

Answers to the Editors about the  
Comptes Rendus Geoscience paper:  
“ The absolute seawater entropy: Part I and II. ”  
by Pascal Marquet / December 1, 2025

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## 1) Answers to the Editors

- **For the second reviewer (Reviewer-2), you explain:**

*“ One of the two negative reviews is not very detailed but highlights the complexity of the subject matter and a tone that is rather inappropriate for a scientific article. ”*

This review of my two-part paper is really both very superficial and very nasty.

For my part, I have never dared to send such a report in my entire scientific career in my past actions as a reviewer/referee of major journals such as the *Journal of Atmospheric Science* (USA), the *Monthly Weather Review* (USA) or the *Quarterly Journal of the Royal Meteorological Society* (UK).

The lack of understanding of the paper by this reviewer seems to demonstrate that this Reviewer-2 could not give an objective and relevant opinion regarding the publication (or not) of my paper.

And yet the criticisms by this Reviewer-2 are ferocious and nasty: *“ I deeply think that the purpose of a paper is to communicate one’s science and make it accessible to a reader, otherwise it is useless and will not be read and noticed. ”*

This would therefore imply that I was unable to clearly explain the issues surrounding the calculation of seawater entropy, with the choice we have to comply (or not) with the third law of thermodynamics, and with significant numerical differences if we were to disregard this recommendation.

The fact that the other two reviewers, Reviewer-1 and Reviewer-3, clearly understood the scientific aims of my article promoting the straightforward application of the third law of thermodynamics in ocean studies –even though they requested numerous changes and even rejected any influence of the third law– seems to invalidate the nasty remarks made by Reviewer-2.

In any case, I have provided Reviewer-2 with a summary of all the changes made to both parts of the paper. I hope this will help this reviewer to understand the scientific purpose of my paper.

- **For the second reviewer (Reviewer-1), you explain:**

*The third review (positive) is quite detailed, even though the author indicates “ The presentation is exhaustive and I only gave it a high level review. ” This expert also notes that the article is sometimes written in a polemical style and that one of the sections remains highly speculative.*

For Reviewer-1, you indicate a positive aspect associated with the sentence: *“ well written and thorough manuscripts ”* and I also see the following positive sentence: *“ The topic is somewhat esoteric, and the presentation is deliberate, but always clear, and commendable for its precision ”*

There is no statement in this (positive) part of Reviewer-1’s text that what I wrote is “polemical” (displaying a critical or aggressive attitude?), but rather a statement that my considerations are complex but “always clear, and commendable for its precision” (which is, in my opinion, purely complimentary).

This “polemical” aspect is described in more detail in the following section of the text: *“ My major comment is that the implications of the results for standard practice could be better drawn out and contextualized. This would also avoid the danger of the paper being interpreted as a polemic. ”*

Unless I am mistaken, I see in these sentences from Reviewer-1 a desire to improve the text of my paper in two parts, changes that I have willingly and scrupulously carried out, I believe. It seems to me that Reviewer-1 is not saying that what I wrote is “polemical” , but only that it could be interpreted as such. I think this difference is important to mention. However, in order to address the risks mentioned by both Reviewer-1 and Reviewer-3 of a “polemical” interpretation of my comments, I have chosen to tone down wherever possible any wording that might suggest that the current version of ocean entropy (available as an output from TEOS10-GSW) is lower or inaccurate or contrary to the third law (even though this is of course scientifically the case, but without the right to say so, it seems):

“(...) violate” the third law → “(...) differ from” the third law;  
“(...) unless to violate the entropy budget (...)” → “(...) unless to modify the entropy budget (...)”;  
“(...) have the flaw of being in contradiction with” → “(...) can be amended to correspond to”;  
“(...) correcting” → “(...) amending”;  
“(...) prohibitive for the use of the standard entropy” → (removed) ;  
“(...) preferred to any other arbitrarily modified definition” → “(...) should impact” ;  
“(...) imposing the absolute values” → “(...) using the absolute values”;  
“(...) correcting and generalising the current (...)” → “(...) amending, if needed, the current (...)”;  
“(...) to compute the true value of (...)” → “(...) to compute the absolute value of (...)”; ...

The scientific aim of my two-part paper is to promote the straightforward application of the third law of thermodynamics in ocean studies, nothing more, nothing less. There should be nothing “polemical” about this a priori. I believe that this debate is legitimate and should be the subject of a scientific paper, even if, of course, there can (and should) be a contradictory scientific debate, however harsh and sometimes passionate it may be.

• **For the second reviewer (Reviewer-3), you explain:**

*“ The second (negative) review questions the relevance and value of the entropy calculations you propose.”*

Reviewer-3’s accusations are even more serious than that, as he mentions: “ ... significant concerns regarding the scientific objectivity, clarity, and accuracy of the present treatment”

Conversely, I believe I have been able to respond point by point to the sharp remarks made by Reviewer-3, and also in greater detail in the large files in Supplementary Materials.

Reviewer-3’s also writes: “ Without such rigorous testing, it is difficult to assess whether an absolute determination of entropy is more meaningful than a relative one. For these reasons, the determination of absolute entropy remains largely of academic interest, and it is understandable that TEOS10 has chosen not to address it in detail. (...) However, given the concerns raised in the review of Part I regarding the definition of absolute entropy, it is difficult to assess the scientific merit of Part II in detail.”

This is an arbitrary position taken by Reviewer-3 against any possible interest in the third law of thermodynamics, despite the notable differences shown in Part II of the paper, a position taken by Reviewer-3 that is partly contradicted by the positive opinion of Reviewer-1, and with statements by Reviewer-3 concerning me and indicating a ‘lack of rigorous testing’ and ‘concerns’ that I believe I have been able to criticise, defend and rationally refute in my point-by-point responses to Reviewer-3.

In particular, in order to address the risks mentioned by both Reviewer-1 and Reviewer-3 of a “polemical” interpretation of my comments, I have chosen to tone down wherever possible any wording that might suggest that the current version of ocean entropy (available as an output from TEOS10-GSW) is lower or inaccurate or contrary to the third law (even though this is of course scientifically the case, but without the right to say so, it seems):

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- **As a synthesis, you explain:**

*All of the reviewers (...) recognise that the two parts of the paper are closely linked and that reading both is necessary in order to fully understand their scope (...) Nevertheless, I wonder whether it might be in your interest to significantly reduce the length of these two manuscripts and combine them into a single article (...) It is also important to avoid any polemical tone in a scientific text, which must remain factual and objective. Significantly reducing the length of the text would probably be a way of achieving this.*

- I have given a lot of thought to and studied the solution you propose (a single article of 20 pages or so). I had actually started combining the two articles into one very long article to compensate for a possible rejection by C. R. Géosciences, so that I could submit it to another electronic journal as quickly as possible (...)

Your acceptance of a revision for “major revisions” has reshuffled the cards, but I really cannot fit both “theoretical” and “numerical applications” aspects into a single 20-page article for the following reasons.

My paper, in two main parts, should be understood as a synthesis of work carried out over the past 36 years, more precisely since 1989 and my research training period at the LMD at the Ecole Polytechnique, while simultaneously taking DEA (M2) courses in oceanography at Paris-VI. Although I was able to defend my doctoral thesis in 1994 on the subject of atmospheric exergy (SMF Prud’homme prize 1995), this was in parallel with my operational work as an Engineer (IPEF) at Météo-France, where my activities as a modeler and controller of the Arpege weather forecasting model, then of the Arpege-climate model, did not allow me to pursue my theoretical work full time, and in particular on ocean thermodynamics.

However, I had already gathered preliminary documentation in 1989-90 to try to define the seawater exergy, regularly performing exploratory calculations between 1989 and 2014. This work was undertaken with increased fervour (and with greater precision regarding seawater entropy) from 2014 onwards, with initial contact with Rainer Feistel. It was only in 2022 (at the time of my retirement) that I was able to finalize my work on the subject of absolute ocean entropy, after having published all my work on the absolute entropy and enthalpy of the (moist-air) atmosphere between 2010 and 2022, with operational applications discovered since 2021 by Peter Bechtold and now included in the prestigious IFS model at ECMWF.

Although Rainer Feistel initially responded positively between 2012 and 2014 to my ideas on atmospheric aspects and the absolute definition of the moist-air entropy in TEOS10-SIA (but without ever going so far as to include my formulation even as a simple option in TEOS10-GSW) I quickly noticed that Rainer Feistel and Rémi Tailleux (and more recently Trevor McDougall) completely rejected my preliminary work on the absolute seawater entropy, with an explicit refusal to collaborate on this subject for the past 10 years.

In an ideal world, I should have been able to publish articles on the subject of absolute seawater entropy for years now, in collaboration with the oceanographic community. It is the lack of collaboration (through no fault of my own) that explains the length of the two parts of my paper submitted to C. R.

Géosciences, which are the first publications on this subject since those by Millero in 1976-83. I have to (re)explain everything in detail in the first part, showing numerous detailed results in the second, because otherwise no one else will do it. Moreover, it is very likely that this two-part article submitted to your journal will be the last publication of my career, having now been retired for three years.

It is for all these reasons that the two parts (theoretical and numerical applications) that I am submitting for review are longer than I would have written had I been included in a community project involving papers spread over several years.

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• **You further explain that:**

*(...) It is also important to avoid any polemical tone in a scientific text, which must remain factual and objective (...)*

• I believe I have taken into account your request (as well as those of the reviewers) to be “factual and objective” by having (as already stated previously): reduced wherever possible the words suggesting that the current version of ocean entropy output from TEOS10-GSW would be “lower” or “inaccurate” or even “contrary” to the third law of thermodynamics:

“(...) violate” the third law → “(...) differ from” the third law;

“(...) unless to violate the entropy budget (...)” → “(...) unless to modify the entropy budget (...)”;

“(...) have the flaw of being in contradiction with” → “(...) can be amended to correspond to”;

“(...) correcting” → “(...) amending”;

“(...) prohibitive for the use of the standard entropy” → (removed);

“(...) preferred to any other arbitrarily modified definition” → “(...) should impact”;

“(...) imposing the absolute values” → “(...) using the absolute values”;

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“(...) to compute the true value of (...)” → “(...) to compute the absolute value of (...)”; ...

• I believe I have always been able to stay within the framework of a “scientific text” by remaining within a “factual and objective” framework and avoiding “polemical” aspects in the “aggressive” sense of the term, but factually assuming a “critical attitude” which consisted of saying even things that might be displeasing, such as the fact that the current version of TEOS10 is contrary to the third law of thermodynamics.

The third law of thermodynamics is an undeniable scientific fact, but one that I am not allowed to mention... it is very scientifically shocking.

It should be noted, however, that at no point was there any questioning of the substance of my ideas and calculations, in the sense that the absolute entropies of liquid water and ocean salts might not be those I used? Or that there might be a good, specific reason to disregard this third law when calculating the entropy function of the oceans?

It should be noted, however, that the fundamentals of my ideas and calculations are never questioned, in the sense that it is not said that the absolute (third-law) entropies of liquid water and ocean salts I used would be false (like those considered in Millero’s 1976-83 papers), or that there would be a particular reason to disregard the third principle of thermodynamics when calculating the entropy function of the oceans. Differently, my opponents explain: “We know we have the right to use arbitrary-defined entropy reference values ... we have been doing it for a very long time ... and in any case there is no impact of the absolute values on any variables other than entropy itself ...” (all of which are factually useless, if not incorrect assertions).

And if we were to admit in the end (as I show) that the numerical values, vertical profiles and horizontal maps of entropy are different, even very different, for the standard and absolute versions

of ocean entropy, then I am told : “... anyway, we don’t care about calculating and studying ocean entropy, it is what it is and not otherwise...” without the possibility for me to say that entropy is one of the 3 fundamental quantities of thermodynamics (along with temperature and energy), that it is a state function, and that therefore it cannot be defined up to an arbitrary function which varies with salinity.

I believe that this request to “avoid any controversial tone” is too easily used to prevent me from pointing out undeniable scientific facts. All this is difficult to accept, even though : [I ultimately chose to tone down all my comments deemed “controversial” or “polemical”](#). As explained previously, the scientific purpose of my two-part article was to promote the pure and simple application of the third law of thermodynamics in ocean studies, nothing more, nothing less, even if this could lead to contradictory scientific debates, however harsh and sometimes inflamed.

But these (pseudo-controversial) debates should not be able to call into question any of the four fundamental principles of thermodynamics (the "0th" principle for the existence of temperature; the "1st" principle for the conservation of energy; the "2nd" principle for the increase of entropy; and the "3rd" principle for establishing the absolute values of thermal entropy). Or should we also be able to regularly question the principle of conservation of energy, as is too often seen on the internet? (Because, ultimately, there is no "energy thermometer" capable of measuring all possible forms of energy, including all those that might still be unknown to us?)

I can only applaud the position of the French Academy of Sciences in Paris of no longer opening sealed envelopes supposedly demonstrating the existence of all kinds of "perpetual machines" (as often seen on the internet), and therefore supposedly proving the falsity of the first law. I can only lament that almost no one seems concerned about these attacks against the third principle, which are widespread in atmospheric and oceanic studies (apart from, for the ocean, the present paper that I am submitting to the C. R. Géosciences journal, following those by Millero in 1976-1983).

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[Finally, I wrote as requested by the editors :](#)

- [point-by-point responses to the three reviewers of both parts of the article, as well as to the editor;](#)
  - [files generated by “LaTeX-diff” showing deletions in red and additions/modifications in blue for both parts of the paper;](#)
  - [as well as a large file entitled ‘Supplementary Materials’ containing all calculations and additional information that could not be included in the paper itself.](#)
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## A summary of all changes made to Part-1 and Part-2 of the paper

In order to show to the Referees and Editor the whole set of changes made to the two-parts paper, before to answer point by point to the general and specific Comments, I may provide the following summary of all these changes made by myself and suggested by the Referees.

- [I have prepared an external “\*Supplementary Materials\*” document \(Marquet, 2025, uploaded in the Zenodo cite\).](#)
- [I have removed the terms considered as “polemic”:](#)  
“[\(...\) violate](#)” the third law → “[\(...\) differ from](#)” the third law;  
“[\(...\) unless to violate the entropy budget \(...\)](#)” → “[\(...\) unless to modify the entropy budget \(...\)](#)”;  
“[\(...\) have the flaw of being in contradiction with](#)” → “[\(...\) can be amended to correspond to](#)”;  
“[\(...\) correcting](#)” → “[\(...\) amending](#)”;

- “(…) prohibitive for the use of the standard entropy” → (removed);
- “(…) preferred to any other arbitrarily modified definition → “(…) should impact”;
- “(…) imposing the absolute values” → “(…) using the absolute values”;
- “(…) correcting and generalising the current (…)” → “(…) amending, if needed, the current (…)”;
- “(…) to compute the true value of (…)” → “(…) to compute the absolute value of (…)”; ...)
- I have added the new section 3.3 with the new Fig.2, where I describe other more general situations in physics where the absolute values of entropies impact different phenomena (saturation pressures versus latent heat; turbulence; chemical constants for Ozone and Seawater reactions; entropy potential temperature  $\theta_\eta$ ), with detailed computations shown in the Supplementary Materials (Marquet, 2025), as well as answers to FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans.
  - In this new section 3.3 I have added new citations: Planck (1917), Nernst (1918), Planck (1921), Nernst (1926) for the saturation pressure; Richardson (1919) Richardson (1922) Ma and Peltier (2024) Canuto et al. (2002) for the turbulence; (Burkholder et al., 2020) Weiss (1974) Millero (1995) DOE (Departement of Energy, 1994) for Ozone and Seawater chemical reactions; Betts (1973) for the atmospheric liquid-water potential temperature.
  - I have explained that the first resolution accepted during the 5th International Conference on the Properties of Steam in London (5th-ICPS et al., 1956) only concerned the steam water (one component system of constant composition), and not the seawater (multi-components system of variable composition), whereas a second resolution was adopted asking to provide the absolute values of entropies in all subsequent studies (as done in the present study).
  - In the Fig.1 of the Part-1, I have added two zoom versions of the first diagram for very small salinity, to show the impact of the term  $x^2 \ln(x)$  corresponding to  $S_A \ln(S_A)$ .
  - I recall in the conclusion of the Part-1 that the rejection of the third-law by the oceanic community can likely be dated to Fofonoff (1962, p.8), even though Fofonoff cited the previous books of Fowler (1929), Guggenheim (1933) and Guggenheim (1950), who all trusted the third law of thermodynamics and the Sackur-Tetrode translational entropy used in the present paper, and even though Guggenheim has chosen to call the “*absolute value*” of entropy the “*conventional*” entropy.
  - I explain in the Part-1 about  $S(T) = 0 + k \ln(W)$  that: “... the 0 term indicates that no other arbitrary term must be added ...”
  - The wrong title of the Section 4.3 of Part-1 I is duly change into “*The absolute entropy of pure liquid water.*”
  - I have switched to Roman style (where needed) for several (if not most of) indices and superscripts (in particular:  $S_P$ ,  $S_A$ ,  $S_{SO}$ ,  $t_{SO}$ ,  $P_{SO}$ ,  $t_u$ ,  $T_t$ ,  $p_t$ ,  $C_{ps}$ ,  $M_s$ ,  $M_w$ ,  $N_w$ ,  $\mu_{w/s}^0$ ,  $(\dots)_{liq.}$ ,  $(\dots)^{aq.}$ ,  $(\dots)_{std/TEOS10}$ ,  $\eta_{abs}$ ,  $\Delta\eta_s$ ,  $\eta_{Fei08}^{W/S}$ ,  $\eta_w$ ,  $\eta_s$ ,  $\eta_{w0}$ ,  $\eta_{s0}$ ,  $\eta_{v/i/3rd}^{calor./stat.}$ ,  $R_v$ ,  $c_w$ ,  $c_{pd}$ ,  $s_{d0}$ ,  $s_w$ ,  $\theta_s$ ,  $\Delta G_r$ ,  $\Delta H_r$ ,  $L_{sub}$ ,  $p_{sat}$ , ...)
  - I have changed a title and several texts in the Part-2:
    - “... Northeast Atlantic and Mediterranean Seas” (title of section 2.6);
    - “... the Arctic ocean; the Bay of Bengal; and the Northeast Atlantic and Mediterranean Seas.”;
    - “... In the Northeast Atlantic, colder temperature with smaller ...”;
    - “... Black and Caspian Seas; the Northeast Atlantic and Mediterranean Seas, ...”;
    - “... global surface ocean entropy.”
  - In the Fig.1 of Part-2: in the upper-middle vertical profile I have changed the colours and the labels for  $\theta$  (in blue),  $T$  (in purple), and  $\Theta$  (in red); in the lower-left vertical profile the “*min*” and “*max*” curves are removed; in the lower-right  $t$ - $S_A$  diagram the coloured scale is reverse (on the right, with the surface at the top) and dashed-blue curves are added for the standard (TEOS10) seawater entropy.

- In the Figs.2 and 3 of Part-2: in order to avoid spurious extrapolation up to 0 m (were no CTD value is available) the new vertical scales start at the depth of 15 m.
- In the Fig.4 of Part-2: in order to facilitate the localisation of regions with the larger values of the difference between the standard (Std) and absolute (Abs) seawater entropies, I have added the fifth global surface map showing the difference (Abs-Std).
- I have added several citations in the Part-1, first for Thermodynamic Tables Rossini et al. (1952) and Gokcen and Reddy (1996); then for the book of Planck (1911); and then for the papers and books by Cooper and Dooley (2008), Chou (1968), Pitzer (1987), Sharqawy et al. (2010), Stern (1960), Onsager and Fuoss (1932) and McDougall and Barker (2011).
- I recall in the Part-1 that: “*the term “isentropic” (or same entropy) includes possible joint variations in pressure, temperature and salinity, without prejudging any adiabatic (no exchange of heat) or closed (same salinity) aspect of the evolution of ocean parcels. This is analogous to the definition of “isopycnal” processes, where density (or potential density) remains constant regardless of joint variations in pressure, temperature and salinity, with variations in temperature and salinity along isopycnals described with spiciness.*”
- I have removed the first name Franck in all citations of Millero’s papers.
- A large part of the Conclusion of the Part-1 is removed and transferred toward the new section 3.3.
- In order not to offend anyone, I have clearly mention in Part-1 of the paper that: “*The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater itself, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.*”
- I also explain in the Conclusion of the Part-1 that: “*Since Fofonoff (1962, p.8), the prevailing view in the oceanographic community is that the choice of the linear salinity function  $-a_2 - a_4 S$  entering into the TEOS10 definition of the seawater entropy has no practical impact on known oceanographic applications, and that the choice of fixing  $-a_2$  and  $-a_4$  is a matter of convention. However, some people think that the Millero and TEOS10 approaches may be considered valid, and that neither should be subject to general rejection. It is within this last absolute-entropy framework that the present and Millero’s papers are situated.*”
- The length of the Part-1 is increased from 19 to 24 pages (section 3.3 + 2 new Figs.1 + the new Fig.2 + biblio).
- The length of the Part-2 is unchanged (16 pages) in spite a new difference map in the Fig.4.

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**Answers to the Referee 1 about the  
Comptes Rendus Geoscience paper:  
“ The absolute seawater entropy ”**  
by Pascal Marquet / November 29, 2025

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**General remarks to the referee 1.**

In order not to unduly lengthen the responses to the reviewers of both parts of my paper, I have prepared a fairly complete Supplementary Materials file which I will refer to as “SM” in the following. This SM file (Marquet, 2025, uploaded on the Zenodo cite) contains several additional Figures, Tables and details about the computations of my responses, as well as answers to many FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans. The time taken to write this large SM document partly explains the delay in finalizing the revision of this two-part paper.

I also provide a “ $\text{\LaTeX}$ -diff” document in which all changes and corrections to the text are indicated in red (cancelled) and blue (modified/new) coloured text.

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**A summary of all changes made to Part-1 and Part-2 of the paper**

In order to show to the Referees and Editor the whole set of changes made to the two-parts paper, before to answer point by point to the general and specific Comments, I may provide the following summary of all these changes made by myself and suggested by the Referees.

- I have prepared an external “*Supplementary Materials*” document (Marquet, 2025, uploaded in the Zenodo cite).
- I have removed the terms considered as “polemic”:
  - “(…) *violate*” the third law  $\rightarrow$  “(…) *differ from*” the third law;
  - “(…) *unless to violate the entropy budget* (…)”  $\rightarrow$  “(…) *unless to modify the entropy budget* (…)”;
  - “(…) *have the flaw of being in contradiction with*”  $\rightarrow$  “(…) *can be amended to correspond to*”;
  - “(…) *correcting*”  $\rightarrow$  “(…) *amending*”;
  - “(…) *prohibitive for the use of the standard entropy*”  $\rightarrow$  (removed) ;
  - “(…) *preferred to any other arbitrarily modified definition*”  $\rightarrow$  “(…) *should impact*” ;
  - “(…) *imposing the absolute values*”  $\rightarrow$  “(…) *using the absolute values*”;
  - “(…) *correcting and generalising the current* (…)”  $\rightarrow$  “(…) *amending, if needed, the current* (…)”;
  - “(…) *to compute the true value of* (…)”  $\rightarrow$  “(…) *to compute the absolute value of* (…)” ; ...)
- I have added the new section 3.3 with the new Fig.2, where I describe other more general situations in physics where the absolute values of entropies impact different phenomena (saturation pressures versus latent heat; turbulence; chemical constants for Ozone and Seawater reactions; entropy potential temperature  $\theta_\eta$ ), with detailed computations shown in the Supplementary Materials (Marquet, 2025), as well as answers to FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans.
- In this new section 3.3 I have added new citations: Planck (1917), Nernst (1918), Planck (1921), Nernst (1926) for the saturation pressure; Richardson (1919) Richardson (1922) Ma and Peltier

(2024) Canuto et al. (2002) for the turbulence; (Burkholder et al., 2020) Weiss (1974) Millero (1995) DOE (Departement of Energy, 1994) for Ozone and Seawater chemical reactions; Betts (1973) for the atmospheric liquid-water potential temperature.

