Lectures on the Thermodynamics of Seawater and Ice, given at MIT, 2015, by Trevor J. McDougall

(of the School of Mathematics and Statistics,
University of New South Wales, Sydney, Australia)

Motivation for the first several lectures

As heat is exchanged between the atmosphere and the ocean, how can we keep track of "heat" in the ocean? Here is a plot of the isobaric specific heat capacity of seawater.

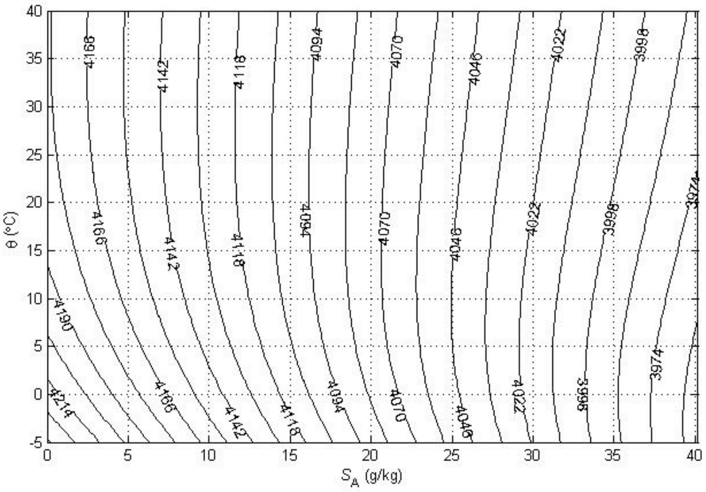


Figure 4. Contours of isobaric specific heat capacity c_p of seawater (in J kg^{-1} K^{-1}), at $p = 0$.

Here is a zoomed-in plot of the isobaric specific heat capacity of seawater.

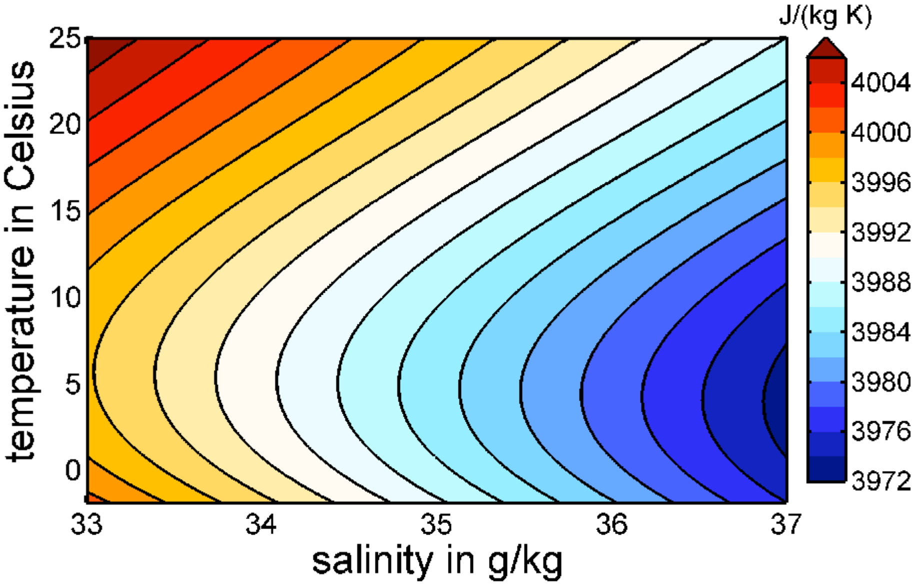


Fig. 1.7 Specific heat of seawater c_p

For the purpose of this introductory lecture, just think of potential temperature θ as simply temperature.

A given air-sea heat flux will affect the potential temperature θ in the ocean at a rate that depends on where you are on this $S_{\mathrm{A}} - \theta$ diagram. That is, the change in temperature at the sea surface due to a Joule of heat being transferred from the atmosphere into a kilogram of seawater, at constant salinity, is equal to the reciprocal of $c_p\left(S_{\mathrm{A}},\theta,0\right)$.

So what variable represents the "heat content per unit mass" of seawater? It clearly is not simply potential temperature θ. Nor is it the product $\theta c_p\left(S_{\mathrm{A}},\theta,0\right)$ (for at least two reasons, (1) because $\theta c_p\left(S_{\mathrm{A}},\theta,0\right) \neq \int c_p\left(S_{\mathrm{A}},\theta,0\right) d\theta$ and (2) because the *"heat content"* of seawater also depends separately on salinity ($\mathrm{d}h_0 = \mathrm{d}h\left(S_{\mathrm{A}},\theta,0\right) = c_p\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}\theta + \tilde{h}_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}$, with the enthalpy h being a credible candidate for "heat content" at this stage).

And even if we were able to answer this question of "what is the *"heat content"* per unit mass" of seawater at $p = 0$, what do we do in the sub-surface ocean where changes in pressure and specific volume v cause changes in the internal energy u and enthalpy h of $-P\mathrm{d}v$ and $v\mathrm{d}P$ respectively?

In short, we are asking the question

"what is "*heat*" in the ocean?";

that is, more specifically, we are asking what is the *"heat content per unit mass"* of seawater, applicable throughout the ocean at all depths. We seek a *"heat content per unit mass"* variable whose transport and turbulent mixing can be used to track the transport and the turbulent mixing of the heat that enters the ocean across the air-sea boundary and across the sea floor (the geothermal heat flux). This paragraph neatly summarizes the purpose of the first several lectures of this course.

The route to answering our question, "what is "*heat*" in the ocean?"

In order to answer this question we need to have a thorough understanding of the First Law of Thermodynamics which in turn, can only be derived from the Conservation Equation for Total Energy, which in turn relies on the Fundamental Thermodynamic Relation, which in turn embodies the definition of entropy and the Second Law of Thermodynamics. In the coming lectures we will derive each of these three equations, but for now, here they are.

The Continuity Equation is

$$\boxed{\rho_t + \nabla\cdot\left(\rho\mathbf{u}\right) = 0} \,. \qquad \text{(A.21.2)}$$

The Fundamental Thermodynamic Relation is

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v = \mathrm{d}h - v\,\mathrm{d}P = \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}} \,. \qquad \text{(A.7.1)}$$

The Conservation Equation for Total Energy is

$$\begin{aligned}\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t &= -\nabla\cdot\left(\left[p+P_0\right]\mathbf{u}\right) - \nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} \\ &\quad + \nabla\cdot\left(\rho v^\mathrm{visc}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right).\end{aligned} \qquad \text{(B.15)}$$

where the total energy $\mathcal{E}$ per unit mass is defined as the sum of the internal, kinetic and gravitational potential energies, that is,

$$\mathcal{E} = u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi \,. \qquad \text{(B.14)}$$

The First Law of Thermodynamics is

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) &= \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right) \\ &= -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\end{aligned}} \,. \qquad \text{(B.19)}$$

Nomenclature

h is specific enthalpy and u is specific internal energy, related by $h = u + Pv = u + \left(p+P_0\right)v$ ("specific" means "per unit mass of seawater")

v is the specific volume

η is specific entropy

μ is the relative chemical potential of seawater

S_A is the Absolute Salinity of seawater

$\mathbf{F}^\mathrm{R}$ is the radiative flux of heat

$\mathbf{F}^\mathrm{Q}$ is the molecular flux of heat

ε is the rate of dissipation of kinetic energy

Equations numbers are from 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. Available from www.TEOS-10.org

Many of the topics that we cover are discussed in more detail in this TEOS-10 Manual. You should download it to your computer; it is over 200 pages.

A comprehensive list of nomenclature (Nomenclature_MATH5185_2014.pdf) is being distributed to the class.

The continuity equation

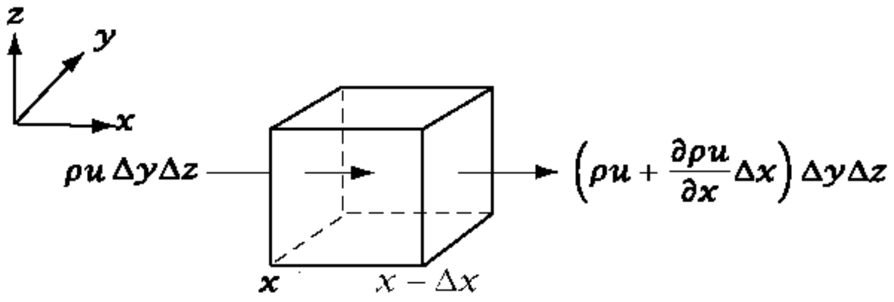


Fig. 1.1 Mass conservation in a cubic Eulerian control volume.

Thus, the accumulation of fluid within the control volume, due to motion in the x-direction only, is

$$\delta y\delta z[(\rho u)_x-(\rho u)_{x+\delta x}]=-\frac{\partial(\rho u)}{\partial x}\delta x\delta y\delta z. \tag{1.25}$$

To this must be added the effects of motion in the y- and z-directions, namely

$$-\left[\frac{\partial(\rho v)}{\partial y}+\frac{\partial(\rho w)}{\partial z}\right]\delta x\delta y\delta z. \tag{1.26}$$

This net accumulation of fluid must be accompanied by a corresponding increase of fluid mass within the control volume. This is

$$\frac{\partial}{\partial t}(\text{Density}\times\text{Volume})=\delta x\delta y\delta z\frac{\partial\rho}{\partial t}, \tag{1.27}$$

because the volume is constant. Thus, because mass is conserved, (1.25), (1.26) and (1.27) give

$$\delta x\delta y\delta z\left[\frac{\partial\rho}{\partial t}+\frac{\partial(\rho u)}{\partial x}+\frac{\partial(\rho v)}{\partial y}+\frac{\partial(\rho w)}{\partial z}\right]=0. \tag{1.28}$$

Because the control volume is arbitrary the quantity in square brackets must be zero zero and we have the *mass continuity equation:*

$$\frac{\partial\rho}{\partial t}+\nabla\cdot(\rho \boldsymbol{v})=0. \tag{1.29}$$

For a finite, arbitrary volume that is fixed in space …

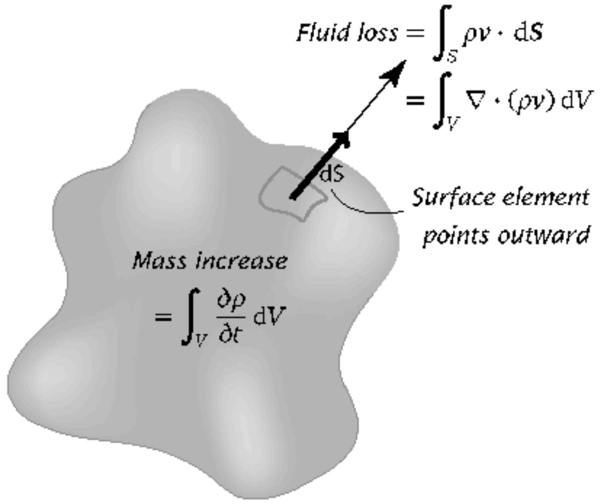


Figure 1.2 Mass conservation in an arbitrary Eulerian control volume V bounded by a surface S. The mass gain, $\int_V(\partial\rho/\partial t)\,\mathrm{d}V$ is equal to the mass flowing into the volume, $-\int_S(\rho\boldsymbol{v})\cdot\mathrm{d}\boldsymbol{S}=-\int_V\nabla\cdot(\rho\boldsymbol{v})\,\mathrm{d}V$.

and if the arbitrary volume moves and changes shape, the continuity equation becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_V\rho\,\mathrm{d}V=\int_S\rho\mathbf{v}\cdot\mathrm{d}\boldsymbol{S}=\int_V\nabla\cdot(\rho\mathbf{v})\mathrm{d}V$$

The material derivative

The material derivative $\frac{\mathrm{d}\phi}{\mathrm{d}t}$ is the derivative following the flow.

