

Final reply to the comments on:

“TEOS-10 and the Climatic Relevance of Ocean-Atmosphere Interaction”

submitted to Ocean Science 2024 by Rainer Feistel

In the **review of Trevor McDougall**, the main criticism was the request to remove from this paper the Section on Potential Enthalpy and Ocean Heat Content. From my perspective, this was a misunderstanding, and as a consequence, this section has been enlarged in order to better explain what it is intended for.

Already in 1888, in his "Theory of Heat", J.C. Maxwell had clearly stated that “We have ... a right to speak of heat as a measurable quantity, ... however, ... we have no right to treat heat as a substance”. In the recent oceanographic and climatological literature, terms like "ocean heat content" are frequently used, giving the impression that "heat content" is something of the same kind as "salt content", "water content" or "CO₂ content" of the ocean. But, thermodynamically, this impression is definitely wrong.

What can properly be measured, in principle, is the amount of heat that goes into or out of the ocean across its interface with the outside world. "Heat content" may be defined by a specific process that transforms the ocean from a certain reference state to the state of interest. Different processes carried out between those states may be associated with different amounts of heat. Remember that heat engines are systems that are permanently supplied with heat even though they return periodically to the same state over and over again. State quantities, by definition, take the same values again if a system returns to its previous state. There cannot exist any ocean state quantity that may properly be identified with the thermodynamic quantity "heat".

Section 3 of this paper presents a conceptual proposal for defining a reference state and a measurable heat exchange process of the ocean which is consistent with the common understanding of "heat content" in the context of TEOS-10. This proposal should be understood as an additional physical justification of the current formal mathematical definitions of "heat content".

The **review of Remi Tailleux** raises a number of specific questions which have already been addressed in the direct response. In addition to that, a key issue again is the definition of heat, its uniqueness and way of description in oceanography. With this respect, I like to refer to the above response to Trevor McDougall's comments.

The way "heat content" is discussed in this paper is certainly only one possible option of doing so. It is the aim here to raise awareness of the fundamental character and ambiguity of the heat problem involved, and to offer a specific proposal as a suggested solution consistent with the common published definitions of "heat content" in the context of TEOS-10.

The **comments of Pasqual Marquet** have the form of an extended counter publication. The numerous technical arguments raised there must be left to be discussed in detail by the scientific community. None of those, however, is capable of rebutting the general physical key statement that residual entropies are neither available from thermodynamic measurements, nor do their quantitative values affect any results of thermodynamic measurements.

Regarding TEOS-10, note that:

No user of TEOS-10 is committed to work with the reference state definitions actually implemented. TEOS-10 equations and source code are open and well documented. It takes only a few numerical

constants to be modified, mutually consistently, in order to install arbitrary other residual entropies. This will not affect, though, results for any measurable thermodynamic properties of the climate system, and is simply unnecessary therefore. However, care must be taken with respect to special quantities such as Ocean Heat Content or Conservative Temperature which are presently defined under the assumption that the enthalpy of the standard ocean state is zero by definition of the TEOS-10 reference state conditions. The current choice of TEOS-10 reference state conditions is optimum with respect to uncertainties and has been supported by the expert group of TEOS-10 developers as well as various IAPWS experts.

Some key arguments are:

- No scientific study has ever revealed a climatic relevance of residual entropies in ocean-atmosphere interaction
- No atmospheric measurement has ever revealed the exact value of the residual entropy of ice Ih
- No atmospheric measurement has ever revealed whether ice Ih (with residual entropy) or ice XI (without) is the proper zero-point equilibrium phase of water
- No technical or scientific application of the IAPWS-95 equation has ever been reported to be quantitatively in conflict with the IAPWS reference state conditions
- Among all the experimental thermodynamic data available and exploited for the development of TEOS-10, none of those permitted the determination of the adjustable coefficients representing the absolute entropies of the substances involved
- Only little is known about possible residual entropies of the various substances contained in dry air and dissolved sea salt. Published "standard molar entropies" may be considered as agreed reference state definitions as their assumed perfect equilibrium state at 0 K is usually not exactly known (and unnecessary to be exactly known)
- Clausius' empirical entropy definition was derived from cyclic processes which permit an arbitrary additive constant of entropy. Heat exchange is defined in terms of entropy differences only
- Isentropic parcel trajectories defined by $S(\mathbf{x}) = S(\mathbf{x}_0)$ remain the same as $S'(\mathbf{x}) = S'(\mathbf{x}_0)$ under the transformation $S' = S + \text{const}$. Such trajectories are physically meaningful only if along the trajectory the parcel does not exchange matter with its surrounding
- Residual entropy has only theoretically been concluded from the equation $S = k \log W$ of the statistical model of Boltzmann, Planck and Pauling, which requires counting of theoretically possible alternative microscopic (molecular) configurations that are consistent with exactly one and the same given macroscopically observed state

Thankfully, the **comments of Olaf Hellmuth** offer valuable additional aspects of the submitted paper.

- Some references to reviews of MOST have been added to the context of eq. (6)
- Reference to Hellmuth & Shchekin (2015) has been added in Section 5.2
- Work of Luo et al. (2024) has additionally been mentioned in Section 6.3