- I have explained that the first resolution accepted during the 5th International Conference on the Properties of Steam in London (5th-ICPS et al., 1956) only concerned the steam water (one component system of constant composition), and not the seawater (multi-components system of variable composition), whereas a second resolution was adopted asking to provide the absolute values of entropies in all subsequent studies (as done in the present study).
- In the Fig.1 of the Part-1, I have added two zoom versions of the first diagram for very small salinity, to show the impact of the term  $x^2 \ln(x)$  corresponding to  $S_A \ln(S_A)$ .
- I recall in the conclusion of the Part-1 that the rejection of the third-law by the oceanic community can likely be dated to Fofonoff (1962, p.8), even though Fofonoff cited the previous books of Fowler (1929), Guggenheim (1933) and Guggenheim (1950), who all trusted the third law of thermodynamics and the Sackur-Tetrode translational entropy used in the present paper, and even though Guggenheim has chosen to call the “*absolute value*” of entropy the “*conventional*” entropy.
- I explain in the Part-1 about  $S(T) = 0 + k \ln(W)$  that: “... the 0 term indicates that no other arbitrary term must be added ...”
- The wrong title of the Section 4.3 of Part-1 I is duly change into “*The absolute entropy of pure liquid water.*”
- I have switched to Roman style (where needed) for several (if not most of) indices and superscripts (in particular:  $S_P$ ,  $S_A$ ,  $S_{SO}$ ,  $t_{SO}$ ,  $P_{SO}$ ,  $t_u$ ,  $T_t$ ,  $p_t$ ,  $C_{ps}$ ,  $M_s$ ,  $M_w$ ,  $N_w$ ,  $\mu_{w/s}^0$ ,  $(\dots)_{liq.}$ ,  $(\dots)^{aq.}$ ,  $(\dots)_{std/TEOS10}$ ,  $\eta_{abs}$ ,  $\Delta\eta_s$ ,  $\eta_{Fei08}^{W/S}$ ,  $\eta_w$ ,  $\eta_s$ ,  $\eta_{w0}$ ,  $\eta_{s0}$ ,  $\eta_{v/i/3rd}^{calor./stat.}$ ,  $R_v$ ,  $c_w$ ,  $c_{pd}$ ,  $s_{d0}$ ,  $s_w$ ,  $\theta_s$ ,  $\Delta G_r$ ,  $\Delta H_r$ ,  $L_{sub}$ ,  $p_{sat}$ , ...)
- I have changed a title and several texts in the Part-2:
  - “... *Northeast Atlantic and Mediterranean Seas*” (title of section 2.6);
  - “... *the Arctic ocean; the Bay of Bengal; and the Northeast Atlantic and Mediterranean Seas.*”;
  - “... *In the Northeast Atlantic, colder temperature with smaller ...*”;
  - “... *Black and Caspian Seas; the Northeast Atlantic and Mediterranean Seas, ...*”;
  - “... *global surface ocean entropy.*”
- In the Fig.1 of Part-2: in the upper-middle vertical profile I have changed the colours and the labels for  $\theta$  (in blue),  $T$  (in purple), and  $\Theta$  (in red); in the lower-left vertical profile the “*min*” and “*max*” curves are removed; in the lower-right  $t-S_A$  diagram the coloured scale is reverse (on the right, with the surface at the top) and dashed-blue curves are added for the standard (TEOS10) seawater entropy.
- In the Figs.2 and 3 of Part-2: in order to avoid spurious extrapolation up to 0 m (were no CTD value is available) the new vertical scales start at the depth of 15 m.
- In the Fig.4 of Part-2: in order to facilitate the localisation of regions with the larger values of the difference between the standard (Std) and absolute (Abs) seawater entropies, I have added the fifth global surface map showing the difference (Abs-Std).
- I have added several citations in the Part-1, first for Thermodynamic Tables Rossini et al. (1952) and Gokcen and Reddy (1996); then for the book of Planck (1911); and then for the papers and books by Cooper and Dooley (2008), Chou (1968), Pitzer (1987), Sharqawy et al. (2010), Stern (1960), Onsager and Fuoss (1932) and McDougall and Barker (2011).
- I recall in the Part-1 that: “*the term “isentropic” (or same entropy) includes possible joint variations in pressure, temperature and salinity, without prejudging any adiabatic (no exchange of heat) or closed (same salinity) aspect of the evolution of ocean parcels. This is analogous to the definition of “isopycnal” processes, where density (or potential density) remains constant regardless*

*of joint variations in pressure, temperature and salinity, with variations in temperature and salinity along isopycnals described with spiciness.”*

- I have removed the first name Franck in all citations of Millero’s papers.
- A large part of the Conclusion of the Part-1 is removed and transferred toward the new section 3.3.
- In order not to offend anyone, I have clearly mention in Part-1 of the paper that: “*The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater itself, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.*”
- I also explain in the Conclusion of the Part-1 that: “*Since Fofonoff (1962, p.8), the prevailing view in the oceanographic community is that the choice of the linear salinity function  $-a_2 - a_4 S$  entering into the TEOS10 definition of the seawater entropy has no practical impact on known oceanographic applications, and that the choice of fixing  $-a_2$  and  $-a_4$  is a matter of convention. However, some people think that the Millero and TEOS10 approaches may be considered valid, and that neither should be subject to general rejection. It is within this last absolute-entropy framework that the present and Millero’s papers are situated.*”
- The length of the Part-1 is increased from 19 to 24 pages (section 3.3 + new Fig.2 + biblio).
- The length of the Part-2 is unchanged (16 pages) in spite a new difference map in the Fig.4.

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## Answers to General Comments of the Referee

*Note that I reviewed both parts together as they really are a continuation of the same line of thought and broken up mostly to more manageably present the material, which I believe is a reasonable choice. These are well written and thorough manuscripts. The topic is somewhat esoteric, and the presentation is deliberate, but always clear, and commendable for its precision.*

- Thank you for your positive comments on my two papers.

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*My major comment is that the implications of the results for standard practice could be better drawn out and contextualized. This would also avoid the danger of the paper being interpreted as a polemic.*

• I take note of your comments, but I do not really understand the potentially “*controversial*” aspect of my approach, since it is mainly a matter of complying with the recommendations provided by a general principle of thermodynamics (the third law), which should not be polemic a priori.

However, following your remarks as well as those of another of the 3 reviewers, I think I have reduced the “*negative*” aspects wherever it was useful, for example by avoiding expressions like “*truth*” or “*errors*” and by replacing the expressions / “*violate*” / “*have the flaw*” / “*in contradiction with*” / “*correcting*” / ... with ... / “*differ from*” / “*can be amended*” / “*amending*” / ... instead...

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*The central point of both manuscripts is that for a multicomponent system the distribution of entropy depends on composition and thus become arbitrary in the absence of some governing principle.*

*The claim is that the third law provides this principle and hence should be used to define the reference entropy.*

*Other definitions make inferences from the distribution of entropy specious.*

- I agree with the reviewer’s analysis.

In fact, this is what I tried to show in this two-parts paper on ocean thermodynamics, as well as in my other papers published between 2011 and 2022 on atmospheric thermodynamics cited in a footnote at the beginning of the Part-1: Marquet (2011, 2014); Marquet and Geleyn (2015); Marquet (2017), Marquet and Dauhut (2018); Marquet and Bechtold (2020); Marquet et al. (2022); and Marquet and Stevens (2022), in particular.

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*The big and open question is whether the using a definition grounded in basic principles supports meaningful inferences from the distribution of entropy.*

*The general view is that this is not the case, although the consequence of this, which is that general entropy principles (like constancy or extrema) then also loose particular meaning, are often ignored.*

- Again, I agree with the reviewer’s analysis.

I agree that the general view is that, like for the atmosphere where most studies of the moist-air entropy consider that it is defined up to an arbitrary linear function of the total-water content ( $q_t = q_v + q_l + q_i$ ), most studies of the seawater entropy (except Millero’s and mine) consider that it is defined up to an arbitrary linear function of the total sea-salts content (the salinity  $S_A$  summarising the cations  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ , ..., and the anions  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ , ..., contents).

I would like to use this section to describe historical facts that may clarify things.

In fact, even though he was not able in his time to carry out explicit calculations of the entropy of a multi-component system, few people know that Gibbs himself had explained that the weighted sum of reference entropies could not be left arbitrary. I recall in the Fig. 1 two excerpts from his fundamental papers (Gibbs, 1875-1878, p.211 and p.217). This figure is from the Fig. 34 (p.122) in the section 12.8 of the Supplementary Material (dealing with FAQ about the Second Law).

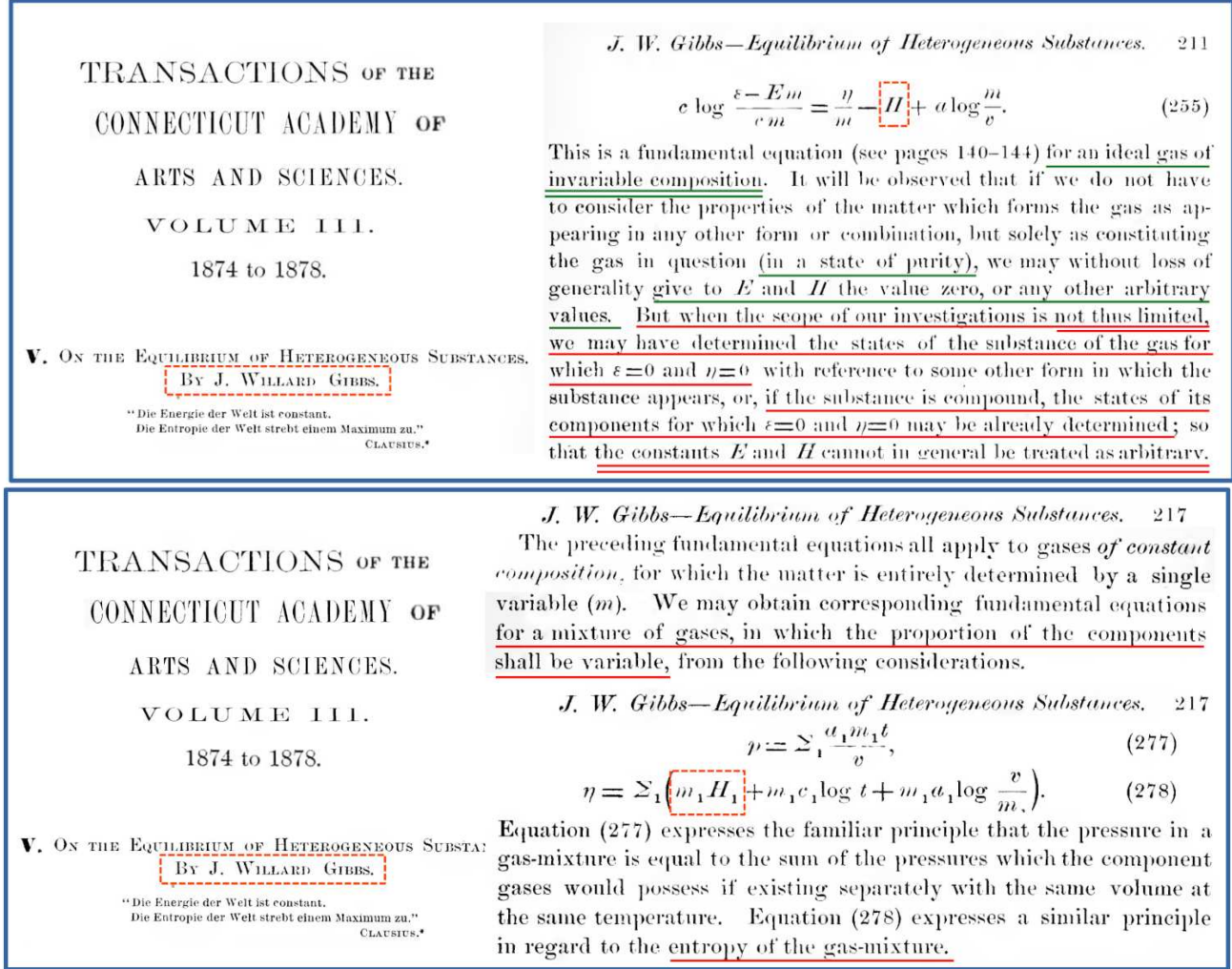
(Gibbs, 1875-1878, Eqs. 25 and 278, p.211 and 217) defined the entropy (noted  $\eta$ ) for a given gas (top) and for a mixture of gases (bottom) with a need to determine the constant of integration noted  $\sum_1 m_1 H_1$  in Eq. 278 and corresponding (with modern notations) to  $\sum_k q_k s_{k0}$  for the atmosphere and  $\sum_k c_k \eta_{k0}$  for the oceans.

(Gibbs, 1875-1878, 211) gave to us the important advice that, except for a given gas of constant composition for which  $H$  is a true constant and may be discarded in physical studies, “...  $H$  cannot in general be treated as arbitrary ...” “... if the substance is compound ...” and need the knowledge of “... the states of its components for which  $\varepsilon$  and  $\eta = 0$  ...” (namely its internal energy and entropy).

The same need to know the reference entropies were recalled by Fowler (1929), Guggenheim (1933) and Guggenheim (1950), who fully trusted the third law of thermodynamics and the corresponding Sackur-Tetrode translational entropy.

Unfortunately, a historical study shows that it was Fofonoff (1962, p.8) who steered all subsequent debates in oceanography by considering without proof, although citing the previous books by Fowler (1929), Guggenheim (1933) and Guggenheim (1950), that (after Eq. 20): “To determine the Gibbs function,  $g$ , completely –except for an arbitrary constant of the form  $(d + aT) + (c + bT)S$ – we would have to know absolute values of the three first derivatives, i.e. entropy  $\eta = -\partial g/\partial T$ , specific volume  $v = \partial g/\partial p$  and chemical potential difference  $\mu = \partial g/\partial S$  as functions of temperature, pressure and salinity.” Moreover, Fofonoff (1962, p.8) added that: “An alternative interpretation of the arbitrary linear function of salinity in the definition of  $\eta$  is obtained by introducing a combined partial entropy of the salts,  $\eta_s = -\partial \mu_s/\partial T$ . Then, the specific entropy,  $\eta$ , is given by  $s \eta_s + (1 - s) \eta_w$ ” (with a typo corrected). This is precisely the method used by Millero and myself to define the seawater entropy. However, Fofonoff (1962) immediately added in this footnote, still without proof, that: “-The partial

Figure 1: The words of Gibbs (1875-1878, p.211) about the choice of the constants  $E$  (for energy) and  $H$  (for the entropy) for a given perfect gas (top) and a mixture of perfect gases (bottom).



entropies,  $\eta_s$ ,  $\eta_w$ , contain arbitrary constants giving rise to an arbitrary linear function of salinity in  $\eta$ " (i.e. the seawater entropy).

These remarks of Fofonoff (1962) are recognisable as those still recalled and accepted without proof in more recent studies, particularly in IAPWS and TEOS10. Indeed, it is similarly explicitly mentioned in the TEOS10 manual McDougall et al. (2010) close to Eq. 2.6.2 and about the idea that: "The Gibbs function contains four arbitrary constants that cannot be determined by any set of thermodynamic measurements. These arbitrary constants mean that the Gibbs function ( $g$ ) is unknown and unknowable up to the arbitrary function of temperature and Absolute salinity"

$$[a_1 + a_2 (T_0 + t)] + [a_3 + a_4 (T_0 + t)] S_A.$$

This lowest-order part of the Gibbs function implies that the specific entropy  $\eta = -\partial g / \partial T$  depends on the lowest-order "arbitrary function"  $-a_2 - a_4 S_A$ .

Nonetheless, as a matter of fact the aspect "unknowable" of  $a_2$  and  $a_4$  is in contradiction with the third-law of thermodynamics, which allows the determination of the absolute entropies for pure water and sea salts since Lewis and Randall (1961) at least, as recalled in Millero and the present paper where the constant term  $-a_4 = (\eta_{s0} - \eta_{w0}) \approx 1633 - 3513 \approx -1880 \pm 17$  J/K/kg can indeed precisely be known, and thus is not "unknowable" by definition, with more precisely the values  $\eta_{s0} \approx 1633 \pm 15$  J/K/kg and

$\eta_{w0} \approx 3513 \pm 1.7$  J/K/kg retained in my present two-parts paper.

Accordingly, the purpose of my present two-Parts paper is to show that the numerical values of the seawater entropy itself, and also its gradients and its time derivative, all depend on these two reference values via the third-law value of the difference  $(\eta_{s0} - \eta_{w0}) \approx 1633 - 3513 \approx -1880 \pm 17$  J/K/kg, which is not “arbitrary” nor “unknowable” since it is precisely known.

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*The author makes the case that if the constituents can transform (electrochemistry in the ocean, ozone chemistry in the atmosphere) then one needs to consider the constituent transformation entropies, but what if the constituents don't transform into one another. The author is uniquely qualified to give a perspective on this, but it would be more compelling if he took on more the role of being his own devils advocate. Here the paragraph starting on line 324 (Part II) is particularly speculative, and seems a bit biased. A more objective stance would be preferable.*

- Since 1988 and my studies of the exergy of the atmosphere and oceans, and then from 2010 of the entropies and enthalpies of the atmosphere and oceans, I have constantly compared my calculations with the observed data, always with the idea that I could have made mistakes, forgotten things already published, or misunderstood things better understood by others...

And it is precisely following common and numerous criticisms received from the atmospheric (ex. Olivier Pauluis and Rémi Tailleux) and oceanographic (ex. Rainer Feistel and Trevor Mc Dougall) communities, saying that the differences between the standard and absolute versions of entropies have no measurable physical impact, that I have tried to find such impacts on measurable and objective quantities. That is why I had tried to explain, perhaps too succinctly and not convincingly enough in the initially submitted version of the paper, that chemical reactions formed examples of such impacts, both for the atmosphere and the ocean.

In order to try to be more clearly understood I describe –with more details than in the initial submitted version of the paper– several validations of the physical impacts of absolute, third-law reference entropy values in the new section 3.3 entitled “General impacts of the Third law in physics” (Part I of the paper).

In particular, I still recall that all constant of chemical reactions do depend on the “entropy of reaction”  $\Delta S^\circ = \sum_k \nu_k S_k^\circ - \sum_{k'} \nu_{k'} S_{k'}^\circ$ , namely the weighted sum of absolute entropies for products minus the weighted sum of absolute entropies for reactants, which must be computed from the same absolute (third-law) values  $S_k^\circ$  and  $S_{k'}^\circ$ , all available in thermodynamical Tables as those used for the present study (and of course for many of them in the book of Lewis and Randall, 1961).

I show in the section 12.2 of the Supplementary Materials (entitled “Validations and physical meaning of absolute entropies / Chemical reactions”) that the constant terms  $A$  in the chemical constants defined as  $\ln(K) = A + B/T + C \ln(T)$  can be defined from the  $S_k^\circ$ ’s and  $S_{k'}^\circ$ ’s for the Ozone-chemistry reactions  $\text{NO} + \text{NO}_2 \longleftrightarrow \text{N}_2\text{O}_3$  and  $\text{Cl} + \text{O}_2 \longleftrightarrow \text{ClO}_2$ , as well as the oceanic reaction  $\text{HCO}_3^- \longleftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ . The consequence is that the concentrations in ozone and sea salts both depends on these absolute (third-law) values of entropies, this providing an additional proof for physical impacts and meanings for these absolute (third-law) values of entropies, because concentrations are observable quantities, as well as temperature in the stratosphere and the surface oceanic layers that are impacted via radiation fluxes by these concentrations.

For the seawater, the chemical reaction  $\text{HCO}_3^- \longleftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  is only one of the so many reactions explaining the observed concentrations in cations and anions recalled in the Table 3 of the present paper. A list of many other reactions can be found in DOE (1994). All these reactions a subject to similar impacts of the third-law absolute values of entropies for reactants and products. On the reverse, the study of the reaction constant  $K$  for  $\text{HCO}_3^- \longleftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  should allow the computation of the absolute (third-law) entropy for  $\text{HCO}_3^-$  from the one for  $\text{CO}_3^{2-}$ , or vice versa, because without lack of

generality the entropy of  $H^+$  is set to 0. I'm not sure that many in the ocean community are aware of these facts, which justifies the desire to describe these facts more precisely in the new section 3.3 of the Part 1.

In the new section 3.3 of the Part 1, I also recall that the absolute (third-law) Sackur-Tetrode values for entropies were first validated before 1926 from observations, with for instance the theoretical value  $C_0 \approx -1.608$  in agreement the experimental value  $C_0 \approx -1.62 \pm 0.03$ . These facts was in particular recalled by: Nernst (1918); Nernst (1921, Nobel prize lecture); Planck (1921); and Nernst (1926). It seems that all of this is forgotten nowadays...

In addition to these old validations of the absolute (third-law) Sackur-Tetrode values for the monatomic (or translational) entropies, I show in new section 3.3 of the Part 1 another existing surprising link between the saturation pressure  $p_{\text{sat}}(T_0)$  and the latent heat of sublimation  $L_{\text{sub}}(T_0)$  over water Ice-Ih at  $T_0 = 273.15$  K ( $0^\circ\text{C}$ ). Indeed, as an extension of the work carried out near absolute zero of temperatures in the years 1910-20 and recalled by Nernst and Planck, I have established since 2022 (and validated for the present article) the relationship that must exist between the latent heat  $L_{\text{sub}}(T_0)$  and the saturation pressure  $p_{\text{sat}}(T_0)$ , with the link between the two being the difference  $\delta\eta(T_0, p_0) \approx 8023 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$  between the absolute entropy for water vapor at  $0^\circ\text{C}$  calculated by the theoretical method (statistical physics), on the one hand, and the entropy of Ice-Ih calculated independently by the experimental method (calorimetric), on the other hand. It turns out that the agreement between  $\delta\eta(T_0, p_0)$  and the values of  $L_{\text{sub}}(T_0)$  and  $p_{\text{sat}}(T_0)$  is good.