Let us suppose that a fluid is characterized by a (given) velocity field $\boldsymbol{v}(\boldsymbol{x}, t)$, which determines its velocity throughout. Let us also suppose that it has another property ϕ, and let us seek an expression for the rate of change of ϕ of a fluid element. Since ϕ is changing in time and in space we use the chain rule:

$$\delta\phi = \frac{\partial\phi}{\partial t}\delta t + \frac{\partial\phi}{\partial x}\delta x + \frac{\partial\phi}{\partial y}\delta y + \frac{\partial\phi}{\partial z}\delta z = \frac{\partial\phi}{\partial t}\delta t + \delta\boldsymbol{x}\cdot\nabla\phi. \tag{1.4}$$

This is true in general for any δt, $\delta\boldsymbol{x}$, etc. Thus the total time derivative is

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{\partial\phi}{\partial t} + \frac{\mathrm{d}\boldsymbol{x}}{\mathrm{d}t}\cdot\nabla\phi. \tag{1.5}$$

If this is to be a material derivative we must identify the time derivative in the second term on the right-hand side with the rate of change of position of a fluid element, namely its velocity. Hence, the material derivative of the property ϕ is

$$\frac{\mathrm{d}\phi}{\mathrm{d}t} = \frac{\partial\phi}{\partial t} + \boldsymbol{v}\cdot\nabla\phi. \tag{1.6}$$

A brief introduction to Absolute Salinity and Practical Salinity

Practical Salinity S_P has been measured and reported by oceanographers for 37 years (since it was defined in 1978). Practical Salinity is found from knowledge of a seawater sample's *in situ* temperature, pressure and electrical conductivity.

In the past ten years it has become acknowledged that the composition of seawater is not constant throughout the world ocean, and that the spatially variable ratio of the constituents leads to horizontal gradients of density that are too large to ignore (leading to ~8% change in the meridional [northward] vertical overturning circulation of the North Atlantic).

This issue is an active area of research, but will not be a central part of this course. We will deal with only one salinity variable, namely Absolute Salinity S_A, as defined by TEOS-10.

For completeness, we will make a few remarks comparing four salinity variables

Practical Salinity, S_P
Reference Salinity, S_R
Absolute Salinity, S_A
Preformed Salinity, S_*

"Standard Seawater" has (reasonably well) known composition, but the Practical Salinity S_P of Standard Seawater is not quite equal to the mass fraction of dissolved material in seawater. Rather, this mass fraction for Standard Seawater is estimated to be the Reference Salinity, S_R, of TEOS-10,

$$S_\mathrm{R} \;=\; \left(\frac{35.165\,04\ \mathrm{g\,kg^{-1}}}{35}\right) S_\mathrm{P} \;=\; u_\mathrm{PS}\, S_\mathrm{P} \;. \qquad (2.4.1)$$

"Standard Seawater" is based on surface water from the North Atlantic, and it contains no nutrients. Deeper in the ocean, and particularly in the deep Southern Ocean and the deep North Pacific, the concentration of nutrients is high (as a result of biogeochemical processes). Nutrients do not conduct electricity very well (particularly silicic acid which is almost non-conductive) and so an estimate of salinity based on a sample's electrical conductivity underestimates the mass fraction of dissolved material and so underestimates the density of seawater.

Given sufficient measurements of nutrients, we can now allow for their presence on the mass fraction (and on the density) of seawater according to

$$\begin{aligned}&\left(S_\mathrm{A}-S_\mathrm{R}\right)/(\mathrm{g\,kg^{-1}}) = \\ &\qquad \left(55.6\,\Delta\mathrm{TA} + 4.7\,\Delta\mathrm{DIC} + 38.9\,\mathrm{NO_3^-} + 50.7\ \mathrm{Si(OH)_4}\right)\Big/(\mathrm{mol\,kg^{-1}})\;.\end{aligned} \qquad (\mathrm{A.4.10})$$

(TA is Total Alkalinity, DIC is Dissolved Inorganic Carbon, $\mathrm{NO_3^-}$ is nitrate and $\mathrm{Si(OH)_4}$ is silicate, or silicic acid).

We normally do not have these measurements, so TEOS-10 also provides an algorithm to evaluate Absolute Salinity from a spatial look-up table of the Absolute Salinity Anomaly Ratio, R^δ,

$$S_\mathrm{A} \;=\; S_\mathrm{R}\left[1 + R^\delta\left(\mathrm{long,\,lat,}\,p\right)\right]. \qquad (\mathrm{A.5.10})$$

The subroutine **gsw_SA_from_SP** converts from Practical Salinity S_P to Absolute Salinity S_A.

The Absolute Salinity S_A is the correct salinity argument to be used to evaluate density and other thermodynamic properties.

The Absolute Salinity Anomaly, $\delta S_{\mathrm{A}} \equiv S_{\mathrm{A}} - S_{\mathrm{R}}$, is the improvement in today's salinity estimates compared to those of the Practical Salinity era (1978 – 2009). This improvement is shown in the following two figures.

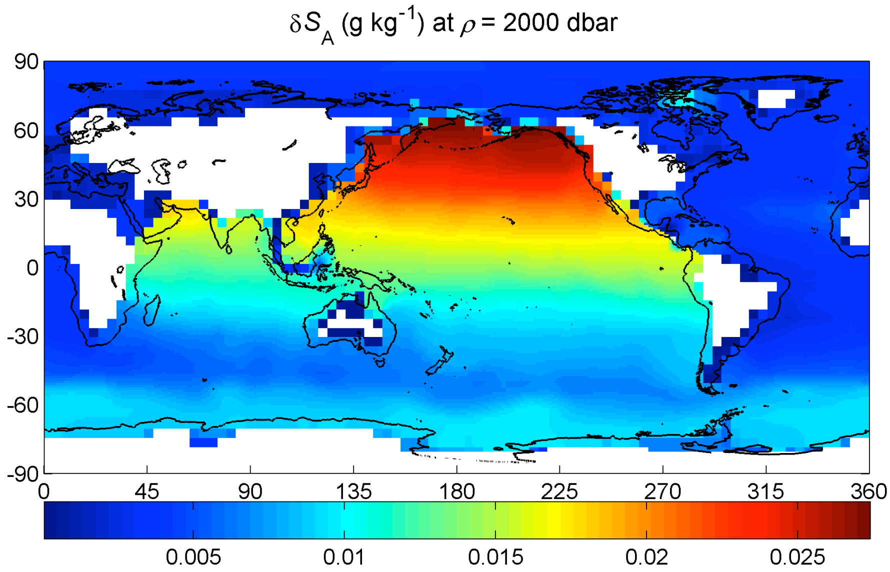


Figure 2 (a). Absolute Salinity Anomaly δS_{A} at p = 2000 dbar.

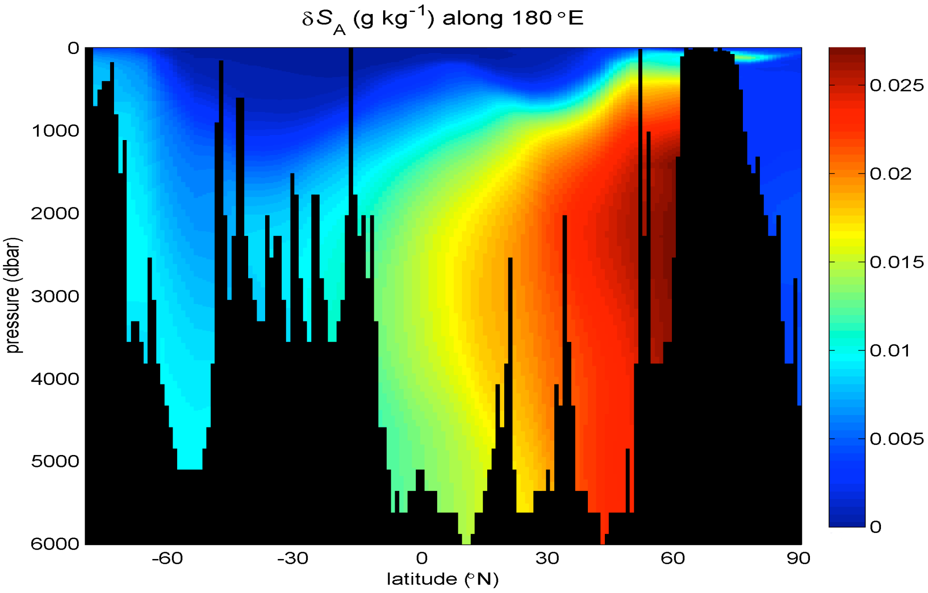


Figure 2 (b). A vertical section of Absolute Salinity Anomaly δS_{A} along 180°E in the Pacific Ocean.

The horizontal gradients of density are responsible for driving the world's deep ocean currents (via the so-called "thermal wind" equation). The neglect of the spatial variation of seawater composition (that is, the use of S_R instead of S_A in the evaluation of density) leads to non-trivial errors in the horizontal density gradient. Globally, half the ocean below 1000 dbar is affected by more than 2% (see **Fig. A.5.1**) while in the North Pacific, half the ocean below 1000 dbar is affected by more than 10%.

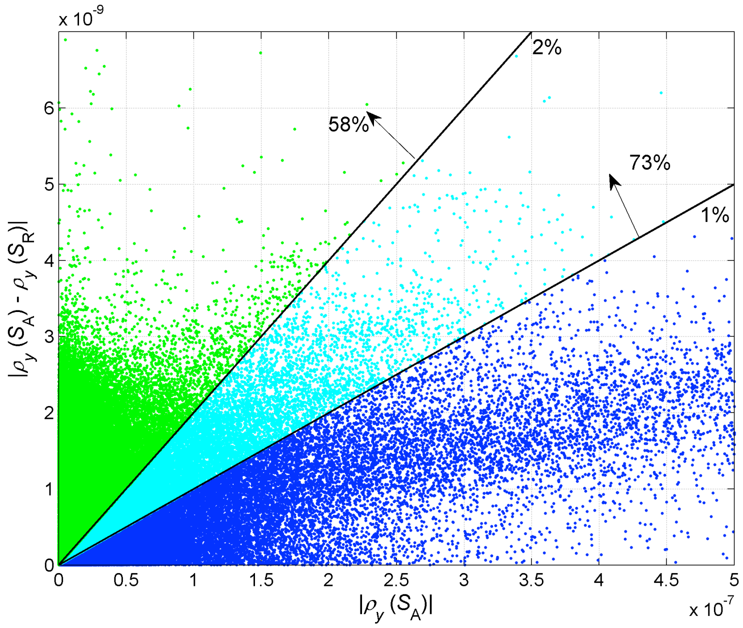


Figure A.5.1. The northward density gradient at constant pressure (the horizontal axis) for data in the global ocean atlas of Gouretski and Koltermann (2004) for $p > 1000\,\text{dbar}$. The vertical axis is the magnitude of the difference between evaluating the density gradient using S_A versus S_R as the salinity argument in the TEOS-10 expression for density.

We now introduce Preformed Salinity S_*. Preformed Salinity S_* is designed to be as close as possible to being a conservative variable. That is, S_* is designed to be insensitive to the *biogeochemical processes* that affect the other types of salinity to varying degrees. S_* is formed by first estimating the contribution of *biogeochemical processes* to S_A, and then subtracting this contribution from S_A. Because it is designed to be a conservative oceanographic variable, S_* is the ideal salinity variable for ocean modeling.

As a practical thing, the difference $S_\mathrm{R} - S_*$ is taken to be $0.35\left(S_\mathrm{A} - S_\mathrm{R}\right)$.

Figure A.4.1. Number line of salinity, illustrating the differences between Preformed Salinity S_*, Reference Salinity S_R, and Absolute Salinity S_A for seawater whose composition differs from that of Standard Seawater.

For seawater of Standard Composition, $S_* = S_\mathrm{R} = S_\mathrm{A} = \left(35.165\,04\ \mathrm{g\,kg}^{-1}/35\right)S_\mathrm{P}$, but when the seawater sample has undergone some biogeochemical activity, its nutrient levels will be greater than zero, its conductivity will be increased a little and its Absolute Salinity will be increased more. Specifically, if the increase in Absolute Salinity due to the change in chemical composition, $S_\mathrm{A} - S_*$, is say 1.35 on some scale, then only 0.35/1.35 (~26%) of this increase will be reflected in the sample's electrical conductivity and hence in its Practical Salinity and Reference Salinity.

