law where irreversible processes of heat flux, salt diffusion, and deformation work (dissipation) occur, but is simply a relation among the changes in potentials corresponding to equivalent coordinate changes during reversible processes. Thus, for rates of change, (14a), for example, becomes just

$$T \frac{d\eta}{dt} = \frac{du}{dt} + p \frac{d\alpha}{dt} - \mu \frac{dS}{dt}. \quad (48)$$

In order to calculate oceanographic budgets, it is useful to recast (42), yet again, into control-volume form. To the terms in (42) one applies the identity, based on the continuity equation,

$$\rho \frac{df}{dt} = \frac{\partial(\rho f)}{\partial t} + \nabla \cdot \rho f \mathbf{v}, \quad (49)$$

where $f(x, y, z, t)$ is any function. For example,

$$\rho \mathbf{V} \cdot \nabla \varphi = \rho \frac{d\varphi}{dt} = \frac{(\partial \rho \varphi)}{\partial t} + \nabla \cdot (\rho \varphi \mathbf{V}),$$

since $\partial \varphi / \partial t = 0$. Thus

$$\frac{\partial}{\partial t} \rho \left(u + \varphi + \frac{1}{2} v^2 \right) + \nabla \cdot \rho \left(h + \varphi + \frac{1}{2} v^2 \right) \mathbf{V} = -\nabla \cdot \mathbf{q} + \frac{\partial}{\partial x_j} (v_i \tau_{ij}) - \nabla \cdot \left(\frac{\partial h}{\partial S} \mathbf{F}_s \right). \quad (50)$$

This form of the energy equation is easily integrated over a fixed volume in space, to give the changes and advectations of energies on the left, due to their forcings across the boundary of the volume on the right.

It would be useful to have a name for the advected quantity, $h + \varphi + \frac{1}{2} v^2 \equiv e$. Kestin (1966, p. 223) proposed “methalpy”, but that hasn’t taken hold; Feistel (1993) and McDougall (2003) used “Bernoulli function”, but that sounds off-puttingly mathematical for a physical quantity; without the insignificant kinetic energy, meteorologists sometimes call it “dry static energy” (Bohren and Albrecht, 1998, p. 109), which seems oxymoronic for the ocean. Perhaps Batchelor’s (1967, p. 158) term, “total energy”, is most apt.

For mean conditions in a finite volume it is the advection of ρe that balances the energy inputs on the right of (50). The enthalpy was developed in (29) in terms of the chemical potentials as a clean-cut way of separating the arbitrary from the measurable, but it can be expressed approximately and more conveniently in physical–oceanographic variables by integrating

$$dh = C_p dT + \frac{\partial h}{\partial p} dp + \frac{\partial h}{\partial S} dS$$

from a reference state (T_o, p_o, S_o) to the desired state (T, p, S) . Thus for $T_o = 0^\circ\text{C}$, $p_o = p_a$, and $S_o = 0.035$, and for the salinity range 0.033-0.037, to an accuracy of order 0.1% (Warren, 1999),

$$e - h_R(T_o, p_o, S_o) - C(S - S_o) - \varphi_o = \bar{C}_p(\theta', p_o, S)\theta', \quad (51)$$

where: $h_R(T_o, p_o, S_o)$ and C are the same arbitrary constants as in (29); φ_o is the arbitrary reference value for φ at the geoid; θ' is the Celsius potential temperature $\theta'(T, p, S)$ referenced to pressure p_o ; and $\bar{C}_p(\theta', p_o, S)$ means the average value of $C_p(T, p_o, S)$ over the temperature interval 0°C to θ' . Kinetic-energy contributions to e are insignificant at this level of accuracy. (The accuracy of approximating $u - u_R(T_o, p_o, S_o) - C(S - S_o)$ by $\bar{C}_p\theta'$ is not so good: a few percent.)