In particular, if we rely on the third-law absolute value for  $\delta\eta(T_0, p_0)$ , it is possible to compute either  $L_{\text{sub}}(T_0)$  from  $p_{\text{sat}}(T_0)$ , or vice versa  $p_{\text{sat}}(T_0)$  from  $L_{\text{sub}}(T_0)$ , leading to  $L_{\text{sub}}(T_0) \approx 2834.0 \pm 3.6 \text{ kJ kg}^{-1}$  or  $p_{\text{sat}}(T_0) \approx 609 \pm 20 \text{ Pa}$ , which are indeed in agreement with the experimental values  $L_{\text{sub}}(T_0) \approx 2834.5 \text{ kJ kg}^{-1}$  and  $p_{\text{sat}}(T_0) \approx 611.15 \pm 0.10 \text{ Pa}$ . This means that the third-law absolute values for water entropy control, link and constrain the two measurable quantities  $L_{\text{sub}}(T_0)$  and  $p_{\text{sat}}(T_0)$  impacting the thermodynamic conditions at the surface of the oceans, and thus impacting the measurable evaporation processes.

I also explain in the new section 3.3 of the Part 1 (with more details provided in the section 12.9 of the Supplementary Materials) that the atmospheric turbulence seems to be controlled, as expected by Richardson (1919, 1922), by positive well-founded exchange coefficients when the absolute moist-air entropy is chosen as the thermal variable on which the turbulence is acting (in fact the variable  $\theta_s$  defined in Marquet, 2011, for which the Lewis number is often different from unity). I similarly (better?) introduce in the new section 3.3 of the Part 1 the seawater entropy potential temperature  $\theta_\eta$  (the counterpart of  $\theta_s$ ), which seems to be possibly linked with the “*double diffusion*” turbulent schemes often used in oceanic modelling.

Therefore, I hope that the new section 3.3 of the Part 1 (which somehow replaces the old paragraph starting on line 324 in the Part II) is less “*speculative*” and less “*biased*” and more “*objective*” than in the first submitted version.

More generally, in atmospheric and seawater thermodynamics the Boltzmann  $k = R/N$  and Avogadro  $N = R/k$  constants have physical impacts only via the product  $R = N k$ . Would this means that, since only  $R$  would be measurable in atmospheric and seawater thermodynamics, one could define arbitrarily  $k$  and  $N$ , provided that  $R = N k$  is kept to its usual constant value? I do not think so ... and the same is true for the third-law (absolute) entropies that should always be set to the values available in all thermodynamic Tables.

As another example, let us consider the speed of light in vaccum ( $c$ ), which impacts nothing in the everyday real life (who redo the Rømer, Fizeau, Foucault measurements everyday?): does it means that we could set the speed of light in vaccum to arbitrary values? For instance, in radiation processes only the Stefan-Boltzmann and the second radiation constants  $\sigma = (2 \pi^5 k^4)/(15 h^3 c^2)$  and  $c_2 = h c / k$  impact the (black-body) radiation laws. But like the reaction constant  $K$  that could be kept from



pure measurements without appealing to the third-law absolute entropies to known the constant term  $\Delta S^0$ , we could rely on pure measured values of  $\sigma$  and  $c_2$ , without knowing the values of  $k$ ,  $h$  and  $c$ : would this be desirable? This would mean that both  $\sigma$  and  $c_2$  could be arbitrarily modified? Why not relying on general laws of physics, as far as possible? And similarly, why not relying on the third-law of thermodynamics in atmospheric and oceanic studies, with in particular the Sackur-Tetrode-Planck theoretical value  $\ln[(2\pi)^{3/2} k^{5/2}/(h^3 N^{3/2})] = 18.22285085$  (i.e. the exact 2019 value) controlling all third-law (absolute) values of entropies of atoms and molecules?

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## Answers to Specific Comments of the Referee

*1. Notational standards should be followed for the mathematical presentation, mostly this relates to when and where the italic font is used, i.e., for variables only. e.g., TEOS should be in roman fonts when it appears in subscripts, as it is not the composition of four variables, likewise for things like max, min, abs, etc.*

• I believe I have changed in the two parts of the paper all instances where subscript terms should be in Roman font:  $S_P$ ,  $S_A$ ,  $S_{SO}$ ,  $t_{SO}$ ,  $P_{SO}$ ,  $t_u$ ,  $T_t$ ,  $p_t$ ,  $C_{ps}$ ,  $M_s$ ,  $M_w$ ,  $N_w$ ,  $\mu_{w/s}^0$ ,  $(\dots)_{liq.}$ ,  $(\dots)^{aq.}$ ,  $(\dots)_{std}/TEOS10$ ,  $\eta_{abs}$ ,  $\Delta\eta_s$ ,  $\eta_{Fei08}^{W/S}$ ,  $\eta_w$ ,  $\eta_s$ ,  $\eta_{w0}$ ,  $\eta_{s0}$ ,  $\eta_{v/i/3rd}^{calor./stat.}$ ,  $R_v$ ,  $c_w$ ,  $c_{pd}$ ,  $s_{d0}$ ,  $s_w$ ,  $\theta_s$ ,  $\Delta G_r$ ,  $\Delta H_r$ ,  $L_{sub}$ ,  $p_{sat}$ , ...

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*2. I'm not a fan of the term latent heat. I prefer "specific phase change enthalpies" and the lower case. This would also be better fitting of the precision that that author attaches to other terms.*

• The term "*latent heat*" is used throughout the TEOS10 manual (McDougall et al., 2010), as is the notation using capital letters  $L$ . As I have chosen to use TEOS10 software as a reference for the ocean thermodynamics, I prefer to align myself with the conventions (like  $L_{sub}$  for the latent heat of sublimation) used in this TEOS10 manual. Furthermore, this terminology (latent heat) and notation ( $L$ ) is also used in most of publications on atmospheric thermodynamics.

In particular, the "*latent heat of melting*" is defined in the Section (3.34) entitled "*Latent heat of melting*" of the TEOS10 manual as  $L_p^{WI} = h^W - h^{Ih}$  (Eq. 3.34.1). The same is true for the "*latent heat of sublimation*" defined in the Section (3.36) entitled "*Sublimation enthalpy*" as  $L_p^{VI} = h^V - h^{Ih}$  (Eq. 3.36.1). The same is true for the "*latent heat of evaporation*" defined in the Section (3.39) entitled "*Latent heat of evaporation*" as  $L_p^{VW} = h^V - h^W$  (Eq. 3.39.1).

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*3. §2.6: I find it strange to talk about "Europe's ocean." Maybe "northeast atlantic and mediterranean." Likewise "global surface entropy" could be "global surface ocean entropy."*

- I have changed the title of the §2.6 in the Part-2: "... Northeast Atlantic and Mediterranean Seas."
- ... also with 3 other changes:  
 "... the Arctic ocean; the Bay of Bengal; and the Northeast Atlantic and Mediterranean Seas."  
 "... In the Northeast Atlantic, colder temperature with smaller ..."  
 "... Black and Caspian Seas; the Northeast Atlantic and Mediterranean Seas, ..."
- I have also changed the title of the §2.3 in the Part-2: "... global surface ocean entropy."

4. For Figure 1 (Part II) bottom left, I was initially confused by the discrimination between the max and min, I don't think these add much and their consideration is inconsistent with the lack of consideration of definitional uncertainty in other quantities.

- So many people asked me since 2011 to indicate and study the uncertainty in the absolute-entropy increments (for both the atmosphere and the seawater, with obviously the hope for them that they could be large enough to remove any interest to compute these absolute-entropy increments). This is why I intended in the first submitted version of the paper to provide these max and min curves...

However, in order to take into account the demand of the referee, I have removed these min/max information in the Part 1 and in the Figure 1 of the Part 2, with the new short sentence in the Part II: “Note that the uncertainty of the impact of  $\Delta\eta_s$  is small (not shown), because the relative uncertainty of  $-1880 \pm 17$  in (5) represents only 1 % of the difference between the blue and red curve in the Fig. 1.”

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5. In line 38 in Part 1, it would be helpful to clarify the 0 reference to the right of the equality sign. I think this is meant to designate the caloric reference entropy, but maybe it could be specified as a symbol and the situation when the symbol is zero could be specified. Also ‘he’ -> ‘the’ and I don't understand the use of ‘next’ in line 41.

- I have fixed the typo ‘he’ -> ‘the’
- The term “0” in the statistical formula  $S(T) = 0 + k \ln(W)$  was somehow explained in a next line: “Note that if the original third law corresponds to both  $S(T = 0 \text{ K}) = 0$  in the calorimetric formula and to the 0 term in the statistical one ...”
- However, this may not be clear enough and I have modified the sentence, with in particular: “(...)  $S(T) = 0 + k \ln(W)$ , where the 0 term indicates that no other arbitrary term must be added, (...)”

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6. I found it a bit unconventional to refer to one of the cited authors by first and last name, but not the others, e.g., repeated reference to “Franck Millero” rather than simply “Millero”.

- I have harmonised things and removed all first names (7 times).

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7. The phrase “in order” can almost always be dropped without any loss in meaning.

- I am not sure which sentence is to be cancelled?

I guess it is the sentence in line with the point 4 above, about the max/min of the term  $-1880 \pm 17$  in the absolute-entropy increment?

If so, I have already cancelled most of the information about the max/min of the term  $-1880 \pm 17$ , both in Part I (former Eqs. 16 and 17) and II (Fig. 1).

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8. Part 1, line 275. Most readers will intuitively think of an isentropic process as one in a closed system for which salinity would be preserved. An isentropic process in T-S space is thus somewhat unusual as it mixes compositional with thermal contributions to entropy, which is at the heart of the matter of my more general comments.

- In the atmosphere, when we talk about “isobaric” surfaces, we simply mean that the pressure is constant, even if for moist air, for example, we have a pressure  $p = \rho R T$  that depends not only on the density  $\rho$  and the temperature  $T$ , but also on the humidity variables ( $q_v$ ,  $q_l$ ,  $q_i$ ) via the gas factor  $R = (1 - q_v - q_l - q_i) R_d + q_v R_v$  which depends on the contents in water vapour ( $q_v$ ), liquid water ( $q_l$ ) and ice ( $q_i$ ).

Similarly, when we talk about isopycnal surfaces for the ocean (i.e. surfaces of equal density that depend on pressure, temperature and salinity), we do not make any assumptions about the constancy of salinity in  $T$ - $S$  diagrams.

The same should therefore apply to the concepts of isenthalpic (same enthalpy) and isentropic (same entropy) processes or surfaces, which can mix points with very different temperatures, pressures or salinities, but which lead to the same values for enthalpy or entropy in  $T$ - $S$  diagrams.

I am well aware that in current studies of the atmosphere and the ocean, people tend to confuse isentropic (same entropy) with joint adiabatic (no heat exchange) and closed (no exchange of matter) aspects. However, the three aspects must be clearly differentiated, and my aim is precisely to highlight the regions where the entropy of seawater is homogeneous (isentropic), regardless of variations in pressure, temperature and salinity.

It was by doing this for the atmosphere that I was able to highlight the links between the stability of tropical marine stratocumulus clouds and vertical variations in the moist-air entropy, despite significant joint variations in both temperature and humidity. The critical stratocumulus regime currently taken into account since 2021 in the turbulence scheme of the IFS model at the ECMWF (one of the three best global models in the world) is based precisely on isentropic vertical profiles, where both temperature and water content vary greatly and jointly on the vertical (Marquet and Bechtold, 2020; Bechtold, 2021).

I believe that the isentropic seawater processes I highlight in the part II of my present paper should find some resonance in future ocean studies, including and especially where salinity and temperature jointly vary with depth or at the surface.

To positively address the referee’s comment, I have added an explanatory sentences:

*It should be noted here (like in the Part-II) that the term “isentropic” (or same entropy) includes possible joint variations in pressure, temperature and salinity, without prejudging any adiabatic (no exchange of heat) or closed (same salinity) aspect of the evolution of ocean parcels. This is analogous to the definition of “isopycnal” processes, where density (or potential density) remains constant regardless of joint variations in pressure, temperature and salinity, with variations in temperature and salinity along isopycnals described with spiciness.*

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9. Part 1, line 347: “It is true that most observable...” this statement would be better justified if the observable quantities that do depend on the absolute entropy could be clarified. This an(d) the paragraph on line 369 also touches on my broader points.

- *I hope that the new section 3.3 of the Part 1 (and also the detailed FAQ provided in the Supplementary Materials) may provide better or even new justifications for using “observable quantities that do depend on the absolute entropy:” rate of chemical reactions (for Ozone and seawater ions); turbulence and positive exchange coefficient; old validations close to 0 K –and a new one at 0°C– for the links between absolute (third-law) entropies, latent heats and saturation pressure; ...*

Normally, I should not have had to endure all the criticism and doubts that have been expressed for more than 15 years now. When I was 19, at the beginning of my higher education, I did so much thermochemistry that it became not only a habit but a second nature to consider that absolute entropy values should be used (except, of course, up to a true constant term, and therefore for the trivial cases of a single-component substance like pure liquid water without salt, or dry air without water).

Normally, anyone who has taken advanced courses in thermodynamics should have no questions and should calculate the entropies of the atmosphere and oceans by applying the third law of thermodynamics, without asking any questions. Unfortunately, while a few people immediately accepted the validity of my work (such as Jean-François Geleyn and Jean-François Mahfouf in France), or did so after some explanation (Peter Bechtold at ECMWF and Bjorn Stevens at MPI), I was subjected to a barrage of criticism since 2010, all along the same lines: what is the point of calculating and studying entropy itself? And who is to say that this entropy corresponds to an objective, measurable reality that would allow us to distinguish the accuracy of the absolute version of these entropies from those commonly accepted in atmospheric and oceanic studies?

Accordingly, the reason why I have addressed this topic of “observable” quantities was forced upon me by the numerous criticisms who explained to me that: “... we should only study quantities that are measurable ... there is no “thermometer” for entropy ... therefore we should not compute nor study the (seawater) entropy ... or else with great freedom and with the right to arbitrarily modify the reference values as in TEOS10 ... ”

To respond to all these criticisms, first of all, the corresponding Wikipedia page<sup>1</sup> confirms the (non-quantum) acceptance that: “In physics, an observable is a physical property or physical quantity that can be measured.” In this sense, I was able to show in the new section 3.3 of the Part 1 that, via reaction constants, or via the links between saturation pressures and latent heats, it is possible to measure the entropy differences between different states of systems. We can therefore at least say that differences in entropy can be measured, and that these differences allow us to distinguish between absolute values (consistent with observations) and other values (which contradict them).

However, even for those who persist in not believing these scientific facts, if we follow to the end the reasoning that entropy cannot be measurable (in short there is no “entropy thermometer”) and then must not be studied in the form of the absolute (third-law) version of it, I would say that for the same reasons we should not study the potential vorticity (PV) complex quantity  $PV = [\vec{\zeta}_a \cdot \vec{\nabla}(\psi)]/\rho$  in the atmosphere, since there is no “PV thermometer” (see the section 12.7 in the Supplementary Materials entitled “Validations and physical meaning of absolute entropies / Entropy-meter?” And yet, there have been numerous and rich applications of the studies of PV since the original German papers by Ertel (1942a,b,c) (all translated in English by Schubert et al., 2004) and since the seminal paper by Hoskins et al. (1985). I have recalled since Marquet (2014) that Ertel explicitly suggested for  $\psi$  the three possibilities:

- the dry-air potential temperature ( $\psi = \theta$ ); or
- the dry-air entropy ( $\psi = S = c_{pd} \ln(\theta) + cste$ ); or
- the total water content ( $\psi = q_t = q_v + q_l + q_i$ ).

Other moist-air variables  $\psi$  have been then suggested and studied, such as the virtual ( $\theta_v$ ), equivalent ( $\theta_e$ ), pseudo-adiabatic ( $\theta'_w$ ), or moist-air entropy ( $\theta_s$ ) potential temperatures. Moreover, I have shown in Marquet (2014) that the use of the moist-air entropy can also be used as the variable  $\psi$  in the PV formula, or better the associated potential variable  $\theta_s$  I defined in Marquet (2011), still without associated “PV thermometer” and clearly with the PV not being an “observable quantity.”

As a conclusion of this item, I believe that it is not necessary for a quantity to be “observable” to justify the study of that quantity. Anyhow, I have shown in the new section 3.3 of the Part 1 that several examples exist for which it is possible to validate the physical meaning of the absolute (third-law) version of entropies, with several validations against observations that invalidate the other “conventional” (non third-law) values of the entropies.

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<sup>1</sup> See: <https://en.wikipedia.org/wiki/Observable>

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**Answers to the Referee 2 about the  
Comptes Rendus Geoscience paper:  
“ The absolute seawater entropy ”**  
by Pascal Marquet / November 29, 2025

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**General remarks to the referee 2.**

In order not to unduly lengthen the responses to the reviewers of both parts of my paper, I have prepared a fairly complete Supplementary Materials file which I will refer to as “SM” in the following. This SM file (Marquet, 2025, uploaded on the Zenodo cite) contains several additional Figures, Tables and details about the computations of my responses, as well as answers to many FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans. The time taken to write this large SM document partly explains the delay in finalizing the revision of this two-part paper.

I also provide a “ $\text{\LaTeX}$ -diff” document in which all changes and corrections to the text are indicated in red (cancelled) and blue (modified/new) coloured text.

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**A summary of all changes made to Part-1 and Part-2 of the paper**

In order to show to the Referees and Editor the whole set of changes made to the two-parts paper, before to answer point by point to the general and specific Comments, I may provide the following summary of all these changes made by myself and suggested by the Referees.

- I have prepared an external “*Supplementary Materials*” document (Marquet, 2025, uploaded in the Zenodo cite).
- I have removed the terms considered as “polemic”:
  - “(…) *violate*” the third law  $\rightarrow$  “(…) *differ from*” the third law;
  - “(…) *unless to violate the entropy budget* (…)”  $\rightarrow$  “(…) *unless to modify the entropy budget* (…)”;
  - “(…) *have the flaw of being in contradiction with*”  $\rightarrow$  “(…) *can be amended to correspond to*”;
  - “(…) *correcting*”  $\rightarrow$  “(…) *amending*”;
  - “(…) *prohibitive for the use of the standard entropy*”  $\rightarrow$  (removed) ;
  - “(…) *preferred to any other arbitrarily modified definition*”  $\rightarrow$  “(…) *should impact*” ;
  - “(…) *imposing the absolute values*”  $\rightarrow$  “(…) *using the absolute values*”;
  - “(…) *correcting and generalising the current* (…)”  $\rightarrow$  “(…) *amending, if needed, the current* (…)”;
  - “(…) *to compute the true value of* (…)”  $\rightarrow$  “(…) *to compute the absolute value of* (…)” ; ...)
- I have added the new section 3.3 with the new Fig.2, where I describe other more general situations in physics where the absolute values of entropies impact different phenomena (saturation pressures versus latent heat; turbulence; chemical constants for Ozone and Seawater reactions; entropy potential temperature  $\theta_\eta$ ), with detailed computations shown in the Supplementary Materials (Marquet, 2025), as well as answers to FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans.
- In this new section 3.3 I have added new citations: Planck (1917), Nernst (1918), Planck (1921), Nernst (1926) for the saturation pressure; Richardson (1919) Richardson (1922) Ma and Peltier



(2024) Canuto et al. (2002) for the turbulence; (Burkholder et al., 2020) Weiss (1974) Millero (1995) DOE (Departement of Energy, 1994) for Ozone and Seawater chemical reactions; Betts (1973) for the atmospheric liquid-water potential temperature.

- I have explained that the first resolution accepted during the 5th International Conference on the Properties of Steam in London (5th-ICPS et al., 1956) only concerned the steam water (one component system of constant composition), and not the seawater (multi-components system of variable composition), whereas a second resolution was adopted asking to provide the absolute values of entropies in all subsequent studies (as done in the present study).
- In the Fig.1 of the Part-1, I have added two zoom versions of the first diagram for very small salinity, to show the impact of the term  $x^2 \ln(x)$  corresponding to  $S_A \ln(S_A)$ .
- I recall in the conclusion of the Part-1 that the rejection of the third-law by the oceanic community can likely be dated to Fofonoff (1962, p.8), even though Fofonoff cited the previous books of Fowler (1929), Guggenheim (1933) and Guggenheim (1950), who all trusted the third law of thermodynamics and the Sackur-Tetrode translational entropy used in the present paper, and even though Guggenheim has chosen to call the “*absolute value*” of entropy the “*conventional*” entropy.
- I explain in the Part-1 about  $S(T) = 0 + k \ln(W)$  that: “... *the 0 term indicates that no other arbitrary term must be added ...*”
- The wrong title of the Section 4.3 of Part-1 I is duly change into “*The absolute entropy of pure liquid water.*”
- I have switched to Roman style (where needed) for several (if not most of) indices and superscripts (in particular:  $S_P$ ,  $S_A$ ,  $S_{SO}$ ,  $t_{SO}$ ,  $P_{SO}$ ,  $t_u$ ,  $T_t$ ,  $p_t$ ,  $C_{ps}$ ,  $M_s$ ,  $M_w$ ,  $N_w$ ,  $\mu_{w/s}^0$ ,  $(...)_\text{liq.}$ ,  $(...)_\text{aq.}$ ,  $(...)_\text{std/TEOS10}$ ,  $\eta_\text{abs}$ ,  $\Delta\eta_s$ ,  $\eta_{\text{Fei08}}^{W/S}$ ,  $\eta_w$ ,  $\eta_s$ ,  $\eta_{w0}$ ,  $\eta_{s0}$ ,  $\eta_{v/i/3rd}^{\text{calor./stat.}}$ ,  $R_v$ ,  $c_w$ ,  $c_{pd}$ ,  $s_{d0}$ ,  $s_w$ ,  $\theta_s$ ,  $\Delta G_r$ ,  $\Delta H_r$ ,  $L_\text{sub}$ ,  $p_\text{sat}$ , ...)
- I have changed a title and several texts in the Part-2:
  - “... *Northeast Atlantic and Mediterranean Seas*” (title of section 2.6);
  - “... *the Arctic ocean; the Bay of Bengal; and the Northeast Atlantic and Mediterranean Seas.*”;
  - “... *In the Northeast Atlantic, colder temperature with smaller ...*”;
  - “... *Black and Caspian Seas; the Northeast Atlantic and Mediterranean Seas, ...*”;
  - “... *global surface ocean entropy.*”
- In the Fig.1 of Part-2: in the upper-middle vertical profile I have changed the colours and the labels for  $\theta$  (in blue),  $T$  (in purple), and  $\Theta$  (in red); in the lower-left vertical profile the “*min*” and “*max*” curves are removed; in the lower-right  $t$ - $S_A$  diagram the coloured scale is reverse (on the right, with the surface at the top) and dashed-blue curves are added for the standard (TEOS10) seawater entropy.
- In the Figs.2 and 3 of Part-2: in order to avoid spurious extrapolation up to 0 m (were no CTD value is available) the new vertical scales start at the depth of 15 m.
- In the Fig.4 of Part-2: in order to facilitate the localisation of regions with the larger values of the difference between the standard (Std) and absolute (Abs) seawater entropies, I have added the fifth global surface map showing the difference (Abs-Std).
- I have added several citations in the Part-1, first for Thermodynamic Tables Rossini et al. (1952) and Gokcen and Reddy (1996); then for the book of Planck (1911); and then for the papers and books by Cooper and Dooley (2008), Chou (1968), Pitzer (1987), Sharqawy et al. (2010), Stern (1960), Onsager and Fuoss (1932) and McDougall and Barker (2011).
- I recall in the Part-1 that: “*the term “isentropic” (or same entropy) includes possible joint variations in pressure, temperature and salinity, without prejudging any adiabatic (no exchange of heat) or closed (same salinity) aspect of the evolution of ocean parcels. This is analogous to the definition of “isopycnal” processes, where density (or potential density) remains constant regardless*

*of joint variations in pressure, temperature and salinity, with variations in temperature and salinity along isopycnals described with spiciness.”*

- I have removed the first name Franck in all citations of Millero’s papers.
- A large part of the Conclusion of the Part-1 is removed and transferred toward the new section 3.3.
- In order not to offend anyone, I have clearly mention in Part-1 of the paper that: “*The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater itself, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.*”
- I also explain in the Conclusion of the Part-1 that: “*Since Fofonoff (1962, p.8), the prevailing view in the oceanographic community is that the choice of the linear salinity function  $-a_2 - a_4 S$  entering into the TEOS10 definition of the seawater entropy has no practical impact on known oceanographic applications, and that the choice of fixing  $-a_2$  and  $-a_4$  is a matter of convention. However, some people think that the Millero and TEOS10 approaches may be considered valid, and that neither should be subject to general rejection. It is within this last absolute-entropy framework that the present and Millero’s papers are situated.*”
- The length of the Part-1 is increased from 19 to 24 pages (section 3.3 + new Fig.2 + biblio).
- The length of the Part-2 is unchanged (16 pages) in spite a new difference map in the Fig.4.