In this course we will deal exclusively with Absolute Salinity, and we will also simplify things and consider Absolute Salinity to be a Conservative variable. That is, we will assume that

$$\boxed{\left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho \mathbf{u} S_\mathrm{A}\right) = \rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S}}, \quad \textit{approximate} \tag{A.21.8a}$$

where $\mathbf{F}^\mathrm{S}$ is the molecular flux of salt. It is actually the Preformed Salinity S_* that obeys such a conservative evolution equation, namely

$$\left(\rho S_*\right)_t + \nabla\cdot\left(\rho \mathbf{u} S_*\right) = \rho\frac{\mathrm{d}S_*}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S}. \tag{A.21.1}$$

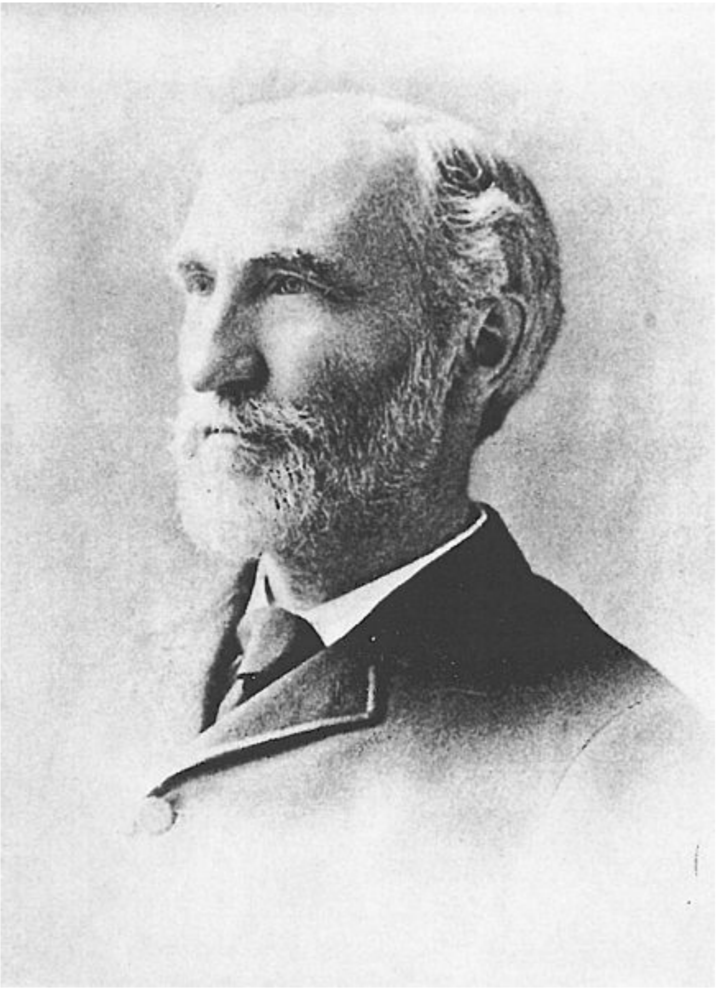
By making the assumption that Absolute Salinity obeys the conservative equation (A.21.8a) rather than the real form of this equation, namely

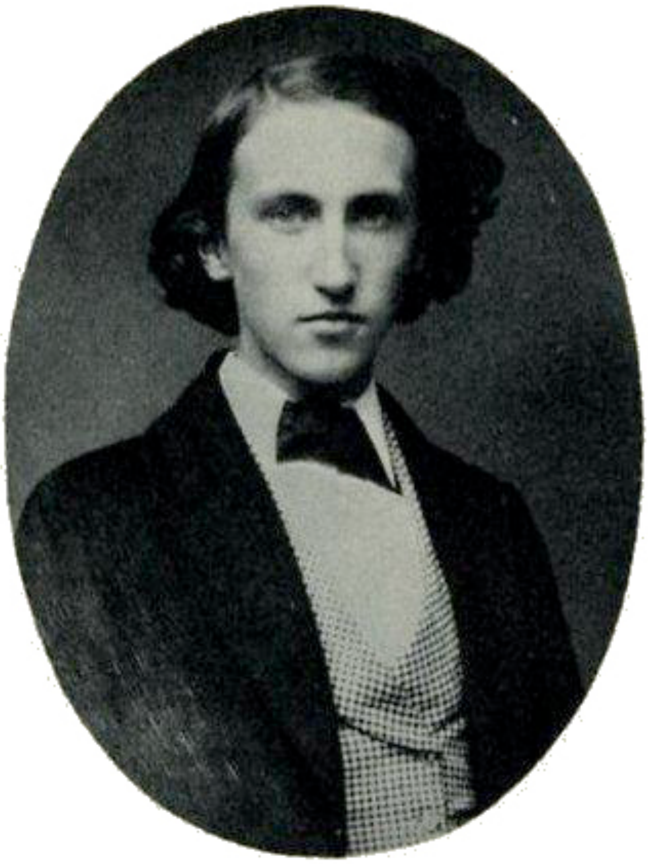
$$\left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho \mathbf{u} S_\mathrm{A}\right) = \rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S} + \rho\, \mathcal{S}^{S_\mathrm{A}} \tag{A.21.8}$$

we are ignoring $\mathcal{S}^{S_\mathrm{A}}$, the non-conservative source term. This non-conservative source term is due to *biogeochemical processes*, for example, the remineralization of biological material; the turning of particulate matter into dissolved seasalt.

For numerical integrations of an ocean model that exceed about a century, this neglect will be significant, leading to errors in the "thermal wind" 1.35 times as large as those described above. For shorter numerical integrations, the errors will be small. For small time, the important thing is that the expression for density is being called with Absolute Salinity as the salinity argument, not Reference or Practical Salinity. Over the first few decades of integration the errors will be small, and then they will build to be 1.35 times those in **Fig. A.5.1** above.

Who was J. W. Gibbs?





Josiah Willard Gibbs (February 11, 1839 – April 28, 1903) was an American scientist who made important theoretical contributions to physics, chemistry, and mathematics. His work on the applications of thermodynamics was instrumental in transforming physical chemistry into a rigorous deductive science. Together with James Clerk Maxwell and Ludwig Boltzmann, he created statistical mechanics (a term that he coined), explaining the laws of thermodynamics as consequences of the statistical properties of large ensembles of particles. Gibbs also worked on the application of Maxwell's equations to problems in physical optics. As a mathematician, he invented modern vector calculus (independently of the British scientist Oliver Heaviside, who carried out similar work during the same period).

In 1863, Yale awarded Gibbs the first American doctorate in engineering. After a three-year sojourn in Europe, Gibbs spent the rest of his career at Yale, where he was professor of mathematical physics from 1871 until his death. Working in relative isolation, he became the earliest theoretical scientist in the United States to earn an international reputation and was praised by Albert Einstein as "the greatest mind in American history".

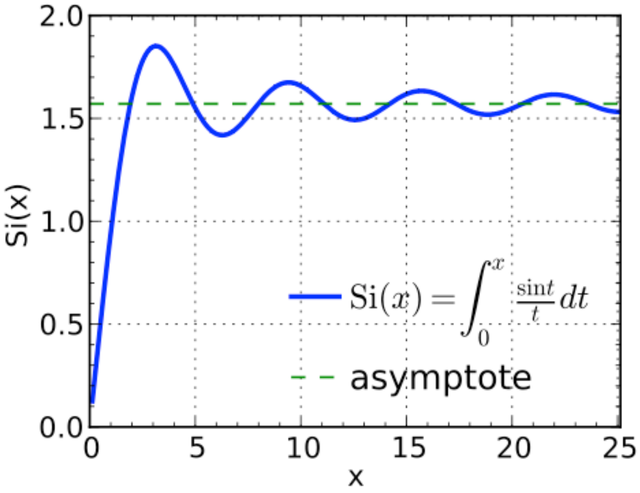
In 1897 he was elected a Member of the National Academy of Sciences in the USA, and as a foreign member of the Royal Society of London, and in 1901 Gibbs received what was then considered the highest honor awarded by the international scientific community, the Copley Medal of the Royal Society of London, "for his contributions to mathematical physics". But Gibbs was so retiring he had the US naval attaché in London collect the medal on his behalf.

Commentators and biographers have remarked on the contrast between Gibbs's quiet, solitary life in turn of the century New England and the great international impact of his ideas. Though his work was almost entirely theoretical, the practical value of Gibbs's contributions became evident with the development of industrial chemistry during the first half of the 20th century. According to Robert A. Millikan, in pure science Gibbs "did for statistical mechanics and for thermodynamics what Laplace did for celestial mechanics and Maxwell did for electrodynamics, namely, made his field a well-nigh finished theoretical structure."

Maxwell was an admirer and collaborator of Gibbs, and Maxwell's early death in 1879, at the age of 48, precluded further collaboration between him and Gibbs. The joke later circulated in New Haven that "only one man lived who could understand Gibbs's papers. That was Maxwell, and now he is dead."

When Dutch physicist J. D. van der Waals received the 1910 Nobel Prize "for his work on the equation of state for gases and liquids" he acknowledged the great influence of Gibbs's work on that subject. Max Planck received the 1918 Nobel Prize for his work on quantum mechanics, particularly his 1900 paper on Planck's law for quantized black-body radiation. That work was based largely on the thermodynamics of Kirchhoff, Boltzmann, and Gibbs. Planck declared that Gibbs's name "not only in America but in the whole world will ever be reckoned among the most renowned theoretical physicists of all times."

The “Gibbs Phenomenon” is another well-known example of his influence; this being the sine integral showing the overshoot and ringing of a Fourier Series approximation to a step function.



Basic Thermodynamic Concepts: internal energy, enthalpy and PdV work

Consider a fluid in a piston arrangement shown below. The fluid receives an amount of heat Q and mechanical work is done on the fluid at the rate W. The internal energy of the fluid U, changes by the amount $\Delta U = Q + W$.

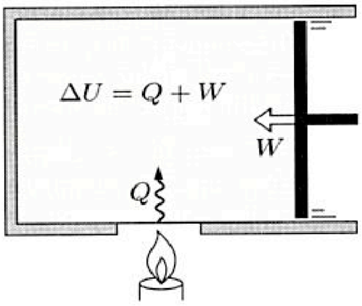


Figure 1.7. The total change in the energy of a system is the sum of the heat added to it and the work done on it.

Internal energy u represents (1) the kinetic energy involved in the vibration of molecules plus (2) the potential energy of chemical bonds and electrostatic charges. For liquids, and especially for water, this second aspect to internal energy is extremely important, while for a perfect gas, only the first part counts. Understanding thermodynamics from the scale of molecular behaviour is the field called "statistical thermodynamics" and we will not touch on this in this course.

The most common type of work W done on or by a fluid is the work done by compression or expansion, as in the following figure. This is how a car internal combustion engine extracts useful work from the high pressure gas that results from igniting the fuel-air mixture in an engine cylinder.

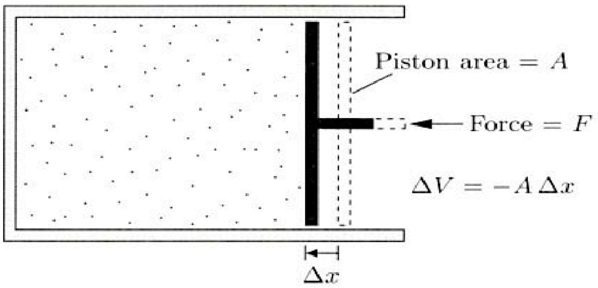


Figure 1.8. When the piston moves inward, the volume of the gas changes by ΔV (a negative amount) and the work done on the gas (assuming quasistatic compression) is $-P\Delta V$.

For infinitesimal changes we can write $\mathrm{d}U + P\mathrm{d}V = \delta Q$. Defining enthalpy H as $H = U + PV$ our attempt at writing down "energy conservation" so far can be written as

$$\mathrm{d}H - V\,\mathrm{dP} = \delta Q\,. \qquad (\sim\text{B.1a})$$

To motivate enthalpy H consider how much energy is required to magically create a blob of fluid out of nothing, and place it at its present location at pressure P.

