Comments on: "A thermodynamic potential of seawater in terms of Conservative Temperature" by McDougall et al.

This is an interesting and useful paper, which I enjoyed reading. I have a few remarks about it though, that the authors may want to address.

- 1. The paper needs a more scholarly review of the theory of thermodynamic potentials. A very good and lucid reference is Alberty (2001). Such a theory highlights at least three key features that the authors appear to have overlooked. The first one is related to the concept of canonical variables. The second one is the theory of Legendre transforms. The third one is the concept of conjugate thermodynamic variables. The first feature is crucial to mention, because a thermodynamic potential contains all possible thermodynamic function only if expressed in terms of canonical variables. The authors should stress the fact that Conservative Temperature (like potential temperature) is not a canonical variable, which is why two functions ($h(\Theta, S, p)$ and $\eta(\Theta, S)$) are needed in that case to predict all possible thermodynamic information about the system. The second feature is crucial to mention, because it is the theory of Legendre transform, and the result that a curve can equivalently be described as the envelope of its tangent lines, which serves to establish the equivalence between the different classical thermodynamic potentials. The third feature is crucial to mention to explain why different thermodynamic potentials have different canonical variables. The author may want to mention that introducing Conservative Temperature (or potential temperature) introduces an external environmental parameter into the system (the reference pressure), which augment the phase space from 3 to 4 dimensions.
- 2. <u>Line 213-214: Note that the FTR follows from this expression for the</u> <u>total derivative of the Gibbs function if and only if one also knows that $g = h - T\eta$; we will return to this later.</u> I don't understand this sentence, because in the theory of thermodynamic potentials, the relation $g = h - T\eta$ is not a matter of knowledge but of definition, in the sense that the relation defines g as the Legendre transform of h. I don't understand what the authors mean by 'if and only if one also knows that [...]'. Do the authors mean: `if one does not know about the theory of thermodynamic potentials and of Legendre transforms'? That seems odd for a paper about thermodynamic potentials.
- 3. I disagree that the new thermodynamic potential is equivalent to the Gibbs function. Indeed, while it is true that the Gibbs function can be recovered from their newly introduced potential via unambiguous mathematical operations (obtain enthalpy and entropy from their new thermodynamic potential; use the result to eliminate conservative temperature and express specific enthalpy in terms of canonical variables; use the Legendre transform to obtain the Gibbs function), it is not possible to recover the newly defined thermodynamic potential from the Gibbs function without introducing external rules along the way. Indeed, since Conservative Temperature is not conjugate to any canonical variable, human intervention is needed to introduce it by specifying the functional relationship linking it to specific entropy and salinity. Moreover, as the authors demonstrate, there is no unique way to construct a thermodynamic potential from $h(S, \Theta, p)$ and $\eta(S, \Theta)$, so that human

intervention (and ingenuity) is required for that last step. Demonstrating the equivalence between two quantities requires discussion of the steps required to obtain one from the other and conversely.

- 4. While I think that explaining how to construct a thermodynamic potential containing all the thermodynamic information when expressed in terms of a non-canonical variable serves a useful purpose, as it clarifies an issue that others may wonder about, I am sceptical that this is of any practical use. As the authors correctly recognise, all necessary information is contained in $h(S, \Theta, p)$ and $\eta(S, \Theta)$, which are independent of each other. It seems pointless (not to say computationally inefficient) to me to construct a thermodynamic potential just as to be able to say that these two functions can be obtained from it. Indeed, the authors make it clear that the thermodynamic potential that they construct is a purely ad-hoc and arbitrary concept with no particular significance. Therefore, while I agree that it is useful to know that such a thermodynamic potential can be constructed in principle, I disagree that it is useful to construct it in practice. To me, it seems more computationally efficient to construct enthalpy and entropy as function of S, CT, and p, and derive all thermodynamic quantities from these two functions without introducing the thermodynamic potential. For this reason, I think that the authors should reconsider the way that they present their material. I think that the correct conclusion that derives from their results is: Yes, it is possible to construct a thermodynamic potential in terms of S, CT, and p, and here is how to do it, which is of theoretical interest for the theory of thermodynamic potentials formulated in terms of non-canonical variables, but this does not appear to offer any practical advantage.
- 5. <u>Line 535. This provides a theoretical boost to using Conservative Temperature</u> <u>as the temperature variable in physical oceanography as recommended by</u> <u>TEOS-10 (Valladares et al., 2011a,b).</u>

I don't understand why for at least two reasons. The first one is that as mentioned before, the authors' thermodynamic potential is clearly an artificial and arbitrary object. As a result, it seems to me that associating Conservative Temperature to an artificial object will just end up highlighting the artificial character of Conservative Temperature, the opposite of a theoretical boost. The second one is that the whole machinery described could obviously be equally applied to potential temperature or any other non-canonical variable. In other words, their results are not specific to Conservative Temperature, so it is unclear why they should favour it more than any other non-canonical variable.

@article{Alberty1994,

author = {R. A. Alberty}, journal = {Chemical Reviews}, number = {6}, pages = {1457--1482}, title = {Legendre transforms in chemical thermodynamics}, volume = {94}, year = {1994}}