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## Answers to the recommendation

*I have read the paper a few times and apologize for taking so long.*

*I repeatedly searched for the goal of the paper and how important/relevant the suggested improvement are. I did not find either of them, except in highly technical terms.*

- I think that the titles indicated the essential motivations and content of the two papers: “*The absolute seawater entropy: Part I. Definition / Part II. Case studies.*”

In the first part I have defined the absolute version of the seawater entropy, showing that current versions based on “*conventional*” (arbitrary) assumptions for the reference entropies of liquid water and sea salts differ from the “*absolute*” (third-law, thermodynamic) version of them.

Then I study in the second part the differences between these two “*conventional*” and “*absolute*” versions of entropy by using observed or analyzed cases of vertical profiles of temperature, salinity and pressure, as well as oceanic surface datasets.

I think I followed a classic scientific approach, with, it seems to me, notable and interesting differences between these “*conventional*” and “*absolute*” versions of the seawater entropy, and with the “*absolute*” version revealing new isentropic regions that could be studied in the future by the oceanic community.

I think I have previously followed a similar scientific approach for the atmospheric thermodynamics between 2011 (Marquet, 2011) and 2022 (Marquet et al., 2022; Marquet and Stevens, 2022), when I was able to demonstrate and published that the absolute definition of the moist-air atmospheric entropy has unique and remarkable properties, with for instance daily use since 2021 in the ECMWF’s IFS model (one of the three best global models in the world) of the analysis of vertical profiles of absolute moist-air entropy to distinguish between stable and unstable marine stratocumulus clouds (Marquet and Bechtold, 2020; Bechtold, 2021). The present paper where I define and study the absolute seawater entropy may be seen as a first step toward similar future applications to oceanic thermodynamics.

*I deeply think that the purpose of a paper is to communicate one's science and make it accessible to a reader, otherwise it is useless and will not be read and noticed.*

*Following this, I recommend rejection of this manuscript.*

- I believe I have provided all the necessary information for anyone to independently calculate and compare the “conventional” and “absolute” seawater entropies for themselves, making them accessible to as many people as possible, whereas in TEOS10, for example, it was difficult to redo the calculations independently.

In this sense, I believe that I have duly communicated my knowledge with all the necessary details and with the aim of contributing to the advancement of scientific knowledge.

I can only hope that the changes made following the numerous recommendations of the two other reviewers (one of whom accepted the publication) will convince you of the scientific value of my approach.

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**Answers to the Referee 3 about the  
Comptes Rendus Geoscience paper:  
“ The absolute seawater entropy: Part I. Definition ”**

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by Pascal Marquet / November 29, 2025

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**General remarks to the referee 3.**

In order not to unduly lengthen the responses to the reviewers of both parts of my paper, I have prepared a fairly complete Supplementary Materials file which I will refer to as “SM” in the following. This SM file (Marquet, 2025, uploaded on the Zenodo cite) contains several additional Figures, Tables and details about the computations of my responses, as well as answers to many FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans. The time taken to write this large SM document partly explains the delay in finalizing the revision of this two-part paper.

I also provide a “ $\text{\LaTeX}$ -diff” document in which all changes and corrections to the text are indicated in red (cancelled) and blue (modified/new) coloured text.

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**A summary of all changes made to Part-1 and Part-2 of the paper**

In order to show to the Referees and Editor the whole set of changes made to the two-parts paper, before to answer point by point to the general and specific Comments, I may provide the following summary of all these changes made by myself and suggested by the Referees.

- I have prepared an external “*Supplementary Materials*” document (Marquet, 2025, uploaded in the Zenodo cite).
- I have removed the terms considered as “polemic”:
  - “(…) *violate*” the third law  $\rightarrow$  “(…) *differ from*” the third law;
  - “(…) *unless to violate the entropy budget* (…)”  $\rightarrow$  “(…) *unless to modify the entropy budget* (…)”;
  - “(…) *have the flaw of being in contradiction with*”  $\rightarrow$  “(…) *can be amended to correspond to*”;
  - “(…) *correcting*”  $\rightarrow$  “(…) *amending*”;
  - “(…) *prohibitive for the use of the standard entropy*”  $\rightarrow$  (removed) ;
  - “(…) *preferred to any other arbitrarily modified definition*”  $\rightarrow$  “(…) *should impact*” ;
  - “(…) *imposing the absolute values*”  $\rightarrow$  “(…) *using the absolute values*”;
  - “(…) *correcting and generalising the current* (…)”  $\rightarrow$  “(…) *amending, if needed, the current* (…)”;
  - “(…) *to compute the true value of* (…)”  $\rightarrow$  “(…) *to compute the absolute value of* (…)” ; ...)
- I have added the new section 3.3 with the new Fig.2, where I describe other more general situations in physics where the absolute values of entropies impact different phenomena (saturation pressures versus latent heat; turbulence; chemical constants for Ozone and Seawater reactions; entropy potential temperature  $\theta_\eta$ ), with detailed computations shown in the Supplementary Materials (Marquet, 2025), as well as answers to FAQs regarding the interest, or not, of studying the absolute entropies of the atmosphere and oceans.
- In this new section 3.3 I have added new citations: Planck (1917), Nernst (1918), Planck (1921), Nernst (1926) for the saturation pressure; Richardson (1919) Richardson (1922) Ma and Peltier

(2024) Canuto et al. (2002) for the turbulence; (Burkholder et al., 2020) Weiss (1974) Millero (1995) DOE (Departement of Energy, 1994) for Ozone and Seawater chemical reactions; Betts (1973) for the atmospheric liquid-water potential temperature.

- I have explained that the first resolution accepted during the 5th International Conference on the Properties of Steam in London (5th-ICPS et al., 1956) only concerned the steam water (one component system of constant composition), and not the seawater (multi-components system of variable composition), whereas a second resolution was adopted asking to provide the absolute values of entropies in all subsequent studies (as done in the present study).
- In the Fig.1 of the Part-1, I have added two zoom versions of the first diagram for very small salinity, to show the impact of the term  $x^2 \ln(x)$  corresponding to  $S_A \ln(S_A)$ .
- I recall in the conclusion of the Part-1 that the rejection of the third-law by the oceanic community can likely be dated to Fofonoff (1962, p.8), even though Fofonoff cited the previous books of Fowler (1929), Guggenheim (1933) and Guggenheim (1950), who all trusted the third law of thermodynamics and the Sackur-Tetrode translational entropy used in the present paper, and even though Guggenheim has chosen to call the “*absolute value*” of entropy the “*conventional*” entropy.
- I explain in the Part-1 about  $S(T) = 0 + k \ln(W)$  that: “... the 0 term indicates that no other arbitrary term must be added ...”
- The wrong title of the Section 4.3 of Part-1 I is duly change into “*The absolute entropy of pure liquid water.*”
- I have switched to Roman style (where needed) for several (if not most of) indices and superscripts (in particular:  $S_P$ ,  $S_A$ ,  $S_{SO}$ ,  $t_{SO}$ ,  $P_{SO}$ ,  $t_u$ ,  $T_t$ ,  $p_t$ ,  $C_{ps}$ ,  $M_s$ ,  $M_w$ ,  $N_w$ ,  $\mu_{w/s}^0$ ,  $(\dots)_{liq.}$ ,  $(\dots)^{aq.}$ ,  $(\dots)_{std/TEOS10}$ ,  $\eta_{abs}$ ,  $\Delta\eta_s$ ,  $\eta_{Fei08}^{W/S}$ ,  $\eta_w$ ,  $\eta_s$ ,  $\eta_{w0}$ ,  $\eta_{s0}$ ,  $\eta_{v/i/3rd}^{calor./stat.}$ ,  $R_v$ ,  $c_w$ ,  $c_{pd}$ ,  $s_{d0}$ ,  $s_w$ ,  $\theta_s$ ,  $\Delta G_r$ ,  $\Delta H_r$ ,  $L_{sub}$ ,  $p_{sat}$ , ...)
- I have changed a title and several texts in the Part-2:
  - “... *Northeast Atlantic and Mediterranean Seas*” (title of section 2.6);
  - “... *the Arctic ocean; the Bay of Bengal; and the Northeast Atlantic and Mediterranean Seas.*”;
  - “... *In the Northeast Atlantic, colder temperature with smaller ...*”;
  - “... *Black and Caspian Seas; the Northeast Atlantic and Mediterranean Seas, ...*”;
  - “... *global surface ocean entropy.*”
- In the Fig.1 of Part-2: in the upper-middle vertical profile I have changed the colours and the labels for  $\theta$  (in blue),  $T$  (in purple), and  $\Theta$  (in red); in the lower-left vertical profile the “*min*” and “*max*” curves are removed; in the lower-right  $t-S_A$  diagram the coloured scale is reverse (on the right, with the surface at the top) and dashed-blue curves are added for the standard (TEOS10) seawater entropy.
- In the Figs.2 and 3 of Part-2: in order to avoid spurious extrapolation up to 0 m (were no CTD value is available) the new vertical scales start at the depth of 15 m.
- In the Fig.4 of Part-2: in order to facilitate the localisation of regions with the larger values of the difference between the standard (Std) and absolute (Abs) seawater entropies, I have added the fifth global surface map showing the difference (Abs-Std).
- I have added several citations in the Part-1, first for Thermodynamic Tables Rossini et al. (1952) and Gokcen and Reddy (1996); then for the book of Planck (1911); and then for the papers and books by Cooper and Dooley (2008), Chou (1968), Pitzer (1987), Sharqawy et al. (2010a), Stern (1960), Onsager and Fuoss (1932) and McDougall and Barker (2011).
- I recall in the Part-1 that: “*the term “isentropic” (or same entropy) includes possible joint variations in pressure, temperature and salinity, without prejudging any adiabatic (no exchange of heat) or closed (same salinity) aspect of the evolution of ocean parcels. This is analogous to the definition of “isopycnal” processes, where density (or potential density) remains constant regardless*

*of joint variations in pressure, temperature and salinity, with variations in temperature and salinity along isopycnals described with spiciness.”*

- I have removed the first name Franck in all citations of Millero’s papers.
- A large part of the Conclusion of the Part-1 is removed and transferred toward the new section 3.3.
- In order not to offend anyone, I have clearly mention in Part-1 of the paper that: “The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater itself, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.”
- I also explain in the Conclusion of the Part-1 that: “Since Fofonoff (1962, p.8), the prevailing view in the oceanographic community is that the choice of the linear salinity function  $-a_2 - a_4 S$  entering into the TEOS10 definition of the seawater entropy has no practical impact on known oceanographic applications, and that the choice of fixing  $-a_2$  and  $-a_4$  is a matter of convention. However, some people think that the Millero and TEOS10 approaches may be considered valid, and that neither should be subject to general rejection. It is within this last absolute-entropy framework that the present and Millero’s papers are situated.”
- The length of the Part-1 is increased from 19 to 24 pages (section 3.3 + new Fig.2 + biblio).
- The length of the Part-2 is unchanged (16 pages) in spite a new difference map in the Fig.4.

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## Answers to Summary and recommendation

*Oceanographers describe the thermodynamic properties of seawater in terms of the TEOS10 Gibbs function  $g(S, T, p)$ , which is defined up to the function  $a_1 + a_2 T + a_3 S + a_4 S T$  involving four arbitrary constants  $a_1, a_2, a_3, a_4$  whose values cannot be constrained by standard thermodynamics. As a consequence, it only defines entropy  $\eta = -\partial g / \partial T$  up to the linear function of salinity  $-a_2 - a_4 S$ . According to the third law of thermodynamics, it is in principle possible to fix the values of  $a_2$  and  $a_4$  so that the corresponding determination of  $\eta$ , referred to as absolute entropy, vanishes at absolute zero. However, since no known oceanographic applications require the knowledge of the unknown function  $a_2 + a_4 S$ , the problem of determining it has not received much attention so far. Only Millero and Leung (1976) (ML76 hereafter) appear to have previously attempted to determine the absolute entropy of seawater, but their result is valid only for one atmosphere and is based on somewhat different assumptions than those underlying the TEOS10 Gibbs function. The main aim of this paper is to build on Millero and Leung (1976) to determine the constant  $a_4$ , leading to a new determination for the absolute entropy  $\eta_{\text{marquet}}$ , which is related to the TEOS-10 determination by the relation:*

$$\eta_{\text{marquet}} \approx \eta_{\text{teos10}} - 1.8 (S - S_0) \quad (1)$$

*with  $S_0$  a reference salinity, salinity in g/kg, and entropy in J/(K kg).*

- I agree with this summary of my article.

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*The question of how to compute the absolute entropy of seawater is theoretically interesting. However, I have significant concerns regarding the scientific objectivity, clarity, and accuracy of the present treatment.*

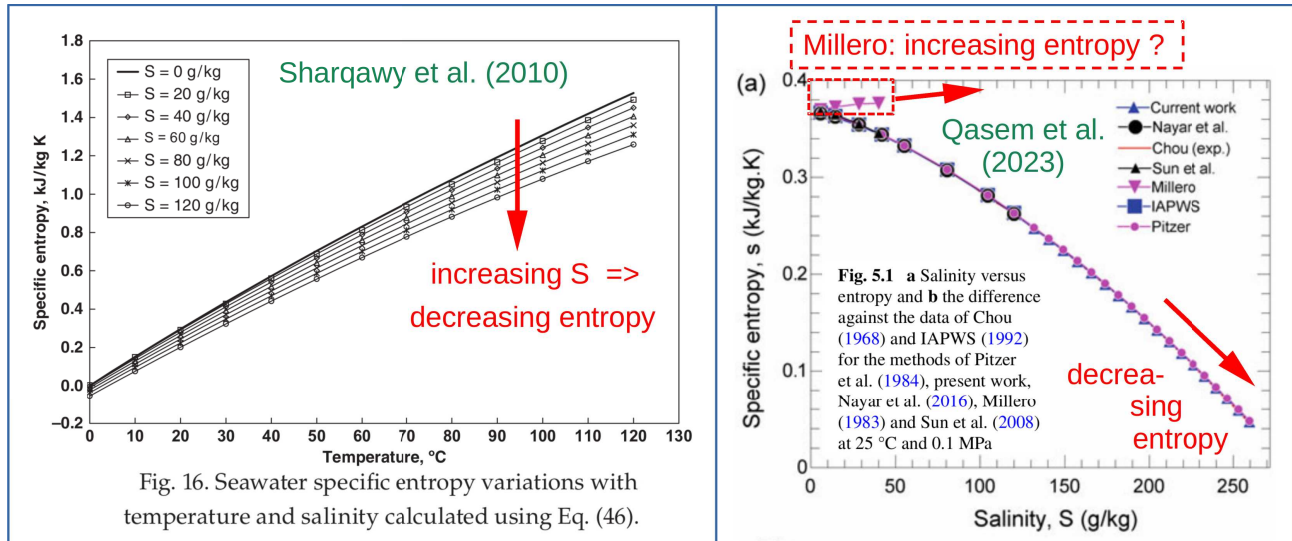
- The accusation of a lack of scientific objectivity, clarity, and accuracy is serious, and I will try to respond point by point to the criticisms made by the referee, in order to show that my judgement is based on an objective scientific study after 36 years (since 1989) spent re-reading and studying all available books and papers dealing with the subject of calculating the seawater (absolute) entropy.



*In particular, the paper presents its approach as a minor improvement on ML76, while in fact proposing a definition of absolute entropy that is incompatible with that of ML76. For example, the present approach predicts that absolute entropy decreases with salinity, whereas ML76's approach predicts an increase. Since absolute entropy is generally interpreted as a measure of disorder, the result of ML76 appears more physically intuitive, as dissolving salts is typically associated with increased disorder. The paper does not provide a critical discussion of the reasons for this discrepancy, nor does it propose objective tests to resolve it. This is one of several important issues, which I discuss in more detail below.*

- I explain in point 6 below that I have studied extensively the papers written by Millero, who unfortunately does not give all the details of his calculations that led him to his numerical formula which, in fact, is atypical as to the sign of the impact of salinity on entropy (see the Fig. 1 where I show the Fig. 5.1 plotted by Qasem et al., 2023). Along with Qasem et al. (2023) I can therefore only note the differences in signs between the formulas of Millero and that of IAPWS/TEOS10 and others with regard to this impact, after having scrupulously ensured that Millero's formula is consistent with all the elements published in his articles (see the point 6 below).

Figure 1: *The impacts on the seawater entropy of the change in salinity. On the left: the Fig. 16 of Sharqawy et al. (2010b, p.374); On the right: the Fig. 5.1 of Qasem et al. (2023, p.125).*



The processes of dissolution of oceanic salts must indeed increase disorder and must be associated with an increase in entropy. To illustrate this I recall in point 6 (correcting Millero's and referee's values) that the change in entropy of the reaction  $\text{NaCl}_{cr} \rightarrow (\text{Na}^+)_{aq} + (\text{Cl}^-)_{aq}$  is from 72.14 J/K/mol for a crystal of NaCl to the sum  $59.00 + 56.36 = 115.36$  J/K/mol for  $(\text{Na}^+)_{aq} + (\text{Cl}^-)_{aq}$ , with a difference +43.22 J/K/mol representing the impact on the entropy of the dissolution of the NaCl crystal into the separate ions  $(\text{Na}^+)_{aq}$  and  $(\text{Cl}^-)_{aq}$ .

Differently, the impact of an increase in salinity on the entropy of seawater does not measure this "entropy of the dissolution" but rather the impact of an input of already dissolved salts. It is a question of calculating the impact of a mixture of water masses of different salinities (with salts already dissolved), and not the impact of the dissolution of salts from crystals in pure water. This is similar to the entropy changes in moist air caused by the addition/removal of water vapor from an existing moist-air sample (for example, due to entrainment, molecular or turbulent mixing processes). In this case, water is added that is already in the form of vapor, without starting from a piece of crystals (of ice-Ih).

For the moist-air atmosphere, I was able to show in my papers that this impact on the moist-air entropy depends on a term of the form  $(s_{vr} - s_{dr}) \Delta q_v$ , where  $\Delta q_v$  is the change in water-vapour specific content,  $s_{vr}$  is the reference entropy of water vapour, and  $s_{dr}$  is the reference entropy of dry air. Similarly, I recall in the present paper that the impact of the reference entropies on the seawater entropy is of the form  $(\eta_{s0} - \eta_{w0}) \Delta S_A/1000$ , with the (minor component) water-vapour replaced by the sea-salts reference entropy, and the (major component) dry-air replaced by the pure liquid-water reference entropy.

The main difference between the moist air and the seawater is that the first-order term  $(s_{vr} - s_{dr}) \approx +5893 \text{ J/K/kg}$  is positive, whereas the first-order term  $(\eta_{s0} - \eta_{w0}) \approx -1880 \text{ J/K/kg}$  is negative, indicating that  $\eta_{s0} \approx 1633.3 \text{ J/K/kg}$  is smaller than  $\eta_{w0} \approx 3513.4 \text{ J/K/kg}$ , and explaining why the seawater entropy must decrease due to this first-order term and when the salinity  $S_A$  increases, with a larger proportion of sea-salts (with its lower entropy) in a given kg of seawater. This could not be guessed without knowing the absolute numerical values of  $\eta_{s0}$  and  $\eta_{w0}$ , and thus with a non-intuitive negative sign of  $(\eta_{s0} - \eta_{w0})$ .

- We can only observe that Millero's formula is atypical compared to all the others, as recalled in the Fig. 1, where I show the Fig. 16 of Sharqawy et al. (2010b, p.374) and the Fig. 5.1 of Qasem et al. (2023, p.125). In order to address the reviewer's criticisms, I have included some additional explanations regarding the atypical aspect of Millero's formulation (see the last two paragraphs at the end of the section 3.1).

- I would like to point out to the referee that I appreciate that you try to interpret the changes in entropy with salinity in a physical way. However, this is somewhat contradictory to considering that one can arbitrarily define the reference entropies  $\eta_{s0}$  and  $\eta_{w0}$ , namely as done in IAPWS and TEOS10 (with a too small decrease of the seawater entropy with  $S_A$ ) and as due to probable errors in Millero's papers (with the surprising increase of the seawater entropy with  $S_A$ ).

I encourage the reviewer to take note of these probably important physical effects (increase or decrease of the entropy in a given domain or layer) due to the absolute definition of the reference entropies, physical effects which could motivate further studies and based on the first case studies that I indicate in the part 2 of the paper.

These effects must therefore influence the second law of thermodynamics, insofar as the value or even the sign of the increases in entropy in a domain  $d/dt(\int \eta dm) = \int (d\eta/dt) dm$  are impacted by the value and the sign of  $\int [(\eta_{s0} - \eta_{w0})/1000] (dS_A/dt) dm$ , which cannot be arbitrarily defined unless to arbitrarily modify  $d/dt(\int \eta dm)$ .

---

*Regarding methodology, the approach appears to rely on heuristic, term-by-term comparisons between the fits used by Millero and TEOS10 to describe entropy. However, these fits are based on different assumptions and use different functional forms. For instance, Millero's expression for the salinity derivative  $\partial\eta/\partial S$  remains finite as salinity vanishes, whereas TEOS10's becomes infinite. Reconciling these approaches is nontrivial and would require deep expertise in the physical chemistry of electrolytes.*

- I will give some evidence to prove that I have followed a scientific methodology, that my approach did not rely on the sole comparison between Millero's and TEOS10' fits, that I know the motivations and origins of the hypotheses concerning the thermodynamics of electrolytes used to establish the formulation in TEOS10, and that the study of all these hypothesis confirms that the reference entropies only impact the coefficients  $a_2$  and  $a_4$  in the linear function noted  $a_2 + a_4 S$  by the referee.