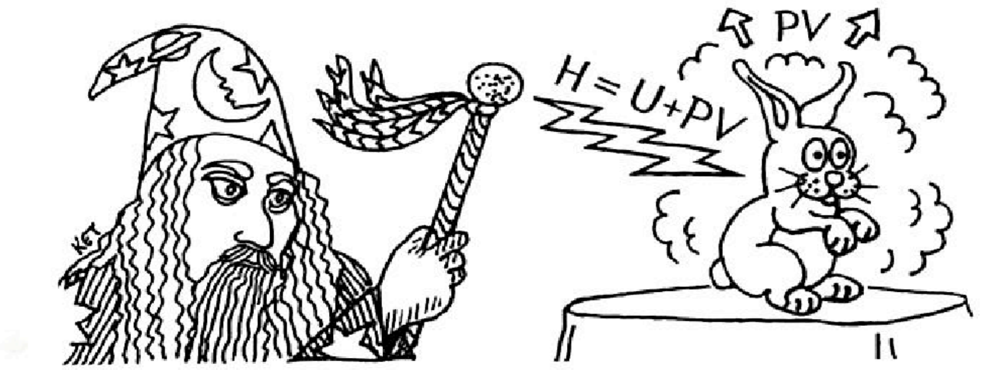


Figure 1.15. To create a rabbit out of nothing and place it on the table, the magician must summon up not only the energy U of the rabbit, but also some additional energy, equal to PV, to push the atmosphere out of the way to make room. The *total* energy required is the **enthalpy**, $H = U + PV$.

Entropy and the Second Law of Thermodynamics

A "closed system", such as the piston illustration on the previous page, is one where there is exchange of heat with the environment, and there is mechanical work done between the system and the environment, but there is no exchange of mass of any species. That is, for seawater, a "closed system" is a seawater parcel with fixed mass of both water and of salt, and having no exchange of water or salt with the surrounding fluid.

We begin by repeating our progress so far with the conservation of energy for a "closed system", but now written in terms of "specific" variables, that is variables that represent the amount of stuff per unit mass of seawater,

$$\mathrm{d}h - v\,\mathrm{dP} = \delta q \,. \tag{\sim B.1b}$$

For a "closed system" the Second Law of Thermodynamics states that

1. there is a <u>state variable</u> entropy $\eta = \eta\left(S_{\mathrm{A}}, T, P\right)$ whose infinitesimal changes obey
$$\mathrm{d}\eta = \frac{\delta q}{T}, \qquad \textit{for a closed system} \qquad (2^{\mathrm{nd}}\_\mathrm{Law})$$
2. and that irreversible processes (like diffusion and turbulent mixing) always result in the <u>production</u> entropy.

Entropy represents the amount of "disorder" in a system, and things naturally become more disordered in nature.

Note that δq itself is a complicated animal (which I passionately dislike). It is not the divergence of a flux; for example the dissipation of turbulent kinetic energy, ε, is part of δq. I emphasise that this dissipation ε heats the fluid but it is not the divergence of a heat flux. This nasty nature of δq is why it is written as δq rather than $\mathrm{d}q$. δq is <u>not</u> a total differential and q is <u>not</u> a state variable, that is $q \neq q\left(S_{\mathrm{A}}, T, P\right)$.

We can combine Eqns. (~B.1b) and (2^{nd}_Law) to find

$$\mathrm{d}h - v\,\mathrm{dP} = T\mathrm{d}\eta \qquad \textit{for a closed system} \qquad (\mathrm{Fundamental\_Closed})$$

This is the Fundamental Thermodynamic Relation for a closed system; it applies when there are no variations of Absolute Salinity (e.g. it applies to a lake). It is a differential relationship between three state variables, specific enthalpy, specific volume and specific entropy.

The Fundamental Thermodynamic Relation (or Gibbs relation)

Now we will generalize this relationship to an "open system" where the system exchanges not only heat and work energy with its environment, but it also exchanges mass. That is, a seawater parcel that is an "open system" exchanges not only "heat" and "work", both also water and salt with its environment.

Consider a situation where we have a seawater parcel exchanging water and salt with its environment at constant temperature and pressure. It is simplest to assume that there is no change in the parcel's total mass. Specifically, envisage two seawater parcels that are in contact with each other, having different Absolute Salinities but the same temperature and pressure. A small part of each parcel is now exchanged with the other parcel, with the amount exchanged in both directions having the same mass.

We now define the "system" as being one of these two seawater parcels. If the system were closed we would have the relation $\mathrm{d}h - v\,\mathrm{dP} = T\mathrm{d}\eta$ but now the change in the seawater sample's enthalpy and entropy must incorporate the change in the Absolute Salinity $\mathrm{d}S_\mathrm{A}$. By Taylor series expansion of $h(S_\mathrm{A},T,P)$ and $\eta(S_\mathrm{A},T,P)$, the changes in enthalpy and entropy are related to those of the corresponding closed system by

$$\mathrm{d}h = \mathrm{d}h^{\mathrm{closed}} + \left.\frac{\partial h}{\partial S_\mathrm{A}}\right|_{T,P} \mathrm{d}S_\mathrm{A} \,, \qquad (\mathrm{d}h)$$

$$\mathrm{d}\eta = \mathrm{d}\eta^{\mathrm{closed}} + \left.\frac{\partial \eta}{\partial S_\mathrm{A}}\right|_{T,P} \mathrm{d}S_\mathrm{A} \,. \qquad (\mathrm{d}\eta)$$

We know that $\mathrm{d}h^{\mathrm{closed}} - v\mathrm{dP} = T\mathrm{d}\eta^{\mathrm{closed}}$ and these three equations can be combined to find

$$\mathrm{d}h - v\mathrm{dP} = T\mathrm{d}\eta + \left(\left.\frac{\partial h}{\partial S_\mathrm{A}}\right|_{T,P} - T\left.\frac{\partial \eta}{\partial S_\mathrm{A}}\right|_{T,P} \right)\mathrm{d}S_\mathrm{A} \,. \qquad (\mathrm{d}h - T\mathrm{d}\eta)$$

This is the Fundamental Thermodynamic Relation. We can write it in more familiar nomenclature once we have defined the Gibbs function (also called “free enthalpy” and sometimes “free energy”) by

$$\boxed{g(S_\mathrm{A},T,P) = g \equiv h - T\eta \equiv u + Pv - T\eta} \,. \qquad (\text{definition\_of\_g})$$

We also use the symbol μ for the *relative chemical potential of seawater* defined as the partial derivative of the Gibbs function with respect to Absolute Salinity,

$$\mu = \left.\frac{\partial g}{\partial S_\mathrm{A}}\right|_{T,P} \qquad (\text{or } \mu = g_{S_\mathrm{A}}). \qquad (\text{rel chem pot})$$

This gives the usual form of the Fundamental Thermodynamic Relation (FTR)

$$\boxed{\mathrm{d}u + (p+P_0)\mathrm{d}v = \mathrm{d}h - v\mathrm{d}P = (T_0+t)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}} \,. \qquad (\text{FTR})$$

Here we have written the Absolute Pressure P as $p + P_0$ where $P_0 \equiv 101325$ Pa is the pressure of one standard atmosphere and p is the “sea pressure”, and we have written the Absolute Temperature $T = T_0 + t$ as the sum of the Celsius zero point $T_0 \equiv 273.15$ K and the temperature t in degrees Celsius.

In Tutorial class you will be asked to prove that (using $g = g(S_\mathrm{A},T,P)$)

$$\eta = -g_T, \quad v = g_P \quad \text{and} \quad c_p = \left.\frac{\partial h}{\partial T}\right|_{S_\mathrm{A},P} = -(T_0+t)g_{TT} \,. \qquad (\eta, v \text{ and } c_p)$$

The Gibbs function is a thermodynamic potential, from which all thermodynamic properties can be found by simple operations such as differentiation.

The alternative name of “free enthalpy” comes from considering again the amount of energy required to create our seawater parcel out of nothing. The total amount of energy required per unit mass is h but some of this energy, namely $T\eta$, can be extracted from the environment if the parcel is created slowly enough so it is always at the temperature T of the environment.

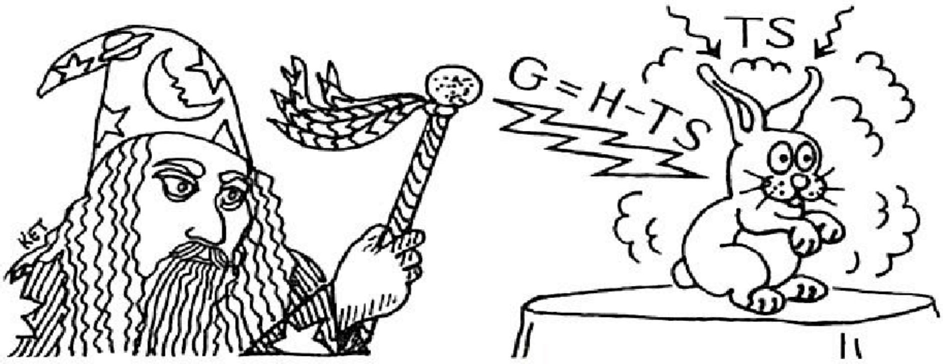


Figure 5.1. To create a rabbit out of nothing and place it on the table, the magician need not summon up the entire enthalpy, $H = U + PV$. Some energy, equal to TS, can flow in spontaneously as heat; the magician must provide only the difference, $G = H - TS$, as work.

Review of the last lecture

We learnt that the Practical Salinity variable, defined in 1980, is essentially a measure of the electrical conductivity seawater, but is blind to spatial variations of the concentrations of nutrients which affect the density and the electrical conductivity of a seawater sample differently to how the major dissolved ions affect density and conductivity.

This has now been addressed, and beginning in 2010 oceanographers have a new variable, Absolute Salinity, S_A, which better represents thermodynamic quantities such as density. This recent definition of seawater salinity and the Gibbs function of seawater goes by the name of the

International Thermodynamic Equation Of Seawater – 2010,
or TEOS-10, see www.TEOS-10.org.

We derived the Gibbs Relation, or Fundamental Thermodynamic Relation

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v \;=\; \mathrm{d}h - v\,\mathrm{d}P \;=\; \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}}\,. \qquad \text{(FTR)}$$

which is a relationship between the total differentials of several state variables, u, v, h, η and μ.

We defined the Gibbs function in terms of enthalpy and entropy by

$$\boxed{g\left(S_\mathrm{A},T,P\right) = g \equiv h - T\eta \;\equiv\; u + Pv - T\eta}\,. \qquad \text{(definition\_of\_g)}$$

All the thermodynamic properties of a fluid can be derived from this one "parent" function, $g\left(S_\mathrm{A},t,p\right)$, by simple mathematical operations such as differentiation. Hence the fundamental importance of the Gibbs function for a substance.

As for understanding the difference between enthalpy h, internal energy u and the Gibbs function g we learnt that enthalpy is a better estimate of the total amount of thermodynamic energy in a fluid parcel, recognizing that the parcel's creation involved pushing its environment out of the way (because it occupies volume v (per unit mass) at ambient Absolute Pressure P). Enthalpy h is useful for understanding processes that occur at constant pressure, while internal energy u is useful for understanding processes that occur at constant volume.

The Gibbs function $g \equiv h - T\eta$ is the part of enthalpy h that is "free" or "available". The part $T\eta$ of h is not available "for sale" on the energy market, because it is not "available" to do any useful work. Hence the Gibbs function is sometimes called "free enthalpy" or "free energy". The adjective "available" makes sense if you are selling the energy of the seawater parcel to someone who wants to use the energy of the parcel to do some useful work in say an energy cycle machine. The adjective "free" makes sense if you consider yourself to be the magician, creating the seawater parcel out of nothing, and getting a free ride from the environment to the extent $T\eta$.

