

Review of

A Thermodynamic Potential of Seawater in terms of Conservative Temperature

by McDougall, Barker, Feistel, and Roquet

Ocean Sciences manuscript <https://doi.org/10.5194/egusphere-2023-1568>

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August 6, 2023

1 Recommendation

This is an impressive work that comes after decades of investigations by the authors into the fundamentals and practices of seawater thermodynamics. I suspect that this paper will be read for decades to come. I fully support publication, and offer comments targeting clarification in hopes that a few more readers will feel inspired to enter into the seawater thermodynamics club, including those readers who are experts in thermodynamics and yet not versed in the ocean notation (e.g., a theoretical physical chemist).

Before starting the formal review, I note that another reviewer pointed out the need to give a name to $\hat{\phi}(S_A, \Theta, P)$. A generic name could be "Seawater Thermodynamic Potential (STP)", which is a somewhat more concise term than the authors' "thermodynamic potential of seawater in terms of Conservative Temperature". However, there are other thermodynamic potentials assigned a name associated with its proponent (e.g., Gibbs, Helmholtz, Massieu). It is with this view in mind that I recommend we refer to $\hat{\phi}(S_A, \Theta, P)$ as the *McDougall thermodynamic function*. That name is certainly not something for the current paper. But in all seriousness I recommend that the community pick up this terminology moving forward.

2 General comments

Here are some general comments.

2.1 Title

Title: the key novelty in this work is to develop the theory and practice for a thermodynamic potential using Θ rather than *in situ* temperature. This novelty is reflected in the title. However, as noted in the first sentence of the abstract, what is in fact proposed is a thermodynamic potential that is a function of S_A, Θ, p . I encourage the authors to use the more complete: "A Thermodynamic Potential of Seawater in terms of Absolute Salinity, Conservative Temperature, and *in situ* pressure". I am particularly keen to allow readers who are not oceanographers to find this title offers a better sense for what is proposed.

2.2 Notation introduced in lines 75-80

In between lines 75-80 there is a single sentence that introduces notation all within the text (i.e., no equation numbers). For those having read other papers in the TEOS-10 family, the notation will be familiar even if one does not like it. Indeed, I have been an author on such papers. Even so, as a reviewer I put on my non-TEOS-10 aficionado hat in hopes of identifying places where readers can be confused.

1. The symbol "t" is almost universally used for time in physics and chemistry. Indeed, you use it for time in the First Law equation (1). However, on lines 77, 78, 79, t is used for *in situ* temperature measured in Celsius units. Should you wish to retain this non-standard usage, care should be made to reduce confusion when switching between time and temperature, with signposts placed where needed.
2. T_0 is a constant offset from t, presumably since $t + T_0$ is the absolute thermodynamic temperature with t in Celsius units. That point is never made yet it would serve the reader to make it here.
3. T is a symbol attached as a subscript to the Gibbs potential, and yet it is never defined. Presumably $T = t + T_0$ is the thermodynamic temperature, but the reader should not need to guess.

4. The above incomplete discussion of t and T_0 make me wonder if they are even needed at this point of the presentation. Perhaps you prefer to keep them here since you prefer to measure all temperature quantities in Celsius, and so need the T_0 offset. But that is a choice that is not fundamental and can lead to rather awkward equations. Indeed, later in the presentation of the same section, you write $\nabla(1/T)$ rather than the more awkward $\nabla(1/(t + T_0))$.
5. It is stated that subscripts denote partial differentiation, whereas we also find many subscripted symbols that are not derivatives. For example, between lines 75-80 we find P_r , S_{A_r} , and T_0 . I realize the authors are fond of the subscript shorthand for partial derivatives. Even so, I will poke at them by noting that ∂_T and ∂_Θ and ∂_p require only a bit more ink on the printed page and yet they offer far less room for notational ambiguity.
6. What does "forward expression" mean on line 78? This term is also used later at lines 480, 481, 486, and 523. It is only when reaching lines 486 and 523 that we find out that "forward calculation" means that no iteration is needed. Please define this term at line 78.
7. h is used in two separate equations between lines 75-80, and yet it is not defined until line 90 in a different section.

2.3 Clarifying "inconsistencies"

On line 80 it is stated that "While the inconsistencies in temperature are small". Although contained in the build up material prior to lines 75, it should be emphasized that the ambiguity is not related to a problem with seawater thermodynamics. Rather, it is that we can compute t and θ using either the "forward expression" on line 79 or the implicit Gibbs equation on line 77, and yet these two expressions, in practice, lead to slightly different numerical values. If you clean up lines 75-80, for example by splitting this material into two or three sentences, then the reader will be a bit more clear on the inconsistency.

2.4 Further citations for First Law

Line 85-95 presents the First Law of Thermodynamics as applied to moving seawater fluid. Perhaps the most lucid and correct discussion of this equation is given in TEOS-10, with citations given here to the relevant sections. Even so, I recommend including some of the other places that the reader might find it discussed. In particular, it is worth pointing to Chapters 49 and 58 of *Landau and Lifshitz (1987)* so that our physical chemist reader does not presume TEOS-10 is the first occasion where the First Law was properly derived for a moving multi-component fluid.