- Indeed, I have clearly recalled in my paper (before Eq. 2) that, for TEOS10:  
*"The specific free enthalpy  $g = G/m$  (with  $m = 1 \text{ kg}$ ) of a multi-component dilute aqueous electrolyte solution was previously derived according to Feistel and Hagen (1995, Eq. 4.9, p.266) from the practical*

osmotic factor considered in Lewis and Randall (1961, Eq. 23-4, p.334) and Falkenhagen and Ebeling (1971, Eq. 116, p.40), leading to the formulation of Feistel and Hagen (1995, Eq. 4.9, p.266) that can be rewritten as

$$g = (1 - C) \times \mu_w^0(T, P) + C \times \mu_s^0(T, P) + \sum_a \frac{X_a}{M_s} R T C \ln \left[ X_a \frac{C}{1 - C} \frac{M_w}{M_s} \right] - \frac{[\sum_a N_a Z_a^2 e^2 / D(T, P)]^{3/2}}{\sqrt{36 \pi \nu(T, P) k T N_w}}. \quad (2)$$

where:  $C = 1.00488 S = S_A/1000$  is the sea-salts concentration (...) The linear term  $a_2 + a_4 S$  for the entropy indicated by the reviewer in point 11 corresponds to the lower order terms of the first line of (2), whereas the non-linear electrolyte terms are all grouped into the second line.

Figure 2: Excerpts from the book, papers and manual by Lewis and Randall (1961), Falkenhagen and Ebeling (1971), Feistel and Hagen (1995) and McDougall et al. (2010, TEOS10) showing some of the hypotheses concerning the theories of electrolytes.

<p><b>Lewis &amp; Randall (1961)</b></p> <p>Chap. 23. Theories of Electrolyte Solutions 333</p> $\nu RT \ln \gamma_{\pm} = \mu_2 - \mu_2^0 - \nu RT \ln m = \mu_2^{el} \quad (23-1)$ $\ln \gamma_{\pm} = \frac{\mu_2^{el}}{\nu RT}$ $(1 - \phi) \nu m RT \frac{M_1}{1000} = \mu_1^{el} \quad (23-2)$ $1 - \phi = \frac{\mu_1^{el}}{\nu m RT} \frac{1000}{M_1}$ <p>334 Thermodynamics for the very dilute solution</p> $1 - \phi = \frac{\pi}{3} \left[ \left( \frac{N}{V} \right)^{1/2} \frac{z^2 e^2}{D k T} \right]^{3/2} \quad (23-4)^*$	<p><b>Falkenhagen &amp; Ebeling (1971)</b> H. Falkenhagen and W. Ebeling</p> <p>40</p> $F^* = -kTV \left\{ \frac{\kappa^3}{12\pi} + \frac{\pi}{3} \sum_{ab} n_a n_b \left( \frac{e_a e_b}{kT} \right)^3 \ln(\kappa R_{ab}) + 2\pi \sum_{ab} n_a n_b R_{ab}^3 K_0(\xi_{ab}) + O(n^{3/2} \ln n) \right\}. \quad (99)$ $b = e_1^2 / D_0 k T a. \quad (100)$ $1 - g = \frac{1}{6} \mu + \frac{1}{2} \mu^2 [k_0(b)/b^3] + \dots, \quad (105)$ $\mu = (e_1^2 \kappa / D_0 k T). \quad (107)$ $(1 - g) = A_2(T) \sqrt{c} + B_2(T) c + O(c^{3/2} \ln c), \quad (116)$
<p>266 <b>Feistel &amp; Hagen (1995)</b> R. FEISTEL and E. HAGEN</p> $m G = N(H_2O) \mu^0(T, P) + \sum_a N(a) \{ kT \ln(N(a)/N(H_2O)) + \mu_a(T, P) \} - \{ [\sum_a N(a) Z(a)^2 e^2 / D(T, P)]^3 / [36 \pi \nu(T, P) N(H_2O) kT] \}^{1/2} \quad (4.9)$ $G(S, t, p) = G_0 + G_1 S \ln(S) + G_2 S + G_3 S \sqrt{S} + \dots \quad (4.10)$ $G = (C000 + C010 \cdot t) + (C100 + C110 \cdot t) S \ln(S) + (C200 + C210 \cdot t) S + \text{higher powers in } S, t, p \quad (4.17)$	<p><b>McDougall et al. (2010) TEOS10</b></p> $g(S_A, t, p) = g^W(t, p) + g^S(S_A, t, p) \quad (2.6.1)$ $g^W(t, p) = g_u \sum_{j=0}^7 \sum_{k=0}^6 g_{jk} y^j z^k \quad (G.1) \quad g_{00} \text{ and } g_{10} \text{ arbitrary}$ $g^S(S_A, t, p) = g_u \sum_{j,k} \left\{ g_{1jk} x^2 \ln x + \sum_{i>1} g_{ijk} x^i \right\} y^j z^k \quad (H.1)$ <p>The coefficients <math>g_{200}</math> and <math>g_{210}</math> were determined to exactly achieve Eqns. (2.6.7) and (2.6.8)</p> $[a_1 + a_2(T_0 + t)] + [a_3 + a_4(T_0 + t)] S_A \quad (2.6.2) \quad \text{arbitrary function}$

I think I have followed a scientific approach and I took time to understand the origin and significance of the Debye-Huckel theory and the three terms  $S \ln(S)$ ,  $S$  and  $S\sqrt{S}$  in the study of electrolyte solutions, with a careful reading of: Debye and Hückel (1923a,b), Onsager (1926a,b, 1927), Onsager and Fuoss (1932), Robinson and Stokes (1955), Fuoss and Onsager (1957), Robinson and Stokes (1959), Fuoss et al. (1965), Fuoss and Hsia (1967), Barthel (1968), Justice (1975), Chen and Onsager (1977), Chen (1977), Ebeling et al. (1978), Feistel (1978), Ebeling et al. (1979), Sändig and Feistel (1979).

I provide in the section 12.10 of the SM (*Validations and physical meaning of absolute entropies / Non-linearities?*) a list and a summary of all these old papers and book, in order to prove that I have

carefully looked for any chance of one of these authors dealing with the problem of determining the possible impact of the reference energies and entropies. As a matter of fact, this was not the case. Therefore, I can confirm from all my careful reading that even for an electrolyte, the linear salinity function  $a_2 + a_4 S$  mentioned by the reviewer is the only place where the reference entropies of liquid water and ocean salts come into play in TEOS10 (see the Fig. 2).

- On the other hand, my study is not based solely on the comparison of the approaches and results of Millero and TEOS10. As far as the consideration of the thermodynamics of electrolytes is concerned, there is no need to look at what Millero did, where only the consideration of the “absolute” aspects of the reference entropies was dully addressed, even if in an ultimately unsatisfactory manner likely due to errors in the fitting processes.

I have just chosen to scrupulously preserve almost all the assumptions retained for TEOS10, except the reference entropy aspects which are well isolated in the linear term  $a_2 + a_4 S$  as indicated by the reviewer in point 11, with the other non-linear terms as a function of  $S$ ,  $t$  and  $p$  being additive other terms independent of this linear term.

Since, according to the referee and to the TEOS10 recommendations as well, the coefficients  $a_2$  and  $a_4$  could be freely set to this or that values, they can equally almost be cancelled as in the present TEOS10 formulation, on the one hand, or set to the values in agreement with the third law of thermodynamics, on the other hand. Since both the referee and the TEOS10 team seem to agree with this alternative, I do not understand why I would not be allowed to just modify the two coefficients  $a_2$  and  $a_4$ , without the need to check or modify any of the other (non-linear and electrolyte) terms.

Anyhow, the comparison between Millero’s and TEOS10’s formulations are only shown in the Part-I of the paper, with likely several issues in the Millero’s papers, whereas the oceanographic study I show in the second part of the paper only concerns comparisons between the standard versus absolute entropy TEOS10’s formulations, without reference to Millero’s formulations.

- As for the infinite values for  $\partial\eta/\partial S$  for  $S = 0$ , according to Eqs. 4.10 and 4.17 of Feistel and Hagen (1995, p.266) recalled in the Fig. 2, the leading-order terms of the TEOS10’s Gibbs function must correspond to:

$$G = C_{000} + C_{010} t + (C_{200} + C_{210} t) S + (C_{100} + C_{110} t) S \ln(S) + (\text{higher powers in } S, t, p) .$$

This means that the entropy  $\eta = -\partial G/\partial t$  is:

$$\eta = -C_{010} - C_{210} S - C_{110} S \ln(S) + (\text{higher powers in } S, t, p) ,$$

where therefore the linear term  $a_2 + a_4 S$  corresponds to  $a_2 = -C_{010}$  and  $a_4 = -C_{210}$ . The referee explains that the derivative

$$\frac{\partial \eta}{\partial S} = -C_{210} - C_{110} [1 + \ln(S)] + (\text{higher powers in } S, t, p)$$

is infinite for  $S = 0$ . This is indeed due to the term  $S \ln(S)$  in the entropy formula, leading to the term  $[1 + \ln(S)]$ . It is also true that the Millero’s formula (147) leads to the seawater entropy relationship:

$$\eta = [...] (t) + A(t) S + B(t) S^{3/2} + C(t) S^2 ,$$

leading to:

$$\frac{\partial \eta}{\partial S} = A(t) + \frac{3 B(t)}{2} \sqrt{S} + 2 C(t) S ,$$

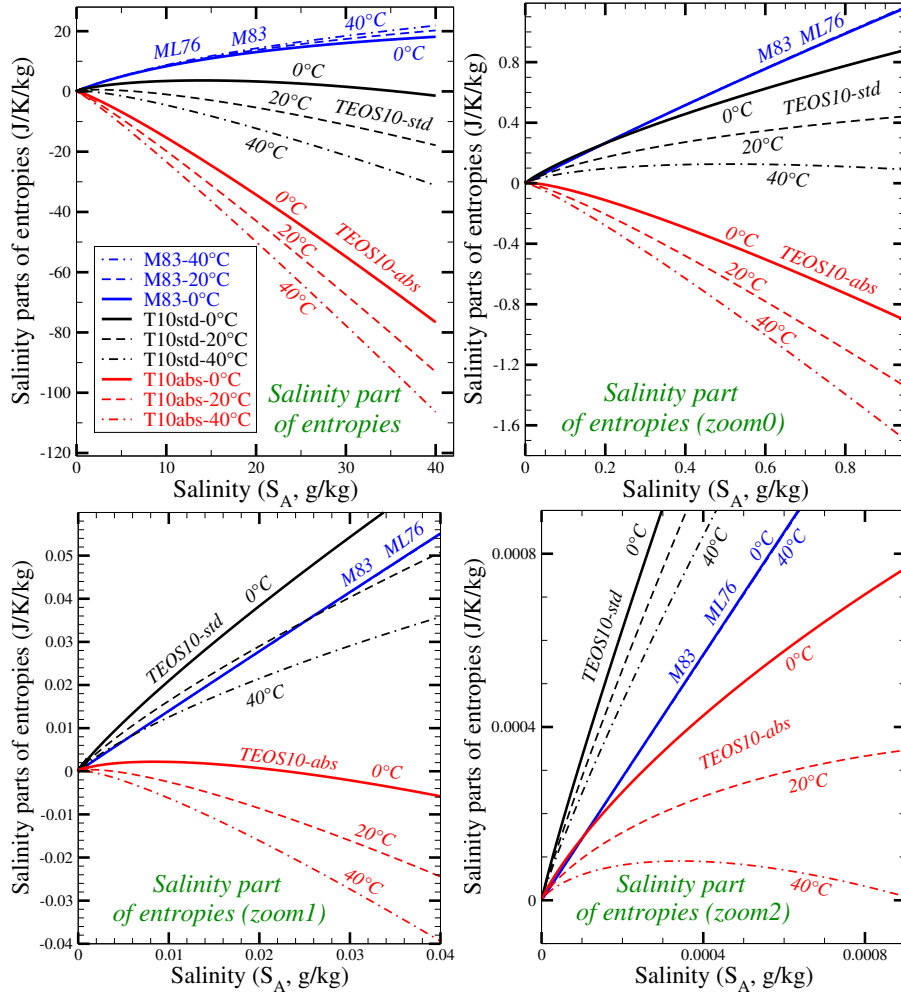
which is indeed finite and equal to  $A(t)$  for  $S = 0$ .

However, the most important feature is that the term  $S \ln(S)$  appearing in the TEOS10’s Gibbs and entropy functions  $G$  and  $\eta$  does not diverge and tends toward 0 for  $S = 0$ . My purpose in the

present paper was just to study the impact of the reference entropy values on the entropy  $\eta$  via the term  $a_4 S = -C_{210} S$ , whatever may be the relevance of the other terms like  $S \ln(S)$  appearing in TEOS10, but not in Millero's papers.

The referee may consider that the term  $S \ln(S)$  could be unusual, although it can be traced back to the term  $c \ln(c)$  due to more exact computations made by Onsager and Fuoss (1932, Eq. 1.1.2, p.2689, see Eq.(299) in the SM Zenodo file). Anyhow, whatever the relevance of the derivative term  $\partial \eta / \partial S = -\partial^2 G / (\partial S \partial t)$  may be, I can only confirm the almost vertical tangents at the origin for the TEOS10 (std and abs) formulations due to the term  $x^2 \ln(x)$ , as shown in the zoomed entropy diagrams in the Fig. 3.

Figure 3: The salinity parts of the Millero's (1976-1983/blue) and TEOS10's (standard/black and absolute/red) seawater entropies plotted against the absolute salinity for three selected temperatures (0, 20 and 40 °C). **Top left:** the same Fig. 1 as in the paper. **Top right and Bottom:** zoomed diagrams toward smaller and smaller values of salinities.



However, we usually have to study the seawater salinities varying at most from 1 to 40 g/kg over the earth and, in this case, as shown in the top-left part of the Fig. 3 included in the paper, the impacts of the term  $x^2 \ln(x)$  corresponding to  $S \ln(S)$  is small for this range of salinities, with almost constant slopes of the TEOS10 (std and abs) formulations and with the absolute entropy (in red) continuously

decreasing with the salinity.

- Therefore, I chose to add to the Part-1 of the paper the two graphs with zoom1 and zoom2 for very low salinity values, in order to indicate to the reviewer as well as to the possible future readers how the term  $S \ln(S)$  impacts the seawater entropies for (very) low salinities.

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*A further challenge, not discussed in the paper, is that constructing an absolute determination of entropy is fundamentally difficult for at least two reasons. First, it relies on combining experimental measurements with theoretical models of electrolytes, which remain imperfect. Second, there is no universally accepted way to ascertain that a given result is physically meaningful. For example, molecular dynamics simulations (e.g., using GROMACS, see <https://www.gromacs.org/>) could, in principle, be used to test the physical plausibility of a proposed absolute entropy. Without such rigorous testing, it is difficult to assess whether an absolute determination of entropy is more meaningful than a relative one. For these reasons, the determination of absolute entropy remains largely of academic interest, and it is understandable that TEOS10 has chosen not to address it in detail.*

- I have shown in my answer to your previous comment that we can separate the impacts of the two: “experimental measurements” and “theoretical models of electrolytes,” with of course the theoretical predictions to be validated by the experimental facts.

- I have checked that all possible non-linear terms depending on  $S$ ,  $\sqrt{S}$ ,  $S\sqrt{S}$  or  $S \ln(S)$  (and higher-order terms) due to the theoretical models of electrolytes can be jointly tuned by the TEOS10 procedure from experimental measurements, on the one hand. However, on the other hand, the absolute definition of the entropy only rely on the linear terms for both the liquid water and the sea salts, leading to the term  $a_2 + a_4 S$  mentioned by the referee, with no less, but no more, arbitrariness than the hypotheses retained in TEOS10, where it is mainly arbitrarily assumed that  $a_2 = a_4 = 0$ .

- It is true that oceanic experimental measurements cannot be used to determine the two coefficients  $a_2$  and  $a_4$ . However, the absolute definition of the liquid-water and sea-salts reference entropies are not arbitrary, and their theoretical definitions by Walther Nernst, Max Planck, Otto Sackur and Hugo Tetrode have been validated by experimental processes.

I therefore respectfully disagree with the referee on this point that “(...) *there is no universally accepted way to ascertain that a given result is physically meaningful*” and that “*Without such rigorous testing* (e.g., using GROMACS?) *is difficult to assess whether an absolute determination of entropy is more meaningful than a relative one.*”

I will need to take some time to refute each of these points (underlined with dotted lines) with reasoned arguments.

- I may first recall that Max Planck (1917) wrote in the 5th edition of his book on Thermodynamics the sentences: “*For the fifth (1917) edition, I have once more worked through the whole material of the book, in particular the section on Nernst’s heat theorem. The theorem in its extended form* (namely the Third Law of Thermodynamics) *has in the interval received abundant confirmation and may now be regarded as well established.*”

Indeed, I further explained in the section 12.1 of the SM entitled “*Validations and physical meaning of absolute entropies / Nernst (1918-1926)*” that the way the absolute definition of the entropy has been validated experimentally partly relied on the saturation pressure equation valid for very low temperatures and monatomic vapours, and if the specific heat of the condensed phase may be neglected, while the molecular heat of the vapour may be taken as  $C_p = (5/2) R$ , leading to

$$\ln\left(\frac{p_s}{p_u}\right) = \ln(p_s) - \ln(p_u) = -\frac{\lambda_0}{RT} + \frac{5}{2} \ln(T) + \frac{3}{2} \ln(M) + i_0 \quad (3)$$

derived with the previous hypotheses (just like the way the electrolytes impact the Gibbs equation of seawater are subject to certain hypotheses previously recalled), where  $\lambda_0$  is the latent heat of change of phase,  $T$  is the absolute temperature,  $M = N m$  is the molar mass,  $p_u$  a conventional pressure unit (in Atmosphere or Baries or Pascal) and  $i_0$  is the Sackur-Tetrode constant

$$i_0 = \ln \left[ \frac{(2\pi)^{3/2} k^{5/2}}{h^3 N^{3/2}} \right] \approx 18.22285 \quad (4)$$

that only depends on the fundamental constants  $\pi$ ,  $k$  (Boltzmann),  $h$  (Planck) and  $N$  (Avogadro).

This equation (3) for  $\ln(p_s)$  was in particular considered by: Nernst (1918); Nernst (1921, Nobel prize lecture); Planck (1921); and Nernst (1926).

In particular, Nernst (1921) explained in his Nobel prize lecture that:

*“An important practical application of this (heat theorem / third law) now ensues immediately for the behaviour of vapour pressure at very low temperatures. (...) the integration constant “i” is dependent only upon the nature of the gas (...)”* (via  $M$ )

*“It is now of considerable interest that the numerical value of “i” can be obtained from the quantum theory if the validity of my heat theorem (third law) is accepted. As I was now able to demonstrate several cases in which in fact that value can be verified from the quantum theory with tolerable certainty by various persons (Sackur, Stem, Tetrode), I could in this way arrive at a new and, I believe, particularly striking confirmation of the accuracy of my heat theorem”* (i.e. the third law).

*“In all this work we have only dealt so far with a confirmation of my heat theorem for solids or liquids.”* However: *“All those who have probed deeply into these questions will probably accept the fact that it is highly probable that my heat theorem (third law) is directly applicable to mixed crystals and similar matter (...)”*

- More precisely, I show in the Fig. 4 the results recalled by Nernst (1918), Nernst (1923) and Nernst (1926) who published a beautiful validation of the truly constant  $i_0$  via the accurate comparison of the theoretical value  $C_0 = i_0/2.303 = -1.608$  and the experimental value  $C_0 \approx -1.62 \pm 0.03$ .

Note that the corresponding negative values  $i_0 = 2.303 \times C_0 \approx -3.7$  or  $-3.73 \pm 0.07$  are different from the one of about  $+18.223$  recalled in (4), with a difference of about  $+21.95$ . This difference is partly explained by the old c-g-s units used by Nernst:

$$h = 6.55 \times 10^{-27} \text{ erg} \cdot \text{s}, \quad k = 1.347 \times 10^{-16} \text{ erg} \cdot \text{K}^{-1}, \quad N = 6.17 \times 10^{23} \text{ mol}^{-1};$$

whereas the modern (exact, 2017) U.S.I. values are:

$$h = 6.62607015 \times 10^{-34} \text{ J} \cdot \text{s}, \quad k = 1.380649 \times 10^{-23} \text{ J} \cdot \text{K}^{-1}, \quad N = 6.02214076 \times 10^{23} \text{ mol}^{-1}.$$

The use of the old c-g-s units can explain a difference of about  $+8.107$  for  $i_0$ , with an additional impact  $+\ln(p_u)$  due to the use of the atmosphere unit for the pressure in (3), namely  $p_u = 1.040000 \times 10^6$  baryes, leading to a logarithm of about  $13.85$ , and thus to an expected total difference of about  $8.107 + 13.85 \approx +21.96$ . Note that this validation of  $i_0$  up to about 1 % recalled by Nernst (1926) was obtained for a series of very different molar masses  $M$  of about 2, 40 and 200 g/mol for dihydrogen ( $\text{H}_2$ ), Argon (Ar) and Mercury (Hg), respectively, which reinforces the quality of this validation where the term  $(3/2) \ln(M)$  must be taken into account.

The final words of Walther Nernst (1926, p.186) were:

*“The above Table (p.185 in the section 3. Experimental Test), from which we have concluded the most probable value of  $C_0$  to be  $-1.608$  is thus a verification of the Sackur-Tetrode formula which we may well claim to be unexpectedly striking in view of the difficulty of the experimental test. For mercury in particular, for which by far the most accurate data are available, the agreement is perfect.*

*Although no longer surprising in view of the recent development of physics, the result of the investigations, both theoretical and experimental, which have been dealt with in this Chapter appears to be a*

Figure 4: Excerpts from Nernst (1926) to show a validation of the Sackur-Tetrode constant  $i_0$ .

CHAPTER XIII			
THEORETICAL CALCULATION OF CHEMICAL CONSTANTS			
$\log_e p = -\frac{\lambda_0}{RT} + 2.5 \log_e T + i, \quad . \quad . \quad (101) \quad (\text{p.166})$			
$i = \log_e \frac{(2\pi)^{3/2} k^{3/2}}{N^{3/2} h^3} + 1.5 \log_e M = i_0 + 1.5 \log_e M, \quad (104) \quad (\text{p.167})$			
$\log_e p = -\frac{\lambda_0}{RT} + 2.5 \log_e T - \frac{1}{R} \int_0^T \frac{E}{T^2} dT + i. \quad (121)$			
after introducing common logarithms <span style="float: right;">(p.179)</span>			
$\log_{10} p = -\frac{\lambda_0}{4.571T} + 2.5 \log_{10} T - \frac{1}{4.57} \int_0^T \frac{E}{T^2} dT + C \quad (122)$			
$i = 2.303C. \quad (123)$			
3. Experimental	Test.	C	C <sub>0</sub>
H <sub>2</sub>	.	-1.23 ± 0.15	-1.69 ± 0.15
A	.	0.75 ± 0.06	-1.65 ± 0.06
Hg	.	1.83 ± 0.03	-1.62 ± 0.03
$C = C_0 + 1.5 \log_{10} M, \quad C_0 = -1.62 \pm 0.03, \quad (\text{p.185})$			
$C = \frac{i}{2.303} = \log_{10} \frac{(2\pi m)^{3/2} k^{3/2}}{h^3}$			
$C = C_0 + 1.5 \log M = -1.608 + 1.5 \log M \quad (125) \quad (\text{p.186})$			

remarkable one ; for the calculation of the vapour-pressure curves and of chemical equilibria (namely the values of the chemical constant  $K$ ) in which gases take part is rendered possible by means of Planck's constant  $h$  in addition to thermal data, i.e. by a quantity which was originally determined from radiation measurements.