Then the advection of total energy across an oceanographic section (or set of surfaces) can be well represented by the integral of $\rho\bar{C}_p\theta'\mathbf{V}\cdot\mathbf{n}$ over the section (or set of surfaces), but it will be a physically meaningful calculation – producing numbers that can be compared to those on the right side of (50) – only if the corresponding mass and salt transports are each zero, so that the arbitrary constants $h_R(T_o, p_o, S_o)$, C , and φ_o drop out. [Montgomery (1954) made the same point long ago in a slightly different context, but apparently he did not find a large audience. The two conditions are probably redundant in practice, as it is hard to think of a budgetary situation in which the mass transport might be zero without the salt transport being so as well.] Most oceanographers call this integral a “heat flux”. It is not: it is the advection by currents of independently defined energies. The fact that the volume-integrated divergence of $\rho\bar{C}_p\theta'\mathbf{V}$ is usually very nearly equal to that of \mathbf{q} does not make them conceptually identical; rather, the near equality is part of the First Law of Thermodynamics. The (mis)conception of “heat” as some sort of caloric fluid transported by the circulation lingers on from the eighteenth century.

The muddle is compounded when the term “heat content” (caloric, again) is injected, usually in reference to internal energy [or more, exactly, to $u - u_R(T_o, p_o, S_o) - C(S - S_o)$] in the time-derivative term in (50). Internal energy is not defined in terms of heating, it is a different energy quantity from e (it is u , not h , that appears in the time-derivative term), and it is less well approximated by $\bar{C}_p \theta'$. Consistency and clarity recommend against describing e and u as “heat”.

Of course the real heat flux \mathbf{q} has little to do with transporting energy in the open ocean much below the euphotic zone, as it embodies molecular processes whose effects are usually swamped by the advection of total energy by the mean circulation or its eddy components, depending on how one defines averaging times and distances. But, as remarked in Section 5.4, molecular processes can be noticeable in special circumstances like the interfaces between double-diffusive layers (e.g., Caldwell, 1973). And even in small-scale turbulence, when eddy coefficients are defensible, a Fourier-like representation of eddy enthalpy flux can be useful.

The work done by other forces not included here is easily added to the energy-conservation statements. For example, since the luni-solar tidal force is a body force, the work it performs should appear in the full energy equations (42) and (50), and in the mechanical-energy equation (43), but not explicitly in the internal-energy equation (44) – although the deformation work associated with the tidal motions acts to increase the internal energy there.

5.6 Global Energy Balance

The energy balance for the global ocean is found by integrating (50) over its volume, whereby all the divergence terms turn (back) into surface integrals. For the first term on the right—the integrated heat flux—if one neglects the geothermal heat flux through the sea floor, all that counts is the heat flux through the sea surface. Within the meaning of the term, it consists of the net radiation [described in detail by Peixoto and Oort (1992, pp. 116–130) or Curry and Webster (1999, pp. 248–251, 331–337)] and the sensible heat flux (from ocean to atmosphere, nearly everywhere). While the latter is parameterized by eddy coefficients away from the sea

surface, the flux at the air-sea interface itself occurs by molecular conduction—the Fourier law—in laminar layers of order 1 mm thick on either side of the interface [e.g., Curry and Webster (1999, pp. 301–302)]—though the distinction must be obscured in a whitecap-covered sea.

Evaporation from the sea surface entails another contribution to the energetics, that of phase change, not previously discussed here. The water vapor pressure just above the sea surface is usually less than the thermodynamic equilibrium value ("saturation vapor pressure") because the wind eddies blow the water vapor away from the sea surface, so freshwater evaporates continuously from the ocean, essentially adiabatically and isobarically, in the drive toward equilibrium. In a parcel of seawater the freshwater constituent, of specific enthalpy h_w , becomes water vapor of specific enthalpy $h_w + L$, where L is the enthalpy ("latent heat") of vaporization per unit mass. Since the process for the combined system of liquid and vapor conserves enthalpy (no heating occurs), the enthalpy required for the phase change must be drawn from the remaining liquid water. Thus evaporation entails an upward enthalpy flux from the sea surface $\rho_F L E$, where ρ_F is the density of fresh water and E the evaporation rate per unit surface area. [Bohren and Albrecht (1999, pp. 181-201) are their usual highly instructive selves on evaporation and its workings in energetics.] The ocean is "cooled", but not because of any heat flux. Despite that, the evaporative enthalpy flux is always catalogued among the real surface heat fluxes (radiative, sensible) as part of \mathbf{q} -- for convenience in forming budgets, from historical practice, and perhaps from misdirection by the term "latent heat". It does no harm, so long as one understands that the "evaporative heat flux" is not a heat flux.

The second term on the right, the rate of shear-stress working at the boundaries, gets no contribution at the rigid boundaries because of the no-slip boundary condition. It reduces to the rate of wind-stress work on the sea surface.