Warning on Nomenclature. For the state variables such as u, v, h, η we use lower case letters when they are per unit mass ("specific" variables), and upper case when they represent the total amount of that quantity in a mass of fluid of mass M. But the use of upper case P and T is different. These upper case letters stand for Absolute Pressure (in $\mathrm{Pa} = \mathrm{N\,m^{-2}}$) and Absolute Temperature (K), while the lower case letters p and t are for $p = P - P_0$ (often in units of dbar) and $t = T - T_0$ (in degrees Celsius).

$P_0 \equiv 101\,325$ Pa (= 10.1325 dbar), and
$T_0 \equiv 273.15$ K.

A rough derivation of the First Law of Thermodynamics for a pure substance

For a pure fluid in which there is no dissolved material (such as pure water with zero Absolute Salinity) the derivation of the First Law of Thermodynamics usually starts with our Eqn. (~B.1b), namely $\mathrm{d}h - v\mathrm{dP} = \delta q$, written in terms of material derivatives as (where δq is now "per unit volume" rather than "per unit mass")

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \frac{\delta q}{\mathrm{d}t}. \qquad \textit{for pure water} \text{ (B.1)}$$

Now we have to guess what the nasty, obnoxious, odious, $\delta q/\mathrm{d}t$ term might be. We know that there is such a thing as the molecular flux of heat $\mathbf{F}^{\mathrm{Q}} = -\rho c_p k^T \nabla T$ (where k^T is the molecular diffusivity of temperature) whose (negative) divergence one might imagine should be part of $\delta q/\mathrm{d}t$. We know there is such a thing as the radiative heat flux $\mathbf{F}^{\mathrm{R}}$ whose (negative) divergence should also be part of $\delta q/\mathrm{d}t$. We also know that when the kinetic energy of turbulent motions is dissipated by the molecular viscosity, energy changes from its kinetic form to its "heat" form", and the fluid warms up as a result. So we do the sensible thing and add this term to $\delta q/\mathrm{d}t$. This term is written as $\rho\varepsilon$ where ε is the rate of dissipation of kinetic energy per unit mass of fluid. After this educated guesswork we have the First Law of Thermodynamics *for a pure substance,*

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \frac{\delta q}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon. \qquad \textit{for pure water} \text{ (B.2)}$$

So far so good; this educated guesswork has allowed us to arrive at a correct result in this simple case for a fluid that is a *pure substance.*

But we have actually assumed that the molecular flux of heat appears on the right-hand side as $\nabla\cdot\left(\rho c_p k^T \nabla T\right)$. We have no right to assume that. We cannot rule out the form $\rho c_p k^T \nabla\cdot\nabla T$ for example, for this term. So, what will turn out to be the key feature of Eqn. (B.2), namely that apart from $\rho\varepsilon$ the other terms on the right-hand side appear as flux divergences, we have actually assumed, not proven. This is not satisfactory and we must do better.

A false start at deriving the First Law of Thermodynamics for seawater

But lets stay with this rough, hand-waving approach for a little bit longer, and see how we can get with deriving the First Law of Thermodynamics for seawater when there *are* spatial variations of Absolute Salinity. The same traditional discussion of the First Law of Thermodynamics involving the "heating" and the application of compression work (as in Eqn. (~B.1a) above), and now the change of salinity to a fluid parcel shows that the change of enthalpy of the fluid parcel is given by ($\mu - \left[T_0 + t\right]\mu_T$ being $h_{S_\mathrm{A}}\big|_{T,P}$)

$$\mathrm{d}H - V\mathrm{d}P = \delta Q + \left(\mu - [T_0 + t]\mu_T\right) M\,\mathrm{d}S_\mathrm{A}, \qquad \text{(B.3)}$$

where M is the mass of the fluid parcel. When written in terms of the specific enthalpy h, and δQ per unit volume (δq), this equation becomes (using $\rho \mathrm{d}S_\mathrm{A}/\mathrm{d}t = -\nabla\cdot\mathbf{F}^S$)

$$\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}p}{\mathrm{d}t}\right) = \frac{\delta q}{\mathrm{d}t} - \left(\mu - \left[T_0 + t\right]\mu_T\right)\nabla\cdot\mathbf{F}^{\mathrm{S}}. \qquad \text{(B.4)}$$

Does this help with the task of constructing an expression for the right-hand side of (B.4) in terms of the dissipation of mechanical energy and the molecular, radiative and boundary fluxes of "heat" and salt? If the "heating" term $\delta q/\mathrm{d}t$ in Eqn. (B.4) were the same as in the pure water case, Eqn. (B.2), then we would have successfully derived the First Law of Thermodynamics in a saline ocean via this route. However, we will now show that $\delta q/\mathrm{d}t$ in Eqn. (B.4) is not the same as that in the pure water case, Eqn. (B.2).

Substituting the expression for $\delta q/\mathrm{d}t$ from (B.2) into the right-hand side of (B.4) we find that the right-hand side is not the same as the First Law of Thermodynamics (B.19) which we derive below (this comparison involves using the correct expression (B.27)) for the molecular flux $\mathbf{F}^{\mathrm{Q}}$). The two versions of the First Law of Thermodynamics are different by

$$\mathbf{F}^{\mathrm{S}}\cdot\nabla\big(\mu-\big[T_0+t\big]\mu_T\big) \;+\; \nabla\cdot\left[\frac{B'\mu_{S_{\mathrm{A}}}}{\rho\, k^{S}\big[T_0+t\big]}\mathbf{F}^{\mathrm{S}}\right]. \tag{B.5}$$

Note that the fact that the right-hand side of Eqn. (B.4) is not the divergence of a flux was already apparent in that equation; this is a damning shortcoming. This inconsistency means that the rather poorly defined "rate of heating" $\delta q/\mathrm{d}t$ must be different in the saline case than in the pure water situation by this amount. We know of no way of justifying this difference, so we conclude that any attempt to derive the First Law of Thermodynamics via this route involving the loosely defined "rate of heating" $\delta q/\mathrm{d}t$ is doomed to failure. This is not to say that Eqn. (B.4) is incorrect. Rather, the point is that it is not useful, since $\delta q/\mathrm{d}t$ cannot be deduced directly by physical reasoning.

In particular, the expression in (B.5) is not the divergence of a flux and so when two parcels are mixed at constant pressure, enthalpy will not be conserved (see later). We were able to correctly guess the form of the right-hand side of the First Law of Thermodynamics in the case of pure substance, but in the presence of salinity gradients, our intuition fails us. Let's stop this guessing game and derive the First Law of Thermodynamics properly.

The proper derivation of the First Law of Thermodynamics for seawater

Since there is no way of deriving the First Law of Thermodynamics that involves the "heating" term $\delta q / \mathrm{d}t$, we follow Landau and Lifshitz (1959) and de Groot and Mazur (1984) and derive the First Law via the following circuitous route. Rather than attempting to guess the form of the molecular forcing terms in this equation directly, we first construct a conservation equation for the total energy, being the sum of the kinetic, gravitational potential and internal energies. It is in this equation that we insert the molecular fluxes of heat and momentum and the radiative and boundary fluxes of heat. We know that the evolution equation for total energy must have the conservative form, and so we insist that the forcing terms in this equation appear as the divergence of fluxes.

Having formed the conservation equation for total energy, the known evolution equations for two of the types of energy, namely the kinetic and gravitational potential energies, are subtracted, leaving a prognostic equation for either internal energy or enthalpy, that is, the First Law of Thermodynamics.

We start by developing the evolution equations for gravitational potential energy and for kinetic energy (via the momentum equation). The sum of these two evolution equations is noted. We then step back a little and consider the simplified situation where there are no molecular fluxes of heat and salt and no effects of viscosity and no radiative or boundary heat fluxes. In this "adiabatic" limit we are able to develop the conservation equation for total energy, being the sum of internal energy, kinetic energy and gravitational potential energy. To this equation we introduce the molecular, radiative and boundary flux divergences. Finally the First Law of Thermodynamics is found by subtracting from this total energy equation the conservation statement for the sum of the kinetic and gravitational potential energies.

We start by writing the Fundamental Thermodynamic Relation (FTR) in terms of material derivatives following the instantaneous motion of a fluid parcel $\mathrm{d}/\mathrm{d}t = \partial/\partial t|_{x,y,z} + \mathbf{u}\cdot\nabla$,

$$\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p + P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t} = \frac{\mathrm{d}h}{\mathrm{d}t} - \frac{1}{\rho}\frac{\mathrm{d}P}{\mathrm{d}t} = \left(T_0 + t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} \quad . \tag{B.6}$$

Gravitational potential energy

If the gravitational acceleration g is taken to be constant the gravitational potential energy per unit mass with respect to the height $z = 0$ is simply gz. Allowing g to be a function of height means that the gravitational potential energy per unit mass Φ with respect to some fixed height z_0 is defined by

$$\Phi = \int_{z_0}^{z} g(z')\, dz'. \tag{B.7}$$

At a fixed location in space Φ is independent of time while its spatial gradient is given by $\nabla\Phi = g\mathbf{k}$ where $\mathbf{k}$ is the unit vector pointing upwards in the vertical direction. The evolution equation for Φ is then readily constructed as

$$\left(\rho\Phi\right)_t + \nabla\cdot\left(\rho\Phi\mathbf{u}\right) = \rho\frac{\mathrm{d}\Phi}{\mathrm{d}t} = \rho g w, \tag{B.8}$$

where w is the vertical component of the three-dimensional velocity, that is $w = \mathbf{u}\cdot\mathbf{k}$. (Clearly in this section g is the gravitational acceleration, not the Gibbs function). Note that this local balance equation for gravitational potential energy is not in the form

$$\left(\rho C\right)_t + \nabla\cdot\left(\rho\mathbf{u}C\right) = \rho\frac{\mathrm{d}C}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{C}. \tag{A.8.1}$$

that is required of a conservative variable, since the right-hand side of (B.8) is not minus the divergence of a flux.

Momentum evolution equation

The momentum evolution equation is derived in many textbooks including Landau and Lifshitz (1959), Batchelor (1970), Gill (1982) and Griffies (2004). The molecular viscosity appears in the exact momentum evolution equation in the rather complicated expressions appearing in equations (3.3.11) and (3.3.12) of Batchelor (1970). We ignore the term that depends on the product of the kinematic viscosity ν^{visc} and the velocity divergence $\nabla\cdot\mathbf{u}$ (following Gill (1982)), so arriving at

$$\rho\frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} + f\,\mathbf{k}\times\rho\mathbf{u} = -\nabla P - \rho g\mathbf{k} + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\widehat{\nabla\mathbf{u}}\right), \tag{B.9}$$

where f is the Coriolis frequency, ν^{visc} is the kinematic viscosity and $\widehat{\nabla\mathbf{u}}$ is twice the symmetrized velocity shear, $\widehat{\nabla\mathbf{u}} = \left(\partial u_i/\partial x_j + \partial u_j/\partial x_i\right)$. The centripetal acceleration associated with the coordinate system being on a rotating planet can be taken into account by an addition to the gravitational acceleration in (B.9) (Griffies (2004)).

Kinetic energy evolution equation

The kinetic energy evolution equation is found by taking the scalar product of Eqn. (B.9) with $\mathbf{u}$ giving

$$\begin{aligned}&\left(\rho\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right)\\ &\quad = \rho\,\mathrm{d}\left(\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u}\right)/\mathrm{d}t \;=\; -\mathbf{u}\cdot\nabla P - \rho g w + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}[\mathbf{u}\cdot\mathbf{u}]\right) - \rho\varepsilon,\end{aligned} \tag{B.10}$$

where the dissipation of mechanical energy ε is the positive definite quantity

$$\varepsilon \equiv \tfrac{1}{2}\nu^{\mathrm{visc}}\left(\widehat{\nabla\mathbf{u}}\cdot\widehat{\nabla\mathbf{u}}\right). \tag{B.11}$$

Evolution equation for the sum of kinetic and gravitational potential energies

The evolution equation for total mechanical energy $\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$ is found by adding Eqns. (B8) and (B10) giving

$$\begin{aligned}&\left(\rho\left[\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right]\right)_t + \nabla\cdot\left(\rho\mathbf{u}\left[\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right]\right)\\ &\quad = \rho\,\mathrm{d}\left(\tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right)/\mathrm{d}t \;=\; -\mathbf{u}\cdot\nabla P + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right) - \rho\varepsilon.\end{aligned} \tag{B.12}$$

Notice that the term $\rho g w$ which has the role of exchanging energy between the kinetic and gravitational potential forms has cancelled when these two evolution equations were added.