The point which is most important in connection with the question under treatment in this book is that we are able to show that there is fresh strong evidence for the logical force of our Heat Theorem (i.e. the third law). This evidence lies in the experimental proof that there is really a general significance in the formula, deduced from a somewhat questionable mechanical model of a solid body and from molecular theory, for the calculation of constants of integration not fixed by thermodynamics."

- Of course, we must maintain a critical mind and must be able to reproduce the results obtained by our elders. This is partly why I have patiently undertaken for more than 10 years to recalculate absolute entropies from theoretical and experimental data for the main gases making up the atmosphere (N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub>, dry air, H<sub>2</sub>O).

The theoretical values are obtained with the quantum and statistical physics hypotheses applied to the translational, rotational, vibrational and electronic degrees of freedom of atoms and molecules (see the section 4 of the SM entitled "*Detailed computations of the third-law statistical entropies*").

Differently, and independently, the experimental (calorimetric) values are computed from the experimental values for the specific heats  $c_p(T)$ , the latent heat of change of phases  $L(T_k)$  for each temperature  $T_k$  for these changes of phase, and the saturation pressure of the vapour above the last solid or the liquid phase at 0°C (see the section 3 of the SM entitled "*Detailed computations of the third-law calorimetric*").



*entropies*”).

In particular, the (validated) Sackur-Tetrode constant ( $i_0$ ) is used to define the translational part for all atoms and molecules. The experimental values are obtained by integrating the quantity  $C_p(T)/T$  from 0 K to the standard temperatures  $T_0$  (0°C or 25°C), where  $C_p(T)$  are the observed specific heats, and by taking into account not only the impact  $\sum_k L_k(T_k)/T_k$  of the latent heats of changes of phases occurring at all possible  $T_k$ , but also the possible residual entropies at 0 K (i.e. the quantity  $R \ln(3/2)$  for  $H_2O$  only, due to the hydrogen bounds).

I show in the Fig. 10 (see the specific point 9) the way these absolute entropies can be plotted from 0 K to 340 K, with the experimental (coloured lines) and theoretical (dashed black lines) leading to almost the same results at the standard temperatures  $T_0 = 0^\circ\text{C}$  or  $25^\circ\text{C}$ . In order to better confirm these “almost same results” I also show in the Table 1 the numerical values of the experimental and theoretical absolute entropies I have computed at  $T_0 = 0^\circ\text{C}$  and  $p_0 = 1000$  hPa.

Table 1: *The standard absolute entropies (in J/K/kg) at  $T_{\text{std}} = 273.15$  K (or  $0^\circ\text{C}$ ) and  $p_{\text{std}} = 1000$  hPa for the main atmospheric gases:  $N_2$ ,  $O_2$ , Ar,  $CO_2$ , dry air (with 400 ppmv of  $CO_2$ ) and  $H_2O$ . The true (and relative) uncertainties are provided for all values. In the last column,  $\Delta$  are the true and relative differences between the experimental (calorimetric) and theoretical (quantum-statistical-physics) methods, namely:  $\Delta = (\text{Exper.} - \text{Ther.})$  or  $100 \times (\text{Exper.} - \text{Ther.})/\text{Exper.}$  in %.*

Abs. Entropies	Theory	Experimental	$\Delta(\text{Exp.-Ther.})$
$N_2$	$6748.87 \pm 0.34$ ( $\pm 0.005$ %)	$6754.5 \pm 19$ ( $\pm 0.28$ %)	+5.6 or +0.08 %
$O_2$	$6330.86 \pm 0.33$ ( $\pm 0.005$ %)	$6341.3 \pm 37$ ( $\pm 0.60$ %)	+10.4 or +0.16 %
Ar	$3830.59 \pm 0.30$ ( $\pm 0.008$ %)	$3832.7 \pm 2.5$ ( $\pm 0.06$ %)	+2.1 or +0.06 %
$CO_2$	$4786.17 \pm 0.24$ ( $\pm 0.005$ %)	$4780.6 \pm 12$ ( $\pm 0.25$ %)	−5.6 or −0.12 %
Dry air	$6776.34 \pm 0.49$ ( $\pm 0.007$ %)	$6783.0 \pm 23$ ( $\pm 0.34$ %)	+6.6 or +0.10 %
$H_2O_{(gas)}$	$10317.92 \pm 0.63$ ( $\pm 0.006$ %)	$10319.9 \pm 13$ ( $\pm 0.13$ %)	+2.0 or +0.02 %
$H_2O_{(ice)}$		$2295.2 \pm 13$ ( $\pm 0.56$ %)	

Clearly the agreement between the experimental and theoretical values are very good (typically up to  $\pm 0.1$  %), even though so many hypotheses are made for modelling the impacts of rotations and vibrations of molecules, and in spite of the difficulty of the experimental measurements of the specific heats  $c_p(T)$  from about 0 K (the Debye’s  $T^3$  region) up to 273.15 K.

- Therefore, I think I have recalled that the absolute entropies are not only “*of academic interest*” but, in fact, have been fully validated via the Sackur-Tetrode constant and have been fully accepted as the third-law of thermodynamics by Walther Nernst, Max Planck, Franz Simon, ... this explaining that we can nowadays dully rely on the absolute-entropy values published and available in all Thermodynamic tables. Moreover, it is probably scientifically justified to use theoretical values for which the range of uncertainty are reduced: up better than 0.01 %. I think that these comparisons between the theoretical and experimental values of the absolute entropies formed a “*test of the physical plausibility of a proposed absolute entropy*” required by the referee, with therefore “*a rigorous testing*” that proves that “*an absolute determination of entropy is more meaningful than a relative one*” since the absolute value are the one in agreement with the quantum and statistical physics concepts that nobody should discard, I guess.

- I really thought that I would have been allowed in this paper to mention without dwelling too much on the reality of the third law/principle of thermodynamic, which should be imposed on everyone as for all physical principles: conservation of energy, constant of the speed of light in vacuum, increase of entropy for isolated systems, the equality of inertial and gravitational mass, the Planck’s constant as a minimum of the exchanges of action, the Boltzmann constant as a proportionality factor between

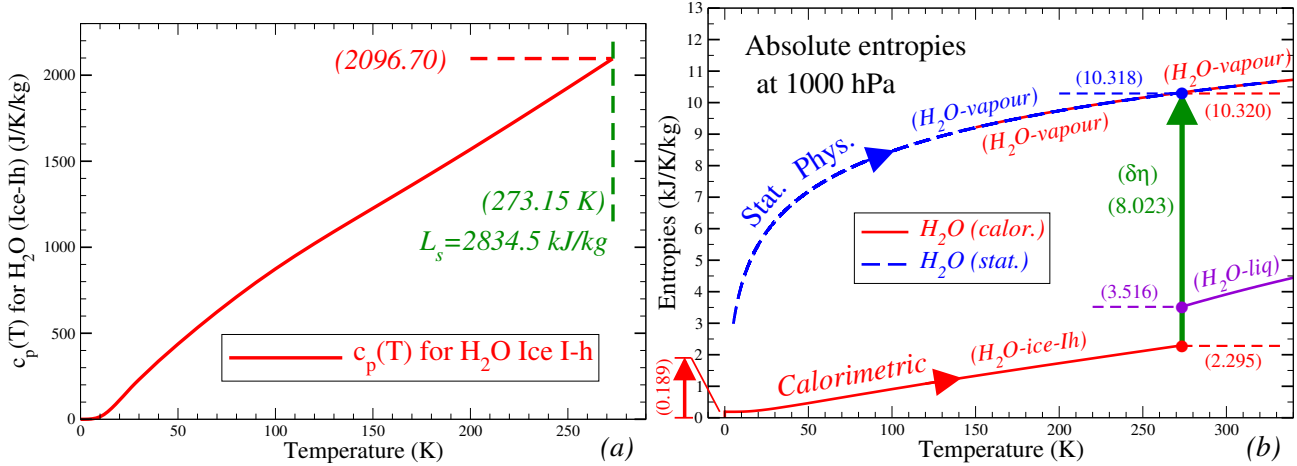
energy and temperature in the equipartition of energy, etc.

Therefore, even though I removed all the words considered as “*controversial*” I have chosen to describe in the new section 3.3 of the Part I of the paper entitled “ General impacts of the Third law in physics” several of existing and explicit physical validation of the absolute, third-law reference entropy values.

I have first recalled the statements described above about the old (1918-26) Nernst’s validation close to 0 K of the theoretical value  $C_0 \approx -1.61$ , which was in agreement with the experimental and calorimetric third-law value  $C_0 \approx -1.62 \pm 0.03$ .

I have also described a new and modern validation I have derived for the present paper (see also the section 12.3 of the SM entitled “ Validations and physical meaning of absolute entropies /  $\text{H}_2\text{O}$  at  $25^\circ\text{C}$ ”) about the computation of the saturation pressures at  $0^\circ\text{C}$  from the third-law absolute entropies if the latent heats are known, or vice versa of the latent heats if the saturation pressures are known, and anyhow the constraint that these observable quantities are linked together through the absolute, third-law values of difference in the calorimetric ice-Ih and statistical-physics water-vapour entropies  $\Delta\eta(T_0, p_0) = \eta_{\text{v}/3\text{rd}}^{\text{stat.}}(T_0, p_0) - \eta_{\text{i}/3\text{rd}}^{\text{calor.}}[T_0, p_{\text{sat}}(T_0)] \approx 8023 \pm 2.5 \text{ J K}^{-1} \text{ kg}^{-1}$  plotted as a green arrow in the Fig 5.

Figure 5: **(a):** The specific heat at constant pressure  $c_p(T)$  for  $\text{H}_2\text{O}$  (Ice-Ih) for absolute temperatures  $T$  from 0 K to  $T_0 = 273.15 \text{ K}$ . **(b):** The absolute entropies for  $\text{H}_2\text{O}$  (Ice-Ih, liquid and vapour) from 0 K to 340 K, with the calorimetric values  $\eta_0 + \int_0^T c_p(T') d\ln(T')$  (solid red lines) including the Pauling-Nagle residual entropy  $\eta_0 \approx 189 \text{ J K}^{-1} \text{ kg}^{-1}$  at 0 K, and the statistical values  $\eta = k \ln(W)$  (dashed blue line) automatically taking into account the residual entropy at 0 K and the latent heat of sublimation  $L_s(T_0) \approx 2834.5 \text{ kJ kg}^{-1}$  at  $273.15 \text{ K}$ . The term  $\Delta\eta \approx 10318 - 2295 = 8023 \text{ J K}^{-1} \text{ kg}^{-1}$  (green arrow) is the difference between the statistical water-vapour and calorimetric Ice-Ih entropies at  $T_0 = 273.15 \text{ K}$ .



I explain in the section of the new section 3.3 of the Part I that: “ These calculations show the predictive power of the statistical (for water vapour) and calorimetric (for Ice-Ih) third-law independent computations leading to the blue and red disks, respectively, and these calculations form a validation of the physical significance of the third-law values of the entropy, by forming a little-known link between the numerical values of  $L_{\text{sub}}(T_0)$  and  $p_{\text{sat}}(T_0)$ , which are generally considered to be independent experimental constants. This creates an unexpected third-law implicit impact on the thermodynamic conditions at the surface of the oceans.”

- I describe other physical validations of the absolute, third-law reference entropy values in the new section 3.3 entitled “ General impacts of the Third law in physics” of the Part I of the paper.

I recall that all constant of chemical reactions do depend on the “entropy of reaction”  $\Delta S^\circ =$

$\sum_k \nu_k S_k^\circ - \sum_{k'} \nu_{k'} S_{k'}^\circ$ , namely the weighted sum of absolute entropies for products minus the weighted sum of absolute entropies for reactants, which must be computed from the same absolute (third-law) values  $S_k^\circ$  and  $S_{k'}^\circ$ , all available in thermodynamical Tables as those used for the present study (see the section 12.2 of the SM entitled “*Validations and physical meaning of absolute entropies / Chemical reactions*”) where I show that the constant terms  $A$  in the chemical constants defined as  $\ln(K) = A + B/T + C \ln(T)$  can be defined from the  $S_k^\circ$ ’s and  $S_{k'}^\circ$ ’s for the Ozone-chemistry reactions  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$  and  $\text{Cl} + \text{O}_2 \rightleftharpoons \text{ClO}_2$ , as well as the oceanic reaction  $\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$ . The consequence is that the concentrations in ozone and sea salts both depends on these absolute (third-law) values of entropies, this providing an additional proof for physical impacts and meanings for these absolute (third-law) values of entropies (concentrations are observable quantities, as well as temperature in the stratosphere and the surface oceanic layers that are impacted via radiation fluxes by these concentrations).

- I further recall in the new section 3.3 of the Part I of the paper that similar impacts exist for the turbulence which, according to Richardson (1919, 1922), should be calculated via a turbulent mixing acting on the absolute entropy variable, and not on the more standard temperature-like variables ( $T$  or  $\theta_v$  or  $\theta_l$  for the atmosphere;  $\theta$  or  $\Theta$  for the ocean). I show with some details in the section 12.9 of the SM entitled “*Validations and physical meaning of absolute entropies / Lewis number?*” that the atmospheric exchange coefficients are well-defined (positive) only for the moist-air absolute entropy variable  $\theta_s$ , and not for the equivalent of the TEOS10 arbitrarily modified value  $\theta_l$  used in all atmospheric numerical models. Moreover, I show in the same section 12.9 of the SM that the Lewis number is above unity for the absolute entropy variable, which corresponds to what is called “double diffusion” in the ocean (i.e. with different turbulent strength for temperature and salinity). These results are important and seem to clearly demonstrate (at least for the atmosphere) that, as predicted by Richardson, only absolute entropy (and the variable  $\theta_s$ ) has physical meaning with regard to turbulence. This property should be verified for the ocean (and the variable  $\theta_\eta$ ).

- By the way, I explain in the section 12.4 of the SM entitled “*Validations and physical meaning of absolute entropies / Absolute-Relative?*” that, as already published in the Section 3 of the JAS paper by Marquet and Dauhut (2018), the concept of “*relative entropy*” cannot be appealed to name the present standard value of TEOS10, because the concept of “*relative entropy*” was already named by Shannon (1948) and Shannon and Weaver (1949), but in a sense different from the information entropy  $S$  function, and rather corresponding to the different concept of Kullback function, Kullback-Leibler mean information, relative information, Contrast, ... (Kullback and Leibler, 1951; Kullback, 1959), which are all linked to the exergy thermodynamic functions depending on both the energy and the entropy of the system via  $(U - U_0) - T_0 (S - S_0)$ , which is different from both  $S$  and  $S - S_0$  (see in particular, for the atmosphere: Marquet, 1990, 1991, 1993, 1994, 1995, 2003a,b).

- I hope that all the preceding objective evidence will convince the reviewer that they constitute: “(...) *rigorous testing* (... which ...) *assess* (... that ...) *absolute determination of entropy is more meaningful than* (... the standard TEOS10 ...) *one*.”

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## Answers to Specific comments

1. *Lines 45-49*: “Differently, almost all other definitions of the quantities called “entropies” in atmospheric and oceanic studies deviate from this method, by choosing other reference values which therefore violate the third law of thermodynamics. More precisely, the alternative definitions are obtained by arbitrarily cancelling out these reference entropy values at the zero Celsius temperature (instead of zero Kelvin) for dry air, liquid water and sea salts.”

*This way of formulating the problem may be misleading, as it presents the concept of “relative entropy” as fundamentally inferior to “absolute entropy”. In modern thermodynamics, both concepts are accepted as valid and legitimate. Absolute entropy naturally appears as the sum of two components: one (the relative entropy) that is determinable by standard thermodynamics, and one that is not. This is analogous to the decomposition of potential energy or enthalpy into available and unavailable parts. Thus, it is not accurate to characterize relative entropy as violating the third law of thermodynamics; rather, it is a distinct and equally legitimate concept.*

- In order to comply with the reviewer’s request, I have mainly replaced “violate” by “differ from” in the new sentence: “Differently, almost all other definitions of the quantities called “entropies” in atmospheric and oceanic studies deviate from this method, by choosing other reference values which therefore differ from both the calorimetric and statistical-quantum values provided by the third law of thermodynamics.”

- However, I disagree on several aspects of the reviewer’s sentences:

- (a) (...) *it presents the concept of “relative entropy” as fundamentally inferior to “absolute entropy”*
- (b) *both concepts are accepted as valid and legitimate*
- (c) *Absolute entropy naturally appears as the sum of two components: one (the relative entropy) ...*
- (d) *... that is determinable by standard thermodynamics, and one that is not*
- (e) (...) *decomposition of potential energy or enthalpy into available and unavailable parts*
- (f) (...) *distinct and equally legitimate concept.*

- Firstly, I have already recalled above (and detailed in the section 12.4 of the SM entitled “*Validations and physical meaning of absolute entropies / Absolute-Relative?*”) that, also according to the Section 3 of Marquet and Dauhut (2018, p.3737-3738):

If the entropy is noted  $S$  as in general thermodynamic:

- 1) the concept of “relative entropy” does not correspond to the arbitrary hypotheses made in TEOS10,
- 2) the concept of “relative entropy” is already defined in thermodynamics,
- 3) but it corresponds to what is called “exergy” or “available energy”  $A = (U - U_0) - T_0 (S - S_0)$ ,
- 4) this explains the decomposition of energy  $U - U_0$  into available  $A$  and unavailable  $T (S - S_0)$  parts,
- 5) in the suggested decomposition  $S_{abs.} = (S_{abs.} - S_{rel.}) + S_{rel.}$  the term  $(S_{abs.} - S_{rel.})$  can be computed.

Therefore, I think that it is not possible to suggest, as done by the referee, that the entropy computed by TEOS10 could be some kind of “relative entropy” defined as a counterpart of the “absolute entropy” I have defined and studied in the present two-parts paper.

By the way, the “relative entropy” or “Kullback-Leibler divergence” are well-known concepts described in several Wikipedia pages like:

[https://en.wikipedia.org/wiki/Kullback%E2%80%93Leibler\\_divergence](https://en.wikipedia.org/wiki/Kullback%E2%80%93Leibler_divergence)

- However, if I accept for a time this possibility suggested by the referee, if the seawater entropy is noted  $\eta$ , in the decomposition  $\eta_{abs.} = \eta_{rel.} + (\eta - \eta_{rel.})$  the first term  $\eta_{rel.}$  would be the TEOS10 value, where the reference values are set to zero at 0.01°C. But in that case the other term  $(\eta - \eta_{rel.})$  would precisely corresponds to the term

$$\Delta\eta_s \approx (-1880 \pm 17) \times \frac{(S_A - S_{S0})}{1000} \quad (5)$$

that I derived in my paper. Therefore, the term  $(\eta - \eta_{rel.})$  is not only “determinable” but has been determined from the Third law of thermodynamics, and the sentence “(...) one term (the relative entropy) that is determinable by standard thermodynamics, and one (absolute entropy) that is not” would contradict the other sentences of the referee that says that the absolute and TEOS10 entropy values are:

*“(...) distinct and equally legitimate concept”*

with

“(…) *different, but equally valid, choice of reference.*”

Indeed, if  $(\eta - \eta_{rel.})$  would not be “determinable” it could not be defined, and could not be legitimate nor valid, although I have been able to precisely compute it in (5).

- I would like to further recall the simple scientific fact that the absolute values for entropies of all elements, cations and anions are available in Thermodynamic Tables. Therefore, to consider that  $(\eta - \eta_{rel.})$  and (5) would not be “determinable” would amount to denying absolute (third-law) entropy its legitimacy, which has, however, been clearly acquired since the work of our elders: Nernst, Planck, Sackur, Tetrode, Simon, Giauque, ...

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2. *Lines 54: “ [...] this TEOS10’s values have the flaw of being in contradiction with the third law of thermodynamics and Franck Millero’s previous papers concerning the calculation of seawater entropy, due to arbitrary redefinitions made in TEOS10 of the reference entropies of liquid water and ocean salts.”*

*I respectfully disagree for the reasons outlined above. The TEOS10 approach is not in contradiction with the third law, but rather reflects a different, but equally valid, choice of reference.*

- In line with the advices of Gibbs (1875-1878), Nernst (1906), Planck (1911, 1914, 1917), Nernst (1918), Giauque and Stout (1936); Giauque (1949) and so many other thermodynamicists, I respectfully disagree with the referee.

Indeed, except in most of the present atmospheric and oceanic studies, I have never seen (unless I am mistaken?) elsewhere in physics such a refusal to consider as a scientific fact the relevance of the values of absolute entropies available in all thermodynamic tables. Moreover, I can recall the existing applications of the absolute-entropy variable  $\theta_s$  that I have defined, published and studied since 2011.

I recall in the section 12.13 of the SM (entitled “ *Validations and physical meaning of absolute entropies / IFS model*”) that Peter Bechtold included an application in 2020 in the IFS model at ECMWF, where the criterion used to distinguish between stratocumulus (Sc) and Cumulus (Cu) topped boundary layers is based since 2021 on a revised version of the EIS (Estimated Inversion Strength) using a proxy of the absolute-entropy variable  $\theta_s$  (Marquet and Bechtold, 2020; Bechtold et al., 2020; Bechtold, 2021)<sup>1</sup>.

I can also cite, as another example, the recent 2025 MWR paper (Hrastinski et al., 2025)<sup>2</sup> by Mario Hrastinski, Ján Mašek, Ivan Bašták Ďurán, Branko Grisogono and Radmila Brožková. This paper describes another application in the turbulence diffusion scheme “ *TOUCANS*” (Bašták Ďurán *et al.*, 2014, 2018) of the absolute-entropy variable  $\theta_s \approx \theta_1 \times \exp(5.87 q_t)$  I have defined since 2011 (in fact with the coefficient  $5.865 \pm 0.004$ ), and more precisely the value of the vertical change of it  $\Delta\theta_s$ . This application in TOUCAN provides another proof of the special conservative feature for the absolute (third-law) moist-air entropy variable  $\theta_s$  that other variables (like the Betts variable  $\theta_1$ , the atmospheric equivalent of the standard TEOS10 entropy) does not possesses, with the term  $+5.865 \pm 0.004$  being the atmospheric counterpart of the term  $-1880 \pm 17$  impacting the salinity increment  $\Delta\eta_s$  in (5) used to compute the absolute seawater entropy  $\eta_{abs}$ , and an equivalent of the term  $-0.446 \pm 0.004$  in the second exponential of the seawater absolute-entropy variable  $\theta_\eta$  defined in Eq. 30 in the revised Part I of the paper.

I have described two examples of concrete applications where there are physical differences between the absolute version of entropy and the one where the reference values of entropies are arbitrarily redefined

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<sup>1</sup> Namely in the IFS-cy47r3 documentation, p.41-42. See also: [http://www.meteo.fr/cic/meetings/2021/AMA/presentations/08\\_04.pdf](http://www.meteo.fr/cic/meetings/2021/AMA/presentations/08_04.pdf), however in French.