The last term looks indeterminate, but the arbitrary constant C is canceled elsewhere. If one disregards the effects of dissolving salt deposits on the sea floor, or gaining salts from hydrothermal vents (which processes add mass to the ocean), the only salt flux is that at the sea surface, due to difference between the rates of evaporation and precipitation, P . In stationary

conditions freshwater mass leaves the sea surface at the rate $\rho_F(E-P)$; this is supplied by an upward net flow w of seawater, at an equal rate of net freshwater transport $\rho w (1-S)$; the accompanying upward sea salt flux $\rho S w$ is returned downward as the diffusive flux F_S ; and thus, in the sea-surface integral of the diffusion term, $(\partial h / \partial S) \mathbf{F}_S \cdot \mathbf{n} = -(\partial h / \partial S) \rho S w$. On the other side of (50) this upward velocity makes a corresponding sea-surface contribution to the advection integral $\int \rho h \mathbf{V} \cdot \mathbf{n} dA$, and the two integrands combine as $[h - (\partial h / \partial S) S] \rho w$. According to (29), the constant C drops out. From another viewpoint, which follows the inference drawn from (15), the enthalpy H of a mass M of seawater is $(\partial H / \partial M_w) M_w + (\partial H / \partial M_s) M_s$; the first term is the enthalpy of the freshwater in the solution, the second term that of the salt. Dividing by the (constant) mass M then shows that $h - (\partial h / \partial S) S = (\partial H / \partial M_w) M_w / M \equiv h_w$. So the vertical advection integral above is just the flux of the freshwater enthalpy (in solution) at the sea surface, in which the constant C does not appear. (This analysis can be extended to a non-stationary sea surface by considering the time-derivative term in (50) as well; the argument is distracting, is not edifying, and produces the same result in the end.)

It is evident, however, that the freshwater cycle (E , P , and runoff) contributes by advection of liquid freshwater to the enthalpy budget (albeit, as it turns out, in a minor way compared to phase change). For the ideal solution, from (29), h_w as above is $h_R(0) + h_D(T, p, 0)$, just the enthalpy h_F of pure water. The physical chemistry is too cumbersome to bother handling h_w exactly in the freshwater cycle, so seawater will be treated as an ideal solution here, and h_w taken as h_F . [The approximation is actually quite good: the difference between h_w and h_F for S near 0.035 is equivalent to a temperature error of only about 0.1°C in h (Feistel and Hagen, 1995, Table A.4).]

At the sea surface $p = p_a$, $\varphi = 0$, and $\theta = T$, so from (51),

$$h_F = h(T, p_a, 0) = h_R(T'_0, p_a, 0) + \varphi_0 + \bar{C}_p(T', p_a, 0) T' \quad (52)$$

where, for clarity and consistency with custom, T' is Celsius temperature, and

$T'_0 = 0^\circ C$. As indicated previously, the net w at the sea surface is $\rho_F(E - P) [\rho(1-S)]^{-1}$. The constant $h_R + \varphi_0$ in (52) may be disregarded because in the global integration the time-mean net mass flux through the sea surface due to evaporation, precipitation, and runoff is zero; even locally, where $E - P \neq 0$, the convergence of surface transport supplying the balance assures no net advection of $h_R + \varphi_0$.

Thus the global sea-surface advection integral reduces to

$$\int \left(h - \frac{\partial h}{\partial S} S \right) \rho w dA = \int \frac{\rho_F \bar{C}_p}{1-S} (T'_S E - T'_a P) dA, \quad (53)$$

where the temperature T' associated with the evaporation is the sea-surface temperature T'_S , and that of the precipitation as it falls out of the atmosphere is T'_a ; the net velocity w has been separated into its upward component E carrying seawater away for evaporation, and its downward component P introducing rainwater, with their two separate enthalpy fluxes; and ρ_F and \bar{C}_p are both freshwater values. To complete the freshwater cycle, this must be supplemented with a near-surface horizontal advection integral for the runoff (including ice breakoff), something of the form $\int \rho \bar{C}_p T'_R R dl$ where R is the rate of runoff per unit length of coastline l , T'_R is the temperature of the runoff water, and the integration is around the entire coastline of the world ocean. The contribution of the freshwater cycle is necessarily small: its magnitude relative to the evaporative enthalpy flux is roughly $C_p \Delta T' / L$, where $\Delta T'$ is the difference between evaporation-weighted T'_S and precipitation-weighted T'_a , and $L = 2.5 \times 10^6 \text{ J kg}^{-1}$ – probably less than one percent.