Conservation equation for total energy $\mathcal{E}$ in the absence of molecular fluxes

In the absence of molecular or other irreversible processes (such as radiation of heat), both the specific entropy η and the Absolute salinity S_A of each fluid parcel is constant following the fluid motion so that the right-hand side of the FTR, Eqn. (B.6), is zero and the material derivative of internal energy satisfies $\mathrm{d}u/\mathrm{d}t = -\left(p+P_0\right)\mathrm{d}v/\mathrm{d}t$ so that the internal energy changes only as a result of the work done in compressing the fluid parcel. Realizing that $v = \rho^{-1}$ and using the continuity Eqn. (A.8.1) in the form $\mathrm{d}\rho/\mathrm{d}t + \rho\nabla\cdot\mathbf{u} = 0$, $\mathrm{d}u/\mathrm{d}t$ can be expressed in this situation of no molecular, radiative or boundary fluxes as $\mathrm{d}u/\mathrm{d}t = -\rho^{-1}\left(p+P_0\right)\nabla\cdot\mathbf{u}$. Adding this equation to the inviscid, non-dissipative version of the mechanical energy equation, Eqn. (B.12), gives

$$\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t = -\nabla\cdot\left(\left[p+P_0\right]\mathbf{u}\right), \quad \textit{no molecular fluxes} \qquad \text{(B.13)}$$

where the total energy

$$\mathcal{E} = u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi \qquad \text{(B.14)}$$

is defined as the sum of the internal, kinetic and gravitational potential energies.

Note that this is the first variable that we have considered so far which has the right-hand side being the divergence of a flux. This was not true of the gravitational potential energy, Eqn. (B.8), it was not rue of the kinetic energy equation, (B.10), and it was not true of the sum of the kinetic and gravitational potential energies, Eqn. (B.12). Note that the divergence-as-right-hand-side is not true of either (B.8), (B.10) or (B.12), even for flows without molecular fluxes. That fact that we have now found a variable, $\mathcal{E}$, whose evolution equation (B.13) has a right-hand-side which is the divergence of something in this adiabatic isohaline limit is extremely important. For example, if we substitute enthalpy h for internal energy u in the quantity $\mathcal{E}$, we lose this property.

Conservation equation for total energy in the presence of molecular fluxes

Now, following section 49 Landau and Lifshitz (1959) we need to consider how molecular fluxes of heat and salt and the radiation of heat will alter the simplified conservation equation of total energy (B.13). The molecular viscosity gives rise to a stress in the fluid represented by the tensor $\boldsymbol{\sigma}$, and the interior flux of energy due to this stress tensor is $\mathbf{u}\cdot\boldsymbol{\sigma}$ so that there needs to be the additional term $-\nabla\cdot\left(\mathbf{u}\cdot\boldsymbol{\sigma}\right)$ added to the right-hand side of the total energy conservation equation. Consistent with Eqn. (B.9) above we take the stress tensor to be $\boldsymbol{\sigma} = -\rho\nu^{\mathrm{visc}}\widehat{\nabla\mathbf{u}}$ so that the extra term is $\nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right)$. Also heat fluxes at the ocean boundaries and by radiation $\mathbf{F}^{\mathrm{R}}$ and molecular diffusion $\mathbf{F}^{\mathrm{Q}}$ necessitate the additional terms $-\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}}$. At this stage we have not specified the form of the molecular diffusive flux of heat $\mathbf{F}^{\mathrm{Q}}$ in terms of gradients of temperature and Absolute Salinity; this is done below in Eqn. (B.24). The total energy conservation equation in the presence of molecular, radiative and boundary fluxes is

$$\begin{aligned}\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{E}\right) = \rho\,\mathrm{d}\mathcal{E}/\mathrm{d}t &= -\nabla\cdot\left(\left[p+P_0\right]\mathbf{u}\right) - \nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} \\ &\quad + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right).\end{aligned} \qquad \text{(B.15)}$$

The right-hand side of the $\mathcal{E}$ conservation equation (B.15) is the divergence of a flux, ensuring that total energy $\mathcal{E}$ is both a "conservative" variable and an "isobaric conservative" variable (see appendix A.8 for the definition of these characteristics).

Two alternative forms of the conservation equation for total energy

Another way of expressing the total energy equation (B.15) is to write it in a quasi-divergence form, with the temporal derivative being of $\rho\mathcal{E} = \rho\left(u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi\right)$ while the divergence part of the left-hand side is based on a <u>different</u> quantity, namely the Bernoulli function $\mathcal{B} = h + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$. This form of the total energy equation is

$$\left(\rho\mathcal{E}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{B}\right) = -\nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right). \qquad \text{(B.16)}$$

In an ocean modelling context, it is rather strange to contemplate the energy variable that is advected through the face of a model grid, $\mathcal{B}$, to be different to the energy variable that is changed in the grid cell, $\mathcal{E}$. Hence this form of the total energy equation has not proved popular.

A third way of expressing the total energy equation (B.15) is to write the left-hand side in terms of only the Bernoulli function $\mathcal{B} = h + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$ so that the prognostic equation for the Bernoulli function is

$$\left(\rho\mathcal{B}\right)_t + \nabla\cdot\left(\rho\mathbf{u}\mathcal{B}\right) = \rho\,\mathrm{d}\mathcal{B}/\mathrm{d}t = P_t - \nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right). \qquad \text{(B.17)}$$

When the flow is steady, and in particular, when the pressure field is time invariant at every point in space, this Bernoulli form of the total energy equation has the desirable property that $\mathcal{B}$ is conserved following the fluid motion in the absence of radiative, boundary and molecular fluxes. Subject to this steady-state assumption, the Bernoulli function $\mathcal{B}$ possesses the "potential" property. The negative aspect of this $\mathcal{B}$ evolution equation (B.17) is that in the more general situation where the flow is unsteady, the presence of the P_t term means that the Bernoulli function does not behave as a conservative variable because the right-hand side of (B.17) is not the divergence of a flux. In this general non-steady situation $\mathcal{B}$ is "isobaric conservative" but is not a "conservative" variable nor does it posses the "potential" property.

Noting that the total energy $\mathcal{E}$ is related to the Bernoulli function by $\mathcal{E} = \mathcal{B} - \left(p + P_0\right)/\rho$ and even if we take the whole ocean to be in a steady state so that $\mathcal{B}$ has the "potential" property, it is clear that $\mathcal{E}$ does not have the "potential" property in this situation. That is, if a seawater parcel moves from say 2000 dbar to 0 dbar without exchange of material or heat with its surroundings and with $P_t = 0$ everywhere, then $\mathcal{B}$ remains constant while the parcel's total energy $\mathcal{E}$ changes by the difference in the quantity $-\left(p + P_0\right)/\rho$ between the two locations. Hence we conclude that even in a steady ocean $\mathcal{E}$ does not possess the "potential" property. This means that total energy $\mathcal{E}$ is useless as far as being a marker of fluid flow.

When the viscous production term $\nabla\cdot\left(\rho\nu^{\mathrm{visc}}\nabla\tfrac{1}{2}\left[\mathbf{u}\cdot\mathbf{u}\right]\right)$ in the above equations is integrated over the ocean volume, the contribution from the sea surface is the power input by the wind stress $\boldsymbol{\tau}$, namely the area integral of $\boldsymbol{\tau}\cdot\mathbf{u}^{\mathrm{surf}}$ where $\mathbf{u}^{\mathrm{surf}}$ is the surface velocity of the ocean.

Obtaining the First Law of Thermodynamics by subtraction

The evolution equation (B.12) for the sum of kinetic and gravitational potential energies is now subtracted from the total energy conservation equation (B.15) giving

$$\left(\rho u\right)_t + \nabla\cdot\left(\rho\mathbf{u}u\right) = \rho\,\mathrm{d}u/\mathrm{d}t = -\left(p + P_0\right)\nabla\cdot\mathbf{u} - \nabla\cdot\mathbf{F}^{\mathrm{R}} - \nabla\cdot\mathbf{F}^{\mathrm{Q}} + \rho\varepsilon. \qquad \text{(B.18)}$$

Using the continuity equation in the form $\rho\mathrm{d}v/\mathrm{d}t = \nabla\cdot\mathbf{u}$ and the Fundamental Thermodynamic Relation (B.6), this equation can be written as

$$\boxed{\begin{aligned} \rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right) \\ &= -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon \end{aligned}} . \qquad \text{(B.19)}$$

which is the First Law of Thermodynamics.

The corresponding evolution equation for Absolute Salinity is (Eqn. (A.21.8))

$$\rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = \left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_\mathrm{A}\right) = -\nabla\cdot\mathbf{F}^\mathrm{S} + \rho\,S^{S_\mathrm{A}}, \qquad \text{(A.21.8)}$$

where $\mathbf{F}^\mathrm{S}$ is the molecular flux of salt and $\rho\,S^{S_\mathrm{A}}$ is the non-conservative source of Absolute Salinity due to the remineralization of particulate matter which we are going to ignore in this course. Hence, in this course we take the salt evolution equation to be

$$\boxed{\left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_\mathrm{A}\right) = \rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S}} , \qquad \textit{approximate}\ \text{(A.21.8a)}$$

For many purposes in oceanography the exact dependence of the molecular fluxes of heat and salt on the gradients of Absolute Salinity, temperature and pressure is unimportant, nevertheless, Eqns. (B.23) - (B.27) below list these molecular fluxes in terms of the spatial gradients of these quantities.

At first sight Eqn. (B.19) has little to recommend it; there is a non-conservative source term $\rho\varepsilon$ on the right-hand side and even more worryingly, the left-hand side is not ρ times the material derivative of any quantity as is required of a conservation equation of a conservative variable. It is this aspect of the left-hand side of the First Law of Thermodynamics, namely the presence of the $-\mathrm{d}P/\mathrm{d}t$ term that has scared oceanographers and held up thermodynamic progress for a century.

In summary, the approach used here to develop the First Law of Thermodynamics seems rather convoluted in that the conservation equation for total energy is first formed, and then the evolution equations for kinetic and gravitational potential energies are subtracted. Moreover, the molecular, radiative and boundary fluxes were included into the total energy conservation equation as separate deliberate flux divergences, rather than coming from an underlying basic conservation equation. This approach is adopted for the following reasons. First this approach ensures that the molecular, radiative and boundary fluxes do enter the total energy conservation equation (B.15) as the divergence of fluxes so that the total energy $\mathcal{E} = u + \tfrac{1}{2}\mathbf{u}\cdot\mathbf{u} + \Phi$ is guaranteed to be a conservative variable. This is essential. Second, it is rather unclear how one would otherwise arrive at the molecular fluxes of heat and salt on the right-hand side of the First Law of Thermodynamics since the direct approach which was attempted involved the poorly defined (and obnoxious) "rate of heating" $\delta q/\mathrm{d}t$ and did not lead us to the First Law.

Expressions for the molecular fluxes of heat and salt

The molecular fluxes of salt and heat, $\mathbf{F}^{\mathrm{S}}$ and $\mathbf{F}^{\mathrm{Q}}$, are now written in the general matrix form in terms of the thermodynamic "forces" $\nabla(-\mu/T)$ and $\nabla(1/T)$ as

$$\mathbf{F}^{\mathrm{S}} = A\nabla(-\mu/T) + B\nabla(1/T), \tag{B.21}$$

$$\mathbf{F}^{\mathrm{Q}} = B\nabla(-\mu/T) + C\nabla(1/T), \tag{B.22}$$

where A, B and C are three independent coefficients. The equality of the off-diagonal diffusion coefficients, B, results from the Onsager (1931a,b) reciprocity relation. When these fluxes are substituted into the First Law of Thermodynamics Eqn. (B.19) and this is written as an evolution equation for entropy, the Second Law constraint that the entropy production must be positive requires that $A > 0$ and that $C > B^2/A$.