<sup>2</sup> See: <https://journals.ametsoc.org/view/journals/mwre/153/11/MWR-D-24-0184.1.xml>

(as in the current version of TEOS10). However, in order not to unduly criticise established habits, I have modified the sentence:

*“(...) this TEOS10’s values have the flaw of being in contradiction with the third law of thermodynamics and Millero’s previous papers (...)”*

replaced by:

*“(...) this TEOS10’s values can be amended to correspond to the third law of thermodynamics and Millero’s previous papers (...)”*

and thus with the term “*flaw*” removed.

3. *Lines 78: [...] “I indicate why almost all other ocean studies have so far refused to consider the calculation and study of the absolute version of ocean entropy, even as a mere possibility, before to give some answers to the arguments most often put forward to justify this attitude.”*

*The arguments presented for why most ocean studies have not considered absolute entropy could be more thoroughly engaged with. In particular, the practical irrelevance of the arbitrary constants in most oceanographic applications is a key reason for the prevailing approach.*

- I think that I have “(...) thoroughly (...presented...) arguments (...showing...) why (...) ocean studies (...should...) considered absolute entropy (...)”

In particular, I have previously explained that the constant term of the chemical constant  $K$  of the oceanic reaction  $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  do depend on (and can be computed from) the absolute entropies for  $\text{HCO}_3^-$ ,  $\text{H}^+$  and  $\text{CO}_3^{2-}$ , all available in thermodynamic Tables, with this reaction constant  $K$  (and most of others involved in oceanic chemistry) determining the concentrations of all sea salts. The use of other values for the entropies for  $\text{HCO}_3^-$ ,  $\text{H}^+$  and  $\text{CO}_3^{2-}$  would lead to irrelevant constant  $K$ , and thus at the end to irrelevant concentrations of sea salts.

Therefore, since the seawater entropy do depend on the values of reference entropies for pure liquid water and sea salts, there is no reason to rely on arbitrary definition of them, since the relevant absolute values are all available in thermodynamics Tables and are the only values leading to the observed concentrations of sea salts.

In my opinion, there is an inconsistency between offering the current version of the seawater entropy as output from the TEOS10 software, which is arbitrarily defined, based on the fact that this arbitrariness does not affect the other derived variables. Indeed, this would assume that the TEOS10 version of entropy could be defined up to a linear function of salinity  $-a_2 - a_4 S_A$ , but this cannot be physically valid since in this case it would affect the time derivative or the gradients of entropy ( $d\eta/dt$  or  $\vec{\nabla}\eta$ ), which in this case would depend on the varying terms  $-a_4 dS_A/dt$  or  $-a_4 \vec{\nabla}(S_A)$ .

For the case of the time derivative, I recall in the section 12.8 of the SM (entitled “*Validations and physical meaning of absolute entropies / Second law?*”) that I have verified in detail that the entropy equation does indeed depend on these reference-entropy values, including going back to the very first formulations of the entropy equation for a body or a fluid (from 1875 to 2015): i.e. the papers of Gibbs, Jaumann, Lohr, Onsager, von Meixner, Eckart, de Groot, Mazur, Glansdorff, Prigogine, Dufour and van Mieghem, Prigogine, von Hasse, Herbert, Hauf and Höller, Landau and Lifshitz, Zdunkowski and Bott, Gassmann and Herzog... This thorough analysis confirm that the second law applied to the seawater entropy must depend on  $-a_4 dS_A/dt$  and  $-a_4 \vec{\nabla}(S_A)$  terms, which cannot be left unknown nor arbitrary, and thus with  $-a_4$  to be computed from the difference of the third-law absolute values for sea salts and liquid water ( $\eta_{s0} - \eta_{w0}$ )  $\approx -1880 \pm 17$  J/K/kg.

For instance de Groot (1951) expressed the entropy equation for continuous, multi-components sys-

tems (Chapter VII, Eqs. 21-26, p.98) as

$$\rho \frac{ds}{dt} = - \vec{\nabla} \cdot \vec{J}_s + \sigma, \quad (6)$$

or (Eq. 28, p.99) written as

$$\frac{\partial(\rho s)}{\partial t} = - \vec{\nabla} \cdot (\vec{J}_s + \rho s \vec{v}) + \sigma. \quad (7)$$

If the present value of the entropy production term  $\sigma \geq 0$  does not depend on the reference entropies, all other terms depends on these reference values. Therefore, unless to only compute  $\sigma$  and never consider the tendencies  $ds/dt$  or  $\partial(\rho s)/\partial t$ , nor the divergence terms  $-\vec{\nabla} \cdot \vec{J}_s$  or  $-\vec{\nabla} \cdot (\rho s \vec{v})$ , as a matter of fact the entropy equation depends on the special third-law, absolute difference term  $(\eta_{s0} - \eta_{w0}) \approx -1880 \pm 17 \text{ J/K/kg}$ .

- However, despite all that I could argue and in order to comply with the reviewer's wishes, I have added a sentence in the Introduction section a sentence as suggested by him, in order to explain:

*“The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.”*

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#### 4. Line 120: “[...] in order to compute the true value of the seawater entropy $\eta$ ”

*This phrasing suggests that the concept of relative entropy is less legitimate, which is not consistent with current understanding. Both absolute and relative entropy have their place in thermodynamics, and the choice between them depends on context and application.*

- In line with my comments to your points 1 and 2, I respectfully disagree with the referee about both the term “relative entropy” and “Both absolute and relative entropy have their place in thermodynamics.”

Indeed, I have explained above that the term “relative entropy” has already been defined in general thermodynamics and does not correspond to an entropy  $S$ , but to the Kullback, exergy or available energy functions like  $A = (U - U_0) - T_0 (S - S_0)$ , and thus corresponds to a mix of internal energy  $U$ , entropy  $S$  and the reference or standard values  $U_0$ ,  $T_0$  and  $S_0$ .

Since I have passed my PhD in 1994 on this subject, I obviously agree with the referee that the concept of relative entropy (or Kullback, or available energy, or exergy functions) is legitimate.

However, the arbitrary assumptions made in TEOS10 are of a completely different nature than those leading from the entropy function  $S = -k \sum_k p_k \ln(p_k)$  to the definition of the relative entropy or exergy or available energy function  $A = +k \sum_k p_k \ln(p_k/q_k)$ , with the distribution of the  $q_k$  states corresponding to the reference state  $U_0$ ,  $T_0$  and  $S_0$ .

For the seawater, the hypotheses made in TEOS10 amount to modify the low-order linear values in  $\eta = \eta_{w0} + (\eta_{s0} - \eta_{w0}) S_A + F_{n.l.}(t, S_A, p)$ , with more precisely  $\eta_{s0} = \eta_{w0} = 0$  whereas the whole non-linear contribution  $F_{n.l.}(t, S_A, p)$  is remained unchanged. There is no “relative” aspect when making these assumptions for the seawater entropy  $\eta$ , and the impact on the time or spatial derivatives  $d\eta/dt$  and  $\vec{\nabla}\eta$  of simply cancelling out the varying term  $(\eta_{s0} - \eta_{w0}) S_A$  cannot, and should not, be neglected.

- However, in order to comply with the reviewer's wishes, I have modified the sentence:

*“(...) in order to compute the true value of (...)”*

replaced by:

*“(...) in order to compute the absolute value of (...)”*

without explaining that it is the “true” value.

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5. *Lines 135-136:* “This means that it is not possible to modify or arbitrary set  $\eta_{s0}$  and/or  $\eta_{w0}$  to this or that values, unless to violate the entropy budget  $d\eta/dt = \dots$  and thus the second law of thermodynamics”

*This statement is not correct. The choice of reference values does not violate the second law, as entropy is only defined up to an arbitrary constant (or, in the case of seawater, up to a linear function of salinity).*

- As already explained, if the reference entropies  $\eta_{s0}$  and/or  $\eta_{w0}$  are modified, since the seawater entropy depends on the term  $(\eta_{s0} - \eta_{w0})(S_A/1000)$  depending on the possibly varying salinity  $S_A$ , the second law of thermodynamics is at least modified by any change in  $\eta_{s0}$  and/or  $\eta_{w0}$ , because the change in seawater entropy  $d\eta/dt$  is modified via the term  $[(\eta_{s0} - \eta_{w0})/1000] \times (dS_A/dt)$  by any change in the difference  $(\eta_{s0} - \eta_{w0})$ .

In particular, for a given value of  $\eta_{w0}$  and depending on any large positive or negative value of  $\eta_{s0}$ , a given change in  $S_A$  would corresponds to any arbitrary large increase or decrease in seawater entropy  $\eta$ . This cannot be true because this would demonstrate that, for such an open thermodynamical system, the definition of an increase in seawater entropy, and thus the second law applied to a given portion of the ocean, would be meaningless. The only way to avoid such an issue is to accept the need to properly define the difference  $(\eta_{s0} - \eta_{w0})$ , and thus the two individual values of  $\eta_{s0}$  and  $\eta_{w0}$ , in a non-ambiguous way, namely via the existing absolute values of them available in thermodynamic Tables.

- However, in order to comply with the reviewer’s wishes, I have modified the sentence:

“(...) *unless to violate the entropy budget (...)*”

replaced by:

“(...) *unless to modify the entropy budget (...)*”

with the term “*modify*” less polemic and more factual than “*violate*” I hope.

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6. *Lines 170 and following:* “The absolute entropy of sea-salts at 25°C”

*There appear to be inconsistencies in the reporting of values from Millero and Leung (1976). For example, the molar mass and entropy values are halved in the present paper compared to the original, which does not seem justified. In Millero and Leung, the authors use 95 J/K/mol for the sea salt molar entropy and 62.793 g/mol for sea-salt molar mass. However, in the present paper, the same values are reported as 47.52 J/K/mol and 31.405 g/mol, respectively. This discrepancy requires clarification, as the molar mass of sea salt should be close to  $23 + 35.45 = 58.45$  g/mol (for NaCl), which is much closer to 62.793 than to 31.405. For aqueous NaCl,  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$ , one mole of solid salt gives two moles of solutes, and the standard entropies of  $\text{Na}^+$  and  $\text{Cl}^-$  are 58.45 J/K/mol and 56.6 J/K/mol, respectively, so the molar entropy of dissolved NaCl is 115 J/K/mol, consistent with the value given in Pitzer et al. (1984).*

- I believe that I have not included “*discrepancy*” nor “*inconsistencies in the reporting of values from Millero and Leung (1976).*” It is true that there are many inaccuracies and errors in the apaper by Millero and Leung (1976), and I have only been able to mention them in a perhaps sometimes sibylline manner, and I am sorry for that. Although I unfortunately don’t have the space to say everything in my present papers, I think I have mentioned the essential things.

For instance, I have duly recalled in the section 2.4 that Millero and Leung (1976) considered the “*molar entropy*” and molecular weight of sea salt to be 95.01 J/K/mol and 62.793 g/mol, respectively, with the mean “*molar entropy of sea salt*”  $\sum_i N_i \bar{S}_i^\circ \approx 95.01$  J/K/mol computed in the Table 32 of ML76 with a sum  $\sum_i N_i \approx 1.99944 \approx 2$  clearly different from unity.



I have explicitly explained in the main text of the paper that: “ *The factor  $1.99944 \approx 2$  was due to a definition of concentrations by Millero different from the molar concentration published by McDougall et al. [2010, Table D.3, p.137] and shown in the column  $X(\text{TEOS10})$  in the Table 3.* ” Moreover, I explain in the legend of the Table 3 that: “ *... with about half the values of  $X(\text{M83})$  normalized to a sum of 1* ”

Here is the reason why I have chosen to divide the numerical values 95.01 J/K/mol and 62.793 g/mol by the factor  $1.99944 \approx 2$ : in order to compare the old results of Millero (1974), Millero and Leung (1976), Millero (1982) and Millero (1983) with the more recent results of Millero et al. (2008) and TEOS10 (McDougall et al., 2010).

It is a matter of fact that the molar mass for NaCl is close to  $23 + 35.45 = 58.45$  g/mol ( $M_2 = 58.4428$  g/mol in Pitzer et al., 1984, p.8), which is indeed closer to 62.793 g/mol than to 31.405 g/mol... However, it is the value of 31.405 g/mol that is retained for the “ *Reference Salinity molar mass* ” defined as  $M_S = \sum_j N_j M_j$  or  $M_S = \sum_j X_j M_j$ , with  $N_i$  or  $X_i$  the mole fractions and  $M_i$  the molar masses, with for instance the value  $M_s = 31.4038218$  g/mol retained both in Millero et al. (2008, Table 4, p.62) and in TEOS10 (McDougall et al., 2010, Table D.3 and D.4). Therefore, I would rather consider that the mean value  $0.5 \times 23 + 0.5 \times 35.45 \approx 29.23$  g/mol computed for half a mole of Na and half a mole of Cl (forming one mole of Na + Cl) is closer to the value  $M_s \approx 31.4$  g/mol computed with one mole of all cations, anions and boric acid forming one mole of sea salts.

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Similarly, for the entropy it is true that both Millero and Leung (1976) and Millero (1983) explained that: “ *... the partial molar entropy of sea salt at 25°C (...) 95.0 J/K/mol (...) can be compared to a value of 115.4 J/K/mol for NaCl.* ” However, this “ comparison ” does not provide a justification for the molar value of 95.0 J/K/mol, and moreover the value 115.4 J/K/mol is not the molar entropy for NaCl<sub>cr</sub>, which is the more important thing.

I agree that this value is indeed in agreement with the value  $\bar{S}_2^\circ = 13.886 \times 8.3145 = 115.45$  J/K/mol at 25°C and 1 bar ( $10^5$  Pa) published by Pitzer et al. (1984, Table A-2, p.20) for NaCl(aq) at infinitely dilute solution (see the upper right panel in the Fig. 6). However, this value seems at odds with all other values published before and after this 1984 paper, including in the other paper by Pitzer (1987, Table 1, p.25) where for NaCl(c)  $\bar{S}_2^\circ = 8.676 \times 8.3145 = 72.14$  J/K/mol, and for Na<sup>+</sup> and Cl<sup>-</sup>  $7.096 \times 8.3145 = 59.00$  J/K/mol and  $6.778 \times 8.3145 = 56.36$  J/K/mol, respectively (see the lower left panel in the Fig. 6), with indeed a sum of 115.36 J/K/mol and thus with a difference of about  $115.36 - 72.14 = 43.22$  J/K/mol to be explained...

In fact, the explanation for this difference of about 43 J/K/mol can be found in the Table A-10 of Pitzer et al. (1984, p.65), where the “ Standard entropy of solution of NaCl(aq) ” was indeed of about  $5.207 \times 8.3145 = 43.29$  J/K/mol. This means that the change in entropy of the reaction  $\text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^-$  must include at the same times the change in the molar entropies and the change due to the entropy of solution, with the close budget:  $(59.00 + 56.36) = 115.36 = 72.14 + 43.29$  J/K/mol. The physical meaning of this budget is as follows: the impact on the entropy of the dissolution of NaCl (72.14) crystals into Na<sup>+</sup> and Cl<sup>-</sup> solved aqueous ions (115.36) logically corresponds to an increase in entropy of +43.29 J/K/mol, due to the irreversible increase in disorder.

By the way, I recall in the upper left panel of the Fig. 6 that the absolute entropy for solid NaCl at 25°C (and 1 bar) given by Lewis and Randall (1961, Table A7-3, p.674) was similarly close to 17.33 cal/K/mol, or equivalently 72.5 J/K/mol. This book by Lewis and Randall (1961) was at the basis of the values retained by Millero and Leung (1976) and Millero (1983), who therefore should not have mentioned the other value of about 115.4 J/K/mol... Here is another error in Millero’s papers.

As a synthesis, and including other similar entropy values published in Thermodynamic Tables, the value of the absolute entropy for solid NaCl at 25°C (and 1 bar) was well-known since 1932 at least, and

Figure 6: The absolute entropy for solid NaCl at 25 °C (and 1 bar) published in several books (Thermodynamic Tables) and papers.

**674 Thermodynamics**

**Lewis & Randall (1961)**

TABLE A7-3. SOLID AND LIQUID HALIDES  
Free energies based on  $H_{298}^0$

	$-(F^0 - H_{298}^0)/T, \text{ cal/deg}$			
	298.15°K	500°K	1000°K	1500°K
NaF	12.26	13.57	18.42 m	23.39
NaCl	17.33	18.72	23.85 m	29.92
NaBr	(20.8)	(22.3)	(27.4) m	(33.8)

Table A-2. The Standard Entropies of Water and NaCl(aq), Debye-Huckel Parameter  $A_\phi$  and NaCl Virial Parameters at  $t$  and  $P$ .  $S_1^0(T,P)$  and  $S_2^0(T,P)$  are Absolute Entropies, i.e., they are Referenced to States Approaching Zero Entropy at 0 K.

$t$ °C	$P$ bar	$S_1^0(T,P)/R$	$S_2^0(T,P)/R$
20.0	1.0	8.2597	14.065
25.0	1.0	8.4130	13.886
30.0	1.0	8.5637	13.726

**Pitzer et al. (1984)**

Table A-10. The Standard Entropy of Solution of NaCl(aq), divided by  $R$ . The entropies of column 3 are given for pressures of 1.0 bar below 100°C and saturation pressure (column 2) above 100°C.

$t$ °C	$P_{\text{sat}}$ bar	1.0 bar
20.0		5.490
25.0		5.207
30.0		4.945

**Pitzer et al. (1984)**

Table 1: The Chemical Potentials, Enthalpies of Formation, and Entropies at 298.15 K of the Species and Minerals of the Na-K-Mg-Cl-SO<sub>4</sub>-OH-H<sub>2</sub>O System and the Temperature Functions of the Heat Capacity of the Solids

Substance	Formula	$S^0/R$
Water	H <sub>2</sub> O(l)	8.409
Hydroxide ion	OH <sup>-</sup> (aq)	-1.293
Chloride ion	Cl <sup>-</sup> (aq)	6.778
Sulfate ion	SO <sub>4</sub> <sup>2-</sup> (aq)	2.42
Magnesium ion	Mg <sup>2+</sup> (aq)	-16.64
Calcium ion	Ca <sup>2+</sup> (aq)	-6.39
Sodium ion	Na <sup>+</sup> (aq)	7.096
Potassium ion	K <sup>+</sup> (aq)	12.33
Arcanite	K <sub>2</sub> SO <sub>4</sub> (c)	21.12
Bischofite	MgCl <sub>2</sub> ·6H <sub>2</sub> O(c)	44.03
Epsomite	MgSO <sub>4</sub> ·7H <sub>2</sub> O(c)	44.79
Halite	NaCl(c)	8.676

**Pitzer (1987)**

**Sodium Chloride (NaCl)**

**Chase (1998)**

Enthalpy Reference Temperature = $T_r = 298.15 \text{ K}$				
$T/K$	$C_p^0$	$S^0$	$-[G^0 - H^0(T_r)]/T$	$H$
0	0.	0.	INFINITE	-
100	34.932	23.723	114.140	.
200	46.873	52.605	76.643	.
298.15	50.509	72.115	72.115	.

with an accuracy improving with time:

- 72.2 ± 2 J/K/mol in Bureau des Mines Bulletin-350 (Kelley, 1932, p.41);
- 72.4 J/K/mol in NBS-500 (Rossini et al., 1952, p.450);
- 72.5 ± 0.4 J/K/mol in Bureau des Mines Bulletin-592 (Kelley and King, 1961, p.87);
- 72.5 J/K/mol by Lewis and Randall (1961, p.674);
- 72.12 ± 0.21 J/K/mol in USG-1452 (Robie et al., 1978, p.24);
- 72.13 J/K/mol in NBS-11 (Supp. N°2) (Wagman et al., 1982, p.301);
- 72.16 = 115.45 - 43.29 J/K/mol by Pitzer et al. (1984, p.20 and 65, corrected);
- 72.14 J/K/mol by Pitzer (1987, p.25);
- 72.1 ± 0.2 J/K/mol in USG-2131 (Robie and Hemingway, 1995, p.23);
- 72.115 J/K/mol in NIST-JANAF4 (Chase, 1998, p.789); and
- 72.15 ± 0.20 J/K/mol in NEA 2nd Ed. (Grenthe et al., 2020, p.162).

All these values are indeed different from the sum 115.4 J/K/mol for Na<sup>+</sup> and Cl<sup>-</sup> considered by the referee and Millero's papers, from which it is needed to remove the entropy of solution of NaCl of about 43.3 J/K/mol.

Moreover, the other apparent "discrepancy" or "inconsistencies" between the mean sea-salt molal entropy of about 95 J/K/mol considered by Millero and Leung (1976) and Millero (1983) and the molar entropy 47.52 J/K/mol I have derived in the Table 3, from the values published by Lewis and Randall (1961), are therefore due to the fact that like in Millero et al. (2008) and TEOS10 (McDougall et al., 2010) the molar mean values are computed for one mole of sea salts by the relationships  $M_S = \sum_j N_j S_j$

or  $M_S = \sum_j X_j S_j$ , where  $N_i$  or  $X_i$  are the mole fractions with  $\sum_i N_i = \sum_i X_i = 1$  and where  $S_i$  are the molar entropies, leading to the even more recent and accurate value of  $\eta_{s0} \approx 46.74 \pm 0.40$  J/K/mol.

In fact, these apparent “*discrepancy*” or “*inconsistencies*” regarding the way to take into account the data published by Millero and Leung (1976) and Millero (1983) can be related to the two different concepts of “*mole fraction*” on the one hand, and “*molality*” on the other, as described by Lewis and Randall (1961) who is the source of inspiration for Millero and Leung (1976) and Millero (1983).

Lewis and Randall (1961, p.199-200) explained that for a mixture or solution made of  $n_1, n_2, n_3, \dots$  moles of the substances 1, 2, 3, ..., the mole fractions of a substance  $i$  is  $x_i = n_i/(n_1 + n_2 + n_3 + \dots)$ , with therefore  $\sum_i x_i = 1$  like in Millero et al. (2008) and TEOS10 (McDougall et al., 2010). Differently, the molality  $m_i$  of an aqueous solute  $i$  is the number on moles per 1000 gr (55.51 moles) of water (acting as solvent).

Accordingly, Millero and Leung (1976) and Millero (1983) computed the partial molal entropy of sea salt at 25°C (...) 95.0 J/K/mol (...) with the property  $\sum_i N_i \approx 2$ , where all the  $N_i$  was almost the double of the values that will be retained next by Millero et al. (2008) and and TEOS10 (McDougall et al., 2010), with the consequence that 95.0 J/K/mol is about twice the value  $\eta_{s0} \approx 46.74 \pm 0.40$  J/K/mol retained in the present paper. I explained in the following more precisely how the “*mole fractions*” was defined by Millero in 1976-1983 as about twice the values that will be considered by him after 2008, and thus in TEOS10.

Anyhow, the “*entropy per unit mass*” is exactly the same if it is computed either from the values published in Millero and Leung (1976) and Millero (1983), namely  $95.01/0.062\,793 \approx 1513$  J/K/kg, or from the rescaled (about half) values  $47.52/0.031\,405 \approx 1513$  J/K/kg divided by 1.999 44, values which are both close to the more accurate values I have retained in the present study, namely  $46.74/0.031\,404 \approx 1488$  J/K/kg.