2.5 Infer versus deduce

Line 97 states that Clausius (1876) "deduced" the existence of entropy. I suggest that it is more proper to say that Clausius "inferred" the existence of entropy. It took the later work of Boltzmann to provide a deductive theory for entropy based on mechanistic and probabilistic principles that led to statistical mechanics.

2.6 Quasi-static versus reversible

In much of Section 1.2 (Thermodynamic fundamentals), the authors refer to *reversible processes*. I instead recommend they use the slightly more general, and useful, term *quasi-static*, following the usage given in Sections 4.2 and 4.3 of *Callen (1985)*, as well as Sections 2.9 and 2.10 of *Reif (1965)*. In these books, the authors define a quasi-static process as a process that moves along a locus of equilibrium states, and with a quasi-static process approximated by a realizable physical process that occurs through steps that are each arbitrarily close to thermodynamic equilibrium. By formulating the notion of a quasi-static process, we are afforded a precise definition for intensive properties such as *in situ* temperature, pressure, and chemical potential, whereas such intensive properties are fuzzy concepts for systems out of thermodynamic equilibrium. A reversible process is a quasi-static process that occurs without net entropy change, and yet not all quasi-static processes are reversible since entropy can generally increase in a quasi-static process.

Here are the lines of text that prompted me to offer my recommendation to switch from "reversible" to "quasi-static". In practice the distinction might be small. But in the spirit of making the fewest assumptions necessary, I recommend switching from your assumed reversible processes to the more general quasi-static processes.

- Line 102 it is stated that the FTR applies to *reversible processes*, and yet *Callen (1985)* emphasizes that the FTR holds for the more general quasi-static processes.
- line 145 states "a seawater parcel is heated reversibly", which I assume means that the parcel's entropy increases when the surrounding environment entropy decreases by the exact same amount. This sort of process is less general than a quasi-static heating of a parcel, in which we do not need to assume zero net entropy production.

- line 149: again change “reversible” to “quasi-static”.
- Discussion finishing at line 162. If you replace “reversible” with “quasi-static”, then this discussion mirrors that in Section 4.2 and 4.3 of [Callen \(1985\)](#).
- If I am barking up the wrong tree, and you do need reversible, then such disagreement with [Callen \(1985\)](#) and [Reif \(1965\)](#) warrants clarification in your manuscript.

2.7 Gravity with thermodynamics

When introducing gravity on line 180, you make the distinction between the distribution of *in situ* temperature and potential temperature in equilibrium. Although a bit tangential to the current discussion, it is worth noting that pressure in thermodynamic equilibrium is not uniform when in a gravity field. Instead pressure is hydrostatically balanced. My motivation for recommending this insertion is that we do not commonly find thermodynamics discussed in the presence of gravity, even though all geophysical fluids are in a gravity field. The notable exceptions include Chapter 9 of [Guggenheim \(1967\)](#), §25 of [Landau and Lifshitz \(1980\)](#), and Section 1.8 of [Kamenkovich \(1977\)](#) (I thank Rainer Feistel for pointing these resources to me in email correspondence in 2022).

2.8 Criterion of independence

On line 228 you state that $h(S_A, T, P)$ and $\eta(S_A, T, P)$ violate the criterion of independence given that they must satisfy equation (10). You then say that for the Gibbs potential equation (10) is satisfied. I missed how you know that it is not satisfied for $h(S_A, T, P)$ and $\eta(S_A, T, P)$. One or two more sentences might be sufficient.

Also, equations (9) and (10) have S, P subscripts for the partial derivatives. Should that instead read S_A, P ?

2.9 Please build a table of symbols!

There are many symbols that are introduced in the text and in equations. These symbols are easily forgotten, in which case one needs to sift through the text to find them defined. It would greatly help the reader to have a thorough table of symbols for more easy reference.

3 Minor comments

- line 154: I recommend the sentence starting “In practice” should start the beginning of a new paragraph.
- lines 176-177 you state “The hat over a variable indicates that it is being expressed as a function of Conservative Temperature (rather than in situ temperature).” This information would be very useful if stated back around line 75-80 where these symbols are first used.
- line 184 you say “here the cup over a variable’s name indicates that it is being expressed as a function of entropy”. However, in equation (6) you use the same cup symbol to write entropy as a function of S_A, h, P . It would be useful to define this notation back at the point of equation (6).
- Equation (8) has a period whereas there should be none.
- Please see the comments from the other reviewer about lines 253 and 256, where S is written when it should be S_A .
- Line 365 there is $\hat{\eta}(S_A, \Theta, P)$ and $\tilde{\eta}(S_A, \Theta, P)$. I do not know what $\tilde{\eta}(S_A, \Theta, P)$ is. Perhaps it is a typo, or perhaps in my wished-for table of math symbols I could find it defined.
- line 353 starts material that, in my opinion, is better placed in Section 4 when detailing how you compute $\hat{\phi}(S_A, \Theta, P)$ in practice.
- line 366: The sentence starting with “In summary” is a great start to a new paragraph.
- line 493: the authors make use of a semi-colon here, whereas a colon is more appropriate. I believe there are a few other occasions of this sort, but I did not mark them on my draft.

References

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