The part of the salt flux that is proportional to $-\nabla S_{\mathrm{A}}$ is traditionally written as $-\rho k^S \nabla S_{\mathrm{A}}$ implying that $A = \rho k^S T / \mu_{S_{\mathrm{A}}}$. The molecular fluxes of salt and heat, $\mathbf{F}^{\mathrm{S}}$ and $\mathbf{F}^{\mathrm{Q}}$, can now be written in terms of the gradients of Absolute Salinity, temperature and pressure in the convenient forms

$$\mathbf{F}^{\mathrm{S}} = -\rho k^S \left(\nabla S_{\mathrm{A}} + \frac{\mu_P}{\mu_{S_{\mathrm{A}}}} \nabla P \right) - \left(\frac{\rho k^S T}{\mu_{S_{\mathrm{A}}}} \left(\frac{\mu}{T} \right)_T + \frac{B}{T^2} \right) \nabla T \,, \tag{B.23}$$

$$\mathbf{F}^{\mathrm{Q}} = -\frac{1}{T^2}\left(C - \frac{B^2}{A} \right) \nabla T + \frac{B\mu_{S_{\mathrm{A}}}}{\rho k^S T} \mathbf{F}^{\mathrm{S}} = -\rho c_p k^T \nabla T + \frac{B\mu_{S_{\mathrm{A}}}}{\rho k^S T} \mathbf{F}^{\mathrm{S}}, \tag{B.24}$$

where the fact that $C > B^2/A$ has been used to write the regular diffusion of heat down the temperature gradient as $-\rho c_p k^T \nabla T$ where k^T is the positive molecular diffusivity of temperature. These expressions involve the (strictly positive) molecular diffusivities of temperature and salinity (k^T and k^S) and the single cross-diffusion parameter B. The other parameters in these equations follow directly from the Gibbs function of seawater.

It is common to introduce a "reduced heat flux" by reducing the molecular flux of heat by $\partial h/\partial S_{\mathrm{A}}\big|_{T,p} \mathbf{F}^{\mathrm{S}} = (\mu - T\mu_T)\mathbf{F}^{\mathrm{S}}$, being the flux of enthalpy due to the molecular flux of salt. This prompts the introduction of a revised cross-diffusion coefficient defined by

$$B' \equiv B + \frac{\rho k^S T^3}{\mu_{S_{\mathrm{A}}}} \left(\frac{\mu}{T} \right)_T \,, \tag{B.25}$$

and in terms of this cross-diffusion coefficient Eqns. (B.23) and (B.24) can be written as

$$\mathbf{F}^{\mathrm{S}} = -\rho k^S \left(\nabla S_{\mathrm{A}} + \frac{\mu_P}{\mu_{S_{\mathrm{A}}}} \nabla P \right) - \frac{B'}{T^2} \nabla T \,, \tag{B.26}$$

and

$$\begin{aligned} \mathbf{F}^{\mathrm{Q}} - (\mu - T\mu_T)\mathbf{F}^{\mathrm{S}} &= -\rho c_p k^T \nabla T + \frac{B'\mu_{S_{\mathrm{A}}}}{\rho k^S T} \mathbf{F}^{\mathrm{S}} \\ &= -\rho c_p K^T \nabla T - \frac{B'\mu_{S_{\mathrm{A}}}}{T} \left(\nabla S_{\mathrm{A}} + \frac{\mu_P}{\mu_{S_{\mathrm{A}}}} \nabla P \right), \end{aligned} \tag{B.27}$$

where K^T, defined by $\rho c_p K^T = \rho c_p k^T + B'^2 / (AT^2)$, is a revised molecular diffusivity of temperature.

The term in (B.26) that is proportional to the pressure gradient ∇P represents "barodiffusion" as it causes a flux of salt down the gradient of pressure. The last term in (B.26) is a flux of salt due to the gradient of *in situ* temperature and is called the Soret effect, while the last term in the second line of Eqn. (B.27) is called the Dufour effect.

If the ocean were in thermodynamic equilibrium, its temperature would be the same everywhere, as would the chemical potentials of water and of each dissolved species; see Eqns. (B.21) and (B.22). Such a situation with $\mathbf{F}^{\mathrm{Q}} = \mathbf{F}^{\mathrm{S}} = 0$ would have entropy and the concentrations of each species being functions of pressure. Turbulent mixing acts very differently, tending to homogenize the concentration of each species and to make entropy constant, but in the process causing gradients in temperature and in the chemical potentials as functions of pressure. That is, turbulent mixing acts to maintain a non-equilibrium state. This difference between the roles of molecular versus turbulent mixing results from the symmetry breaking role of the gravity field; for example, in a laboratory without gravity, turbulent and molecular mixing would have indistinguishable effects.

Reference states

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

$$a_1 + a_2\left(T_0+t\right) + a_3 S_{\mathrm{A}} + a_4\left(T_0+t\right)S_{\mathrm{A}} \ . \qquad (2.6.2)$$

This is equivalent to saying that both enthalpy h and entropy η are unknown and unknowable up to linear functions of Absolute Salinity; enthalpy is unknown up to $a_1 + a_3 S_{\mathrm{A}}$ and entropy is unknown up to $-a_2 - a_4 S_{\mathrm{A}}$.

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

Now we can play

So we've spent 25 pages of lecture notes deriving the Fundamental Thermodynamic Relation and the First Law of Thermodynamics. Now it's time to play. Here is a revision of our underlying equations.

The Continuity Equation is

$$\boxed{\rho_t + \nabla\cdot\left(\rho\mathbf{u}\right) = 0}\ . \qquad \text{(A.21.2)}$$

The Fundamental Thermodynamic Relation is

$$\boxed{\mathrm{d}u + \left(p+P_0\right)\mathrm{d}v = \mathrm{d}h - v\,\mathrm{d}P = \left(T_0+t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}}\ . \qquad \text{(A.7.1)}$$

The First Law of Thermodynamics is

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) &= \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\end{aligned}}\ . \qquad \text{(B.19)}$$

The conservation equation of Absolute Salinity is

$$\boxed{\left(\rho S_\mathrm{A}\right)_t + \nabla\cdot\left(\rho\mathbf{u}S_\mathrm{A}\right) = \rho\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{S}}\ , \qquad \textit{approximate}\ \text{(A.21.8a)}$$

The definition of the Gibbs function

$$\boxed{g\left(S_\mathrm{A},T,P\right) = g \equiv h - T\eta \equiv u + Pv - T\eta}\ . \qquad \text{(definition\_of\_g)}$$

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

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

Enthalpy is "isobaric conservative"

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

$$\left(\rho h\right)_t + \nabla\cdot\left(\rho\mathbf{u}h\right) - \frac{\mathrm{d}P}{\mathrm{d}t} = -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\ . \qquad \text{(A.13.2)}$$

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

This result of non-equilibrium thermodynamics (it is non-equilibrium because of the finite size of the parcels and the finite property differences) has been known since the days of Gibbs in the nineteenth century, and it is of the utmost importance in oceanography. The fact that enthalpy is conserved when fluid parcels mix at constant pressure is the central result upon which all of our understanding of "heat fluxes" and of "heat content" in the ocean now rests.

As important as this result is, it does not follow that enthalpy is the best variable to represent "heat content" in the ocean. Enthalpy is actually a very poor representation of "heat content" in the ocean because it does not posses the "potential" property. It will be seen that potential enthalpy h^0 (referenced to zero sea pressure) is the best thermodynamic variable to represent "heat content" in the ocean.

Review of the past couple of lectures

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

$$\boxed{\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) = \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)}, \qquad \text{(B.6)}$$

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

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

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

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

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

We then looked at the First Law of Thermodynamics, namely

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t} - v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t} + \left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t} + \mu\frac{\mathrm{d}S_\mathrm{A}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^\mathrm{R} - \nabla\cdot\mathbf{F}^\mathrm{Q} + \rho\varepsilon\end{aligned}}\,. \qquad \text{(B.19)}$$

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

"isohaline", "adiabatic" and "isentropic"; reversible and irreversible processes

The adjective "isohaline" means "at constant salinity" and describes a process in which the Absolute Salinity of a fluid parcel is constant because $-\nabla\cdot\mathbf{F}^{\mathrm{S}}$ is zero.

The adjective "adiabatic" is traditionally taken to mean a process during which there is no exchange of heat between the environment and the fluid parcel one is considering. However, with this definition of "adiabatic" it is still possible for the entropy η, of a fluid parcel to change during an isohaline and adiabatic process (see Eqn. (B.19)). This is because the dissipation of mechanical energy ε causes an increase in η.

$$\boxed{\begin{aligned}\rho\left(\frac{\mathrm{d}h}{\mathrm{d}t}-v\frac{\mathrm{d}P}{\mathrm{d}t}\right) &= \rho\left(\frac{\mathrm{d}u}{\mathrm{d}t}+\left(p+P_0\right)\frac{\mathrm{d}v}{\mathrm{d}t}\right) = \rho\left(\left(T_0+t\right)\frac{\mathrm{d}\eta}{\mathrm{d}t}+\mu\frac{\mathrm{d}S_{\mathrm{A}}}{\mathrm{d}t}\right)\\ &= -\nabla\cdot\mathbf{F}^{\mathrm{R}}-\nabla\cdot\mathbf{F}^{\mathrm{Q}}+\rho\varepsilon\end{aligned}} . \tag{B.19}$$

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

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

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

potential temperature of seawater

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

Potential temperature referred to reference pressure p_{r} is often written as the pressure integral of the adiabatic lapse rate (Fofonoff (1962), (1985))

$$\theta = \theta\left(S_{\mathrm{A}},t,p,p_{\mathrm{r}}\right) = t + \int_{P}^{P_{\mathrm{r}}} \Gamma\left(S_{\mathrm{A}},\theta\left[S_{\mathrm{A}},t,p,p'\right],p'\right) dP' \; , \qquad (3.1.1)$$

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

The algorithm that is used in the TEOS-10 code to evaluate potential temperature θ equates the specific entropies of two seawater parcels, one before and the other after the isentropic and isohaline pressure change. In this way, θ is evaluated using a Newton-Raphson type iterative solution technique to solve the following equation for θ

$$\eta\left(S_{\mathrm{A}},\theta,p_{\mathrm{r}}\right) = \eta\left(S_{\mathrm{A}},t,p\right), \qquad (3.1.2)$$

or, in terms of the Gibbs function, g,

$$-\,g_{T}\left(S_{\mathrm{A}},\theta,p_{\mathrm{r}}\right) = -\,g_{T}\left(S_{\mathrm{A}},t,p\right). \qquad (3.1.3)$$

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

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

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

potential enthalpy

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

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

$$\overset{\frown}{h}_\eta \,\mathrm{d}\eta + \overset{\frown}{h}_{S_\mathrm{A}} \mathrm{d}S_\mathrm{A} + \overset{\frown}{h}_P \,\mathrm{d}P - v\,\mathrm{d}P \;=\; \left(T_0 + t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A}\,. \tag{A.11.4}$$

For an isentropic and isohaline process during which $\mathrm{d}\eta = \mathrm{d}S_\mathrm{A} = 0$, this equation reduces to $\overset{\frown}{h}_P \;\equiv\; \partial\overset{\frown}{h}/\partial P\big|_{S_\mathrm{A},\eta} \;=\; v$ which allows us to simplify Eqn. (A.11.4) to

$$\overset{\frown}{h}_\eta \,\mathrm{d}\eta + \overset{\frown}{h}_{S_\mathrm{A}} \mathrm{d}S_\mathrm{A} \;=\; \left(T_0 + t\right)\mathrm{d}\eta + \mu\,\mathrm{d}S_\mathrm{A} \qquad \text{while} \qquad \partial\overset{\frown}{h}/\partial P\big|_{S_\mathrm{A},\eta} = v, \tag{A.11.4}$$