The rest of the integral of the flux-divergence term in (50) is zero because of the no-flux condition at solid boundaries (except, of course, for the runoff). The seasonal sea ice cycle has been disregarded because, while a phase change is involved, the product of the change stays in the ocean system (unlike water vapor), and the original phase is restored in place (apart from surface drift). Phase change during snow melt is mentioned by Curry and Webster (1999, p. 255).

Of course in the mean global ocean budget, the overwhelmingly dominant terms are the radiative heat flux and the evaporative enthalpy flux. For example, an annual-mean evaporation rate of $3.6 \times 10^{14} \text{ m}^3 \text{ yr}^{-1}$ (Peixoto and Oort, 1992, p. 271) implies a rate of enthalpy loss from the ocean of $2.8 \times 10^{16} \text{ W}$; while a mean sensible heat flux from the surface of roughly 10 W m^{-2} (Peixoto and Oort, 1992, p. 235) gives a flux of only $0.36 \times 10^{16} \text{ W}$ over the global ocean (surface area $3.6 \times 10^{14} \text{ m}^2$). As just noted, the freshwater cycle probably contributes less than 1% as much as the evaporative flux. And the wind-stress work is utterly insignificant: for an annual- and areal-mean rate of 0.007 W m^{-2} (Peixoto and Oort, 1992, p. 232), the global ocean value is only $3 \times 10^{12} \text{ W}$.

Similarly, in (44) local deformation work is also inconsequential compared to heating. For example, a relatively large value might be expected in the surface Ekman layer: with the surface stress of order 10^{-1} Pa , and the Ekman thickness and velocity of order 10 m and 10^{-1} m s^{-1} , respectively, the rate of deformation work $\tau \partial v / \partial z$ is of order 10^{-3} W m^{-3} . But with downward radiation at the sea surface of order 10^2 W m^{-2} , absorbed in the euphotic zone of order 100 m thick, the heat-flux divergence is about 1 W m^{-3} , a thousand times greater. In a logical twist, although internal-energy change is defined by adiabatic work, and heat is derived conceptually from the difference between internal-energy change and actual work performed (Section 2), the internal-energy change that really occurs in the ocean is determined by heating (and phase change) and hardly at all by work.

A major objective in this essay has been to demonstrate that indeterminacies in the various First Law equations are real enough, especially in association with salinity variation, but that careful handling can remove them to leave physically meaningful statements. When this is done, the only surviving residuals of the terms having to do with salinity variations are due either to the nonideality of seawater solution or to differences between reference-solution values. These, as has been seen, are insignificant. Whether or not physical oceanographers have always realized it, they have done well not to trouble themselves about the role of salinity in the First Law, except when needing exact values of coefficients like C_p or $\partial \alpha / \partial T$.

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7. APPENDIX. HISTORICAL NOTE ON THE POTENTIAL-TEMPERATURE CONCEPT

Meteorologists and oceanographers approached the concept of potential temperature from opposite directions. Helmholtz (1888) stated the equation (already well known) for the adiabatic expansion of an ideal gas, highlighted the value of absolute temperature reached at sea-level pressure in such a process, and called it “heat content”. Bezold (1888) deprecated that term, and convinced Helmholtz that “potential temperature” was more suitable.

Neither mentioned that some years earlier Lord Kelvin (Thomson, 1857) had derived the general expression for the variation of temperature during adiabatic pressure change [stated here preceding (32)]. On the *Fram* expedition (1893–1896) Nansen was using insulated water bottles both for collecting water samples and for measuring temperatures. He realized that to get the correct *in situ* temperatures the values read on deck had to be *increased* by the amount of adiabatic cooling experienced by the samples as they were raised from depth. Nansen (1902) introduced surface-pressure values of the thermal-expansion coefficient and C_p to Kelvin’s formula, and calculated graphs for making the addition. Ekman (1905) knew that the expansion coefficient actually depended strongly on pressure (C_p much less so), so he integrated Kelvin’s formula with the measurements then available to generate much more accurate graphs for correcting the raw thermometer readings. Shortly afterward, Helland-Hansen (1912) reversed the calculation by *subtracting* Ekman’s correction from measured *in-situ* temperatures to obtain a parameter preserved during adiabatic displacements, which, following the now established meteorological practice, he also called “potential temperature”.

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