Also, from the previous section we know that if S_A and η are constant, then so is potential temperature θ. Hence we also know that

$$\partial h/\partial P\big|_{S_\mathrm{A},\theta} = v\ . \tag{A.11.6}$$

Since we also know that $g_P = v$ we can note that

$$\partial h/\partial P\big|_{S_\mathrm{A},\theta} \;=\; v \;=\; \partial g/\partial P\big|_{S_\mathrm{A},T}\,. \qquad\qquad (\,v = g_P = \tilde{h}_P = \overset{\frown}{h}_P = \hat{h}_P\,)$$

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

$$\begin{aligned} h^0\left(S_\mathrm{A},t,p\right) = h\left(S_\mathrm{A},\theta,0\right) = \tilde{h}^0\left(S_\mathrm{A},\theta\right) \;&=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} v\left(S_\mathrm{A},\theta\left(S_\mathrm{A},t,p,p'\right),p'\right) dP' \\ &=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} \overset{\frown}{v}\left(S_\mathrm{A},\eta,p'\right) dP' \\ &=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} \tilde{v}\left(S_\mathrm{A},\theta,p'\right) dP' \\ &=\; h\left(S_\mathrm{A},t,p\right) - \int_{P_0}^{P} \hat{v}\left(S_\mathrm{A},\Theta,p'\right) dP', \end{aligned} \tag{3.2.1}$$

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

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

$$h^0\left(S_\mathrm{A},t,p\right) \;= h\left(S_\mathrm{A},\theta,0\right) = \; g\left(S_\mathrm{A},\theta,0\right) - \left(T_0 + \theta\right) g_T\left(S_\mathrm{A},\theta,0\right). \tag{3.2.2}$$

Conservative Temperature

Conservative Temperature Θ is defined to be proportional to potential enthalpy,

$$\Theta\left(S_{\mathrm{A}},t,p\right) = \tilde{\Theta}\left(S_{\mathrm{A}},\theta\right) = h^{0}\left(S_{\mathrm{A}},t,p\right)\big/c_p^0 = \tilde{h}^{0}\left(S_{\mathrm{A}},\theta\right)\big/c_p^0 \qquad (3.3.1)$$

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

$$\frac{\left[h\left(S_{\mathrm{SO}},\,25°\mathrm{C},\,0\right) - h\left(S_{\mathrm{SO}},\,0°\mathrm{C},\,0\right)\right]}{(25\ \mathrm{K})} \approx 3991.867\,957\,119\,63\ \ \mathrm{J\,kg^{-1}\,K^{-1}}, \qquad (3.3.2)$$

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

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

The value of c_p^0 in Eqn. (3.3.3) is very close to the average value of the specific heat capacity c_p at the sea surface of today's global ocean. This value of c_p^0 also causes the average value of $\theta - \Theta$ at the sea surface to be very close to zero. Since c_p^0 is simply a constant of proportionality between potential enthalpy and Conservative Temperature, it is totally arbitrary.

potential temperature of a perfect gas

An ideal gas obeys

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

where R is the universal gas constant $R \approx 287 \text{ J kg}^{-1} \text{ K}^{-1}$. For an adiabatic change in pressure (this also being an isentropic processes) the Fundamental Thermodynamic Relation tells us that $\mathrm{d}h = v\mathrm{d}P$. For an ideal gas, specific enthalpy h is equal to $c_p^{\text{gas}} T$ where $c_p^{\text{gas}} = \tfrac{7}{2} R \approx 1004.5 \text{ J kg}^{-1} \text{ K}^{-1}$ for a diatomic gas. Hence for a perfect gas we have

$$c_p^{\text{gas}} \mathrm{dT} = \tfrac{7}{2} R \mathrm{dT} = \frac{RT}{P} \mathrm{d}P \qquad \text{or} \qquad \mathrm{d}(\ln T) = \tfrac{2}{7} \mathrm{d}(\ln P) . \qquad \text{(Perfect\_Gas\_B)}$$

Performing the adiabatic change in pressure from P to P_0 gives

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

specific entropy of a perfect gas

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

$$\mathrm{d}h - v\mathrm{d}P = \left(T_0 + t\right) \mathrm{d}\eta \qquad \text{(A.7.1)}$$

shows that

$$\begin{aligned} d\eta &= c_p^{\text{gas}} \frac{\mathrm{dT}}{T_0 + t} - R \frac{\mathrm{d}P}{P} = c_p^{\text{gas}} \mathrm{d}(\ln\left[T_0 + t\right]) - \tfrac{2}{7} c_p^{\text{gas}} \mathrm{d}(\ln P) \\ &= c_p^{\text{gas}} \mathrm{d}(\ln\left[T_0 + \theta\right]). \end{aligned} \qquad \text{(Perfect\_Gas\_D)}$$

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

$$\begin{aligned} \eta &= c_p^{\text{gas}} \ln\left[T_0 + \theta\right] + \text{constant} \\ &= c_p^{\text{gas}} \ln\left[1 + \theta / T_0\right], \end{aligned} \qquad \text{(Perfect\_Gas\_E)}$$

where the constant is defined so that entropy is zero at a Celsius temperature of $0\,°\mathrm{C}$ (see Eqn. (J.6) and (J.7) of IOC *et al.* (2010)).

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

An approximate specific entropy of seawater

One wonders how accurate a correspondingly simple logarithm expression would be for the entropy of seawater, defined by either $c_p^0 \ln\left[T_0 + \theta\right] + \text{constant}$ or $c_p^0 \ln\left[T_0 + \Theta\right] + \text{constant}$. The constants can be chosen so that it makes the estimate of entropy zero if $\theta = 0\,°\mathrm{C}$ or $\Theta = 0\,°\mathrm{C}$ in the two cases respectively since entropy is defined to be zero for Standard Seawater ($S_{\mathrm{A}} = S_{\mathrm{SO}}$) at these temperatures. Hence we try the two approximations

$$c_p^0 \ln\left[1 + \theta / T_0\right], \qquad \text{(approx\_entropy\_pt)}$$

and

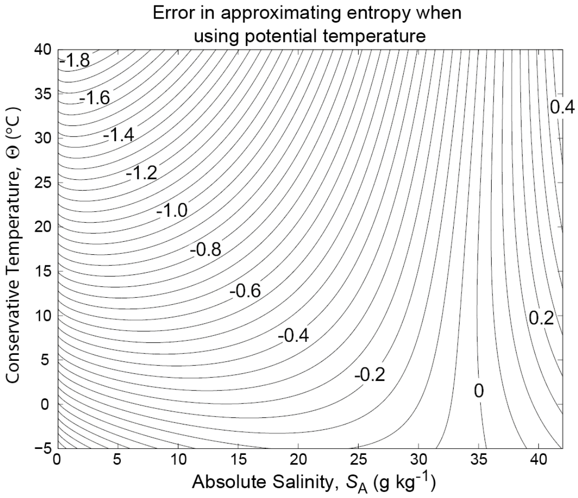
$$c_p^0 \ln\left[1 + \Theta / T_0\right]. \qquad \text{(approx\_entropy\_CT)}$$

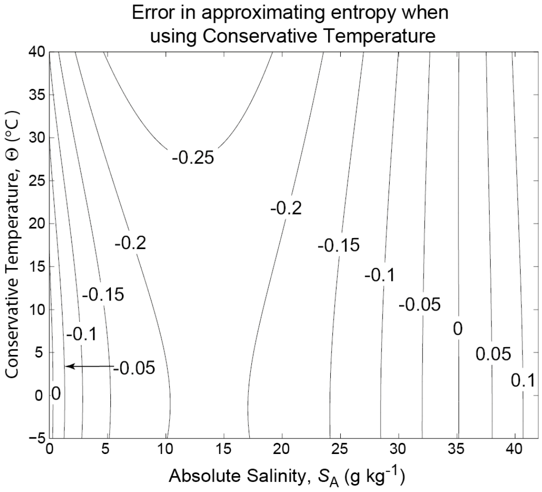
The figures below show the difference between these approximate expressions and the specific entropy of seawater, and each plot has been divided by

$$13.983265450613318 \text{ J kg}^{-1}\mathrm{K}^{-2} = \frac{\hat{\eta}\left(35.16504 \text{ g kg}^{-1}, 25\,°\mathrm{C}\right)}{25\mathrm{K}}, \qquad \text{(scaling\_factor)}$$

(i.e. essentially $14\ \mathrm{J\,kg^{-1}K^{-2}}$) in order to express the error in the approximation in temperature units.

It is seen that the expression involving Conservative Temperature, $c_p^0 \ln\left[1+\Theta/T_0\right]$, is a better approximation to entropy than is the one involving potential temperature, $c_p^0 \ln\left[1+\theta/T_0\right]$. (Note that for seawater, c_p^0 is approximately four times as large as the specific heat capacity of air, c_p^{gas}).





Can we understand the relative performance of these two approximate expressions? Starting from the Fundamental Thermodynamic Relationship

$$\mathrm{d}h - v\,\mathrm{d}P \;=\; \left(T_0+t\right)\mathrm{d}\eta \;+\; \mu\,\mathrm{d}S_{\mathrm{A}}\,, \qquad \text{(A.7.1)}$$

we consider this differential relationship at the fixed pressure of $p=0$ dbar where the *in situ* temperature is equal to the potential temperature θ, so the FTR becomes

$$c_p^0\mathrm{d}\Theta \;=\; \left(T_0+\theta\right)\mathrm{d}\eta \;+\; \mu\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}\,, \qquad \text{(d\_entropy\_1)}$$

or

$$\mathrm{d}\eta \;=\; \frac{c_p^0}{\left(T_0+\theta\right)}\mathrm{d}\Theta \;-\; \frac{\mu\left(S_{\mathrm{A}},\theta,0\right)}{\left(T_0+\theta\right)}\mathrm{d}S_{\mathrm{A}}\,, \qquad \text{(d\_entropy\_2)}$$

or

$$\boxed{\mathrm{d}\eta \;=\; \frac{\left(T_0+\Theta\right)}{\left(T_0+\theta\right)}c_p^0\,\mathrm{d}(\ln\left[T_0+\Theta\right]) \;-\; \frac{\mu\left(S_{\mathrm{A}},\theta,0\right)}{\left(T_0+\theta\right)}\mathrm{d}S_{\mathrm{A}}}\,. \qquad \text{(d\_entropy\_3)}$$

This is the relevant differential expression for entropy in terms of Θ.

Now to develop the corresponding expression in terms of θ we go back to the FTR, Eqn. (A.7.1), evaluated at $p=0$ dbar in the form

$$c_p\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}\theta \;+\; h_{S_{\mathrm{A}}}\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}} \;=\; \left(T_0+\theta\right)\mathrm{d}\eta \;+\; \mu\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}\,. \qquad \text{(d\_entropy\_4)}$$

Since $h = g - Tg_T$ it follows that $h_{S_{\mathrm{A}}} \;=\; g_{S_{\mathrm{A}}} - Tg_{S_{\mathrm{A}}T} \;=\; \mu - T\mu_T$ so we can rewrite this last equation as

$$\boxed{\mathrm{d}\eta \;=\; c_p\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}(\ln\left[T_0+\theta\right]) \;-\; \mu_T\left(S_{\mathrm{A}},\theta,0\right)\mathrm{d}S_{\mathrm{A}}}\,. \qquad \text{(d\_entropy\_5)}$$

Our approximate straw-men expressions for entropy, namely $c_p^0 \ln\left[1+\theta/T_0\right]$ and $c_p^0 \ln\left[1+\Theta/T_0\right]$, amount to ignoring the dependence of entropy on Absolute Salinity in the above boxed equations, as well as

(i) in the case of θ, approximating $c_p\left(S_{\mathrm{A}},\theta,0\right)$ as c_p^0, and

(ii) in the case of Θ, approximating $\left(T_0+\Theta\right)/\left(T_0+\theta\right)$ by unity.

The specific heat capacity $c_p\left(S_{\mathrm{A}},\theta,0\right)$ varies by 5.5% in the ocean whereas the ratio $\left(T_0+\Theta\right)/\left(T_0+\theta\right)$ varies by no more than 0.67%, and this goes some way towards explaining why the approximate expression $\eta \approx c_p^0 \ln\left[1+\Theta/T_0\right]$ outperforms $c_p^0 \ln\left[1+\theta/T_0\right]$ by a factor of about 15.