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Unfortunately, I don’t have the space to say everything in the present papers. I could have explained that the total mole  $N_T$  of sea salts was defined in Millero (1982, Eq 88, p.427) as

$$N_T = \frac{1}{2} \left( \sum_i N_i \right) + N_B = \frac{2 N_B + \sum_i N_i}{2} = \frac{\overbrace{\left( N_B + \sum_i N_i \right)}^{\text{Sum}} + N_B}{2} . \quad (8)$$

I show in the left part of the Fig. 7 that the sum “(Sum +  $N_B$ )” equal to  $2 N_T$  is very close to 2 in the oldest Tables published by Millero (1974), Millero and Leung (1976), Millero (1982) and Millero (1983), with therefore  $N_T = N_B + \sum_i N_i / 2 \approx 1$ , whereas in the more recent Tables published by Millero et al. (2008) and TEOS10 (McDougall et al., 2010) recalled in the right parts of the Fig. 7, the sum of all components is set to unity with in particular  $N_T = N_B + \sum_i N_i \equiv 1$  in TEOS10.

It is therefore in order to compare the old values with the more recent TEOS10’s definitions that I have retained everywhere the relationships  $N_T = N_B + \sum_i N_i = 1$  for the total mole of sea salts,  $M = N_B \times M_B + \sum_i N_i \times M_i$  for the molar mass of sea salts and  $S = N_B \times S_B + \sum_i N_i \times S_i$  for the molar entropy of sea salts.

Strictly speaking I was first inclined according to (8) to leave unchanged the molal fraction  $N_B$  for the boric acid  $B(OH)_3$  and to divide by two all the other molal fractions. However, a close comparison with the mole fractions retained by Millero et al. (2008) and TEOS10 (McDougall et al., 2010) shows that it would be more relevant to divide by 1.999 44 all the molar fractions published by Millero and Leung (1976) and Millero (1983). The motivation is that the value of  $N_B$  is close to  $2800 \times 10^{-7}$  in the

more recent papers, and they cannot be kept to the old molal value of about 0.000 6 or  $6000 \times 10^{-7}$ . Anyhow, the relative uncertainty caused by this alternative should not exceed  $0.000\,6/1.999\,44 \approx 0.000\,3$  or 0.03 %, which is much smaller than the relative accuracy of the sea-salt molar entropy  $\eta_{s0} \approx 46.74 \pm 0.40$  J/K/mol, namely about 0.9 %.

Figure 7: The “mole fractions”  $N_i$  published (from the left to the right) by Millero (1974, Table II, p.20), Millero and Leung (1976, Table 32, p.1071), Millero (1982, Table IV, p.428), Millero (1983, Table X, p.35), Millero et al. (2008, Tables 3 and 4, p.60 and p.62) and McDougall et al. (2010, Table D.3) for almost the same ionic components (cations and anions) and the neutral boric acid  $B(OH)_3$ .

Millero (1974)	Millero and Leung (1976, TABLE 32) and Millero (1983)		Millero (1982)	Millero et al.(2008)		McDougall, ..., Millero et al. (TEOS-2010)	
TABLE II	TABLE X		TABLE IV	Table 3	Table 4	Table D.3.	
$N_i$	Species	$N_i$	$N_i / 1.999\,44$	$N_i$	$10^7 X_i$	$10^7 X_i$ (Definition)	$X(\text{TEOS10})$
0.835890	Na <sup>+</sup>	0.83619	0.4 182 121	0.837341	4 188 071.5	4 188 071	Na <sup>+</sup> 0.418 807 1
0.095068	Mg <sup>2+</sup>	0.09509	0.0 475 583	0.094299	471 677.6	471 678	Mg <sup>2+</sup> 0.047 167 8
0.018340	Ca <sup>2+</sup>	0.01834	0.0 091 726	0.018357	91 822.9	91 823	Ca <sup>2+</sup> 0.009 182 3
0.018222	K <sup>+</sup>	0.01822	0.0 091 126	0.018222	91 158.8	91 159	K <sup>+</sup> 0.009 115 9
0.000163	Sr <sup>2+</sup>	0.00016	0.0 000 800	0.000163	809.6	810	Sr <sup>2+</sup> 0.000 081 0
0.974632	Cl <sup>-</sup>	0.97481	0.4 875 415	0.974590	4 874 838.9	4 874 839	Cl <sup>-</sup> 0.487 483 9
0.050415	SO <sub>4</sub> <sup>2-</sup>	0.05042	0.0 252 171	0.050415	252 152.4	252 152	SO <sub>4</sub> <sup>2-</sup> 0.025 215 2
0.004168	HCO <sub>3</sub> <sup>-</sup>	0.00345	0.0 017 255	0.003321	15 340.4	15 340	HCO <sub>3</sub> <sup>-</sup> 0.001 534 0
0.001508	Br <sup>-</sup>	0.00151	0.0 007 552	0.001501	7520.1	7520	Br <sup>-</sup> 0.000 752 0
0.000737	B(OH) <sub>3</sub>	0.0006	0.0 003 001	0.000588	2806.5	2807	B(OH) <sub>3</sub> <sup>aq</sup> 0.000 280 7
$N_B$	CO <sub>3</sub> <sup>2-</sup>	0.0004	0.0 002 000	0.000346	2133.6	2134	CO <sub>3</sub> <sup>2-</sup> 0.000 213 4
	B(OH) <sub>4</sub> <sup>-</sup>	0.00015	0.0 000 750	0.000149	899.8	900	B(OH) <sub>4</sub> <sup>-</sup> 0.000 090 0
0.000121	F <sup>-</sup>	0.0001	0.0 000 500	0.000121	610.2	610	F <sup>-</sup> 0.000 061 0
1.999 264 (<-Sum->)		1.999 44	1.0 000 000	1.999 413	OH <sup>-</sup> 71.2	71	OH <sup>-</sup> 0.000 007 1
2.000 001 (Sum+ $N_B$ )		2.000 04		2.000 001	CO <sub>2</sub> 86.5	86	CO <sub>2</sub> <sup>aq</sup> 0.000 008 6
					Sum 10 000 000.0	10 000 000	Mean 1.000 000 0

Beyond the apparent “discrepancy” or “inconsistencies” seen by the reviewer, I have studied in detail the true uncertainties and problems contained in the papers by Millero and Leung (1976) and Millero (1983).

Millero and Leung (1976) and Millero (1983) explained that: “Since future workers may wish to look at entropy surfaces in the oceans, the relative specific entropy of seawater has been fitted to a functions of salinity (std deviation 0.0001 J/K/g = 0.01 10<sup>-2</sup> J/K/g)”

$$s \text{ (J/K/g)} = A_s \times S(\%) + B_s \times S(\%)^{3/2} + C_s \times S(\%)^2, \quad (9)$$

$$\text{where } A_s = +1.42185 \times 10^{-3} - 3.1137 \times 10^{-7} \times t(^{\circ}\text{C}) + 4.2446 \times 10^{-9} \times t(^{\circ}\text{C})^2, \quad (10)$$

$$B_s = -2.1762 \times 10^{-4} + 4.1426 \times 10^{-7} \times t(^{\circ}\text{C}) - 1.6285 \times 10^{-9} \times t(^{\circ}\text{C})^2, \quad (11)$$

$$C_s = +1.0201 \times 10^{-5} + 1.5903 \times 10^{-8} \times t(^{\circ}\text{C}) - 2.3525 \times 10^{-10} \times t(^{\circ}\text{C})^2. \quad (12)$$

However, Millero and Leung (1976) and Millero (1983) did not provided the way the coefficients  $A_s$ ,  $B_s$  and  $C_s$  have been fitted from unknown relationships and datasets. It is thus impossible to appreciate the quality and the realism of these coefficients  $A_s$ ,  $B_s$  and  $C_s$ , and thus of the formula (9) for the “relative specific entropy of seawater.” In particular, it is not possible to appreciate if the molal entropy of salt  $\bar{S}_2^{\circ} \approx 95.0$  J/K/mol has been used by Millero as such and associated with the molal entropy of water  $\bar{S}_1^{\circ} \approx 70.0$  J/K/mol?

If we are therefore compelled to trust the numerical methods implemented by Millero and Leung (1976) and Millero (1983) leading to the relationships (9)-(12), it was however not only possible but also needed to try to validate these relationships as far as possible. I show in the top of the Figs. 8 a comparison between, in the left part, the original Fig. 5 (p.1073) of Millero and Leung (1976) for the salinity part of the seawater entropy  $(100/1000) \times s = s/10$ , with  $s$  in units of J/K/kg, to be compared with the personal plot shown in the right part computed from the relationships (9)-(12).

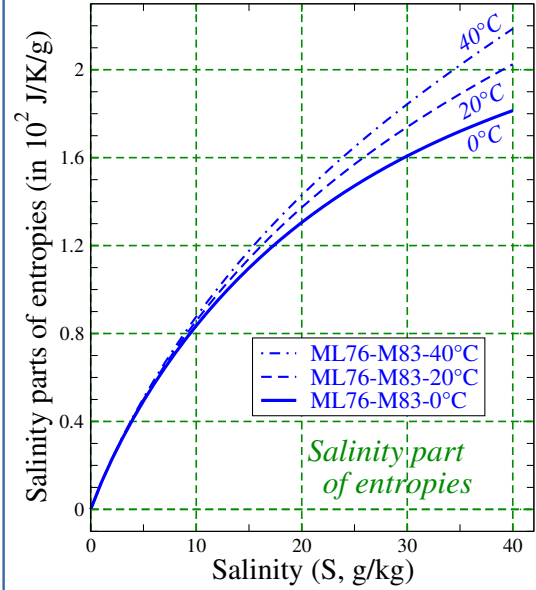
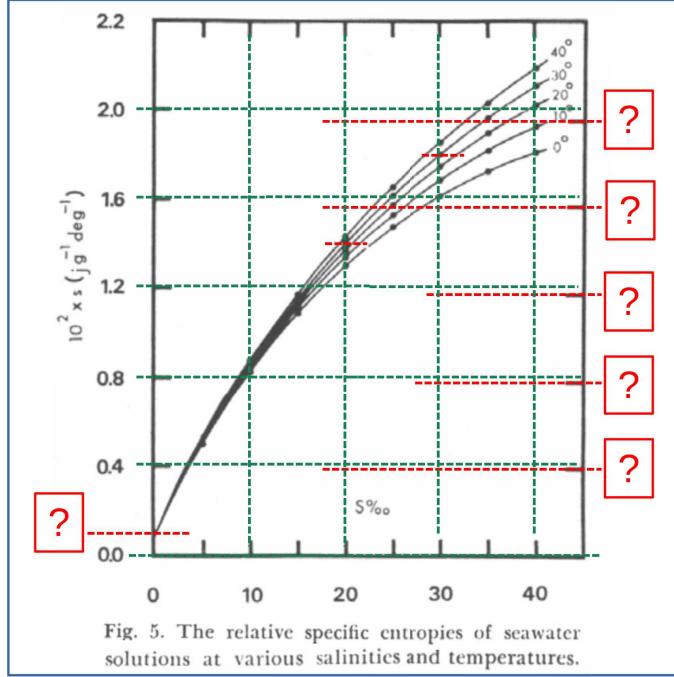
Note that there is a change of sign in the preprint paper by Sharqawy et al. (2010a, Eq. 44, Table 9, p.55) in the Millero's salinity increment  $s_{sw} = s_w - \eta_s(y, x)$ , whereas the original Millero's formula  $s_{sw} = s_w + \eta_s(y, x)$  is retained in the published version by Sharqawy et al. (2010b, Eq. 44, Table 9, p.373).

The fact that the general shapes of the two figures are quite similar indicates that there must be no typo in the relationships (9)-(12). However, it is clear that the Fig. 5 of Millero and Leung (1976) does not satisfy the constraint that  $s = 0$  for  $S = 0\%$  regardless of the Celsius temperature  $t = (0, 20, 40)$ . Furthermore, there is a discrepancy between the ordinates on the left and right sides of Fig. 5 (see red question marks)... I think that these graphical issues only concern the Fig. 5, and not the relationships (9)-(12).

Another way to validate the (9)-(12) is to check the agreement with the numerical values published in the Table 29 (p.1070) of Millero and Leung (1976) for  $s/10$  and for  $t$  from 0 to 40°C by step of 5°C. I show in the bottom of the Fig. 8 that these numerical values recomputed from (9)-(12) are similar to those of the Table 29: see the last Table in the Fig. 8, where the differences are the largest for low salinities with a relative accuracy of about 0.01/0.5 or 2% for  $S = 5\%$ .

- As a conclusion, I think I have precisely shown that I have not included “*discrepancy*” nor “*inconsistencies in the reporting of values from Millero and Leung (1976)*.”

Figure 8: **Upper left:** the Fig. 5 (p.1073) of Millero and Leung (1976) for  $(100/1000) \times s = s/10$ , with  $s$  measured in units of J/K/kg; **Upper right:** the same salinity parts ( $s/10$ ) of the seawater entropy recomputed from the Millero's (1976-1983) relationships (9)-(12), in units of  $10^2$  J/K/kg and plotted against the absolute salinity for the three selected temperatures 0, 20 and 40°C; **Middle:** the Table 29 (p.1070) of Millero and Leung (1976) for  $s/10$  and  $t$  from 0 to 40°C by step of 5°C; **Bottom:** the corresponding Tables for  $s/10$  recomputed from (9)-(12) for the 3 Celsius temperatures  $t = (0, 20, 40)$ , with the last Table showing the differences  $\Delta(s/10)$  between the Table 29 and the recomputed data.



		Salinity							
Temp	0(‰)	5(‰)	10(‰)	15(‰)	20(‰)	25(‰)	30(‰)	35(‰)	40(‰)
0°C	0	0.503 <sub>5</sub>	0.833 <sub>1</sub>	1.091 <sub>8</sub>	1.301 <sub>3</sub>	1.471 <sub>8</sub>	1.609 <sub>5</sub>	1.718 <sub>1</sub>	1.801 <sub>8</sub>
5	0	0.505 <sub>1</sub>	0.838 <sub>8</sub>	1.103 <sub>8</sub>	1.320 <sub>7</sub>	1.500 <sub>5</sub>	1.648 <sub>5</sub>	1.735 <sub>2</sub>	1.865 <sub>2</sub>
10	0	0.507 <sub>1</sub>	0.844 <sub>5</sub>	1.115 <sub>1</sub>	1.338 <sub>9</sub>	1.526 <sub>5</sub>	1.684 <sub>3</sub>	1.814 <sub>9</sub>	1.922 <sub>4</sub>
15	0	0.509 <sub>1</sub>	0.849 <sub>2</sub>	1.125 <sub>5</sub>	1.355 <sub>5</sub>	1.551 <sub>1</sub>	1.716 <sub>7</sub>	1.857 <sub>5</sub>	1.975 <sub>1</sub>
20	0	0.512 <sub>9</sub>	0.855 <sub>9</sub>	1.135 <sub>2</sub>	1.371 <sub>2</sub>	1.573 <sub>3</sub>	1.747 <sub>3</sub>	1.896 <sub>7</sub>	2.023 <sub>1</sub>
25	0	0.512 <sub>5</sub>	0.860 <sub>1</sub>	1.144 <sub>3</sub>	1.386 <sub>9</sub>	1.595 <sub>9</sub>	1.776 <sub>2</sub>	1.932 <sub>7</sub>	2.068 <sub>9</sub>
30	0	0.513 <sub>9</sub>	0.864 <sub>9</sub>	1.153 <sub>8</sub>	1.400 <sub>8</sub>	1.615 <sub>1</sub>	1.803 <sub>9</sub>	1.968 <sub>1</sub>	2.011 <sub>8</sub>
35	0	0.515 <sub>7</sub>	0.869 <sub>9</sub>	1.162 <sub>2</sub>	1.415 <sub>1</sub>	1.635 <sub>3</sub>	1.829 <sub>9</sub>	2.001 <sub>3</sub>	2.120 <sub>9</sub>
40	0	0.517 <sub>5</sub>	0.874 <sub>7</sub>	1.172 <sub>2</sub>	1.428 <sub>5</sub>	1.655 <sub>9</sub>	1.855 <sub>7</sub>	2.034 <sub>5</sub>	2.193 <sub>3</sub>

Temp	0(%)	5(%)	10(%)	15(%)	20(%)	25(%)	30(%)	35(%)	40(%)
0	0.0	0.4931	0.8357	1.0980	1.3053	1.4719	1.6078	1.7200	1.8142
20	0.0	0.5000	0.8575	1.1406	1.3735	1.5700	1.7398	1.8896	2.0250
40	0.0	0.5066	0.8768	1.1765	1.4293	1.6486	1.8436	2.0211	2.1863

Temp	0(%)	5(%)	10(%)	15(%)	20(%)	25(%)	30(%)	35(%)	40(%)
0	0.0	+0.0104	-0.0026	-0.0062	-0.0040	-0.0001	+0.0017	-0.0016	-0.0126
20	0.0	+0.0120	-0.0025	-0.0053	-0.0023	+0.0033	+0.0075	+0.0071	-0.0016
40	0.0	+0.0109	-0.0021	-0.0043	-0.0005	+0.0064	+0.0121	+0.0134	+0.0075

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7. Line 210: “[...] correcting this standard formulation to add the absolute-entropy increment  $\Delta\eta_s$ ”

*The TEOS-10 determination of seawater entropy is not flawed or in error, so it is misleading to present the computation of the increment  $\Delta\eta_s$  as a correction to the existing formulation.*

- I have previously explained, and I provide in the next point 9 other physical motivations and detailed explanations, that the seawater entropy currently provided by TEOS10 is indeed contrary to the third law of thermodynamics.

- However, in order to avoid being too critical of TEOS10’s use of arbitrary definitions of reference entropies, I have replaced the term “correcting” by “amending”.

- I have also modified the other sentence:

“(...) the present paper offers the possibility of correcting and generalising the current standard formulation of TEOS10 (...)”

replaced by:

“(...) the present paper offers the possibility of amending, if needed, the current standard formulation of TEOS10 (...)”

- I have also modified (by cancelling a whole part of it) the other sentence:

“(...) show large differences in magnitude (and even signs) for the changes in seawater entropy that should be considered as prohibitive for the use of the standard entropy version of TEOS10, as far as the salinity is not a constant.”

replaced by:

“(...) show large differences in magnitude (and even signs) for the changes in seawater entropy, as far as the salinity is not a constant.”

- I have also modified the other sentence:

“(...) the absolute definition of seawater entropy must be preferred to any other arbitrarily modified definition, otherwise the entropy budget and therefore the second principle of thermodynamics will be arbitrarily modified.”

replaced by:

“(...) the absolute definition of seawater entropy should impact the second principle of thermodynamics.”

Indeed, let me write at least this small term “should” that I believe to be factual, since I have recalled that the linear term  $-a_2 - a_4 S_A$  cannot be left unknown nor arbitrary, due to the impacts  $-a_4 dS_A/dt$  and  $-a_4 \vec{\nabla}(S_A)$  on the second-law seawater entropy equation  $d\eta/dt = (\dots)$ .

- I have also modified the other sentence:

“It would be valuable to redo the tuning of the TEOS10’s formulation by imposing the values of both  $\eta_{w0}$  and  $\eta_{s0}$  at  $0^\circ\text{C}$ , rather than (...)”

replaced by:

“Increased accuracy could be achieved by re-adjusting the tuning of the TEOS10’s formulation by using the absolute values of both  $\eta_{w0}$  and  $\eta_{s0}$  at  $0^\circ\text{C}$ , rather than (...)”

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8. Lines 253-257: “The positive increasing values for the Millero’s formulation disagree with the decreasing values of the TEOS10 standard entropy. The red lines corresponding to the TEOS10 absolute entropy values are even more decreasing with both  $t$  and  $S_A$ . As entropy is a thermodynamic state function, its variations with salinity must have well-defined, non-ambiguous values, and the red curves and the absolute version of the reference entropies must be preferred to any others.”

*This paragraph does not fully account for the fact that entropy is only defined up to a linear function of salinity  $-a_2 - a_4 S$ . The variations with salinity depend on the approach used to compute entropy.*

*To determine if two different determinations of entropy are consistent, one needs to check whether their difference is a linear function of salinity. My own checks suggest that, for any given temperature, Millero's saline entropy part approximately differs from the TEOS10 saline part by a linear function of salinity, with a temperature-dependent slope. For instance, at  $t = 25^\circ\text{C}$ ,*

$$\eta_{\text{millero}} \approx \eta_{\text{teos10}} - 1.06 S_A + \text{constant} \quad (13)$$

*while at  $t = 0^\circ\text{C}$ ,*

$$\eta_{\text{millero}} \approx \eta_{\text{teos10}} - 0.5 S_A + \text{constant} \quad (14)$$

*This suggests that the difference is not simply a matter of improved values, but rather reflects a fundamental incompatibility between the approaches. Given that the composition of seawater considered by Millero and Leung (1976) is not very different from that considered by TEOS10, the source of the discrepancy deserves further discussion. Physically, it is generally expected that adding salt to pure water increases disorder, and thus absolute entropy, which is consistent with Millero's result.*

- I already disagree with the first sentence of this specific comment: “*(...) the entropy is only defined up to a linear function of salinity  $-a_2 - a_4 S$ .*”

Once again, this is a claim that remains to be demonstrated by the facts, but since the linear term denoted as  $-a_2 - a_4 S_A$  has an impact on the entropy values, even if it does not have an impact on the other quantities obtained via the partial derivatives of the Gibbs function (at constant  $S_A$ ), to admit that  $-a_2 - a_4 S_A$  can remain unknown (or be defined arbitrarily) would amounts to admit that the seawater entropy may not need to be calculated precisely. Unless I am mistaken, this attitude is not found anywhere else in physics except in the fields of atmospheric and oceanic studies.

Differently, I have recalled in the present two-parts paper that  $-a_4 = (\eta_{s0} - \eta_{w0}) \approx -1880 \pm 17 \text{ J/K/kg}$  can be precisely computed by applying the general third law of thermodynamic. The linear  $-a_2 - a_4 S$  is therefore far from being unknown and cannot be arbitrarily set to this or that values, unless to arbitrarily modify the values of the seawater entropy itself.

- I also disagree with the other sentence of this specific comment: “*To determine if two different determinations of entropy are consistent, one needs to check whether their difference is a linear function of salinity.*”

In fact, there is no reason why the dependence of the seawater entropy should be only a linear function of salinity.

Differently, the present formulation of seawater entropy in TOES10 already have a clear dependence on the salinity, but via the non-linear terms depending on  $t$ ,  $S_A$  and  $p$ , with the linear lowest-order term you note as  $-a_2 - a_4 S_A$  almost or entirely cancelled out.

Perhaps you meant that one could always try to appreciate the effects of salinity through a linear, linearized tangent version as a function of  $S_A$ ? That would be consistent with the rest of the remarks anyway...

- But I am also afraid that *the evaluations (13) and (14) made by the referee have the wrong sign.* On my own side, I find for  $10 < S_A < 40 \text{ g/kg}$  and at  $t = 25^\circ\text{C}$ :

$$\eta_{\text{Millero}} \approx \eta_{\text{Teos10}} + 1.05 S_A + \text{constant} , \quad (15)$$

while at  $t = 0^\circ\text{C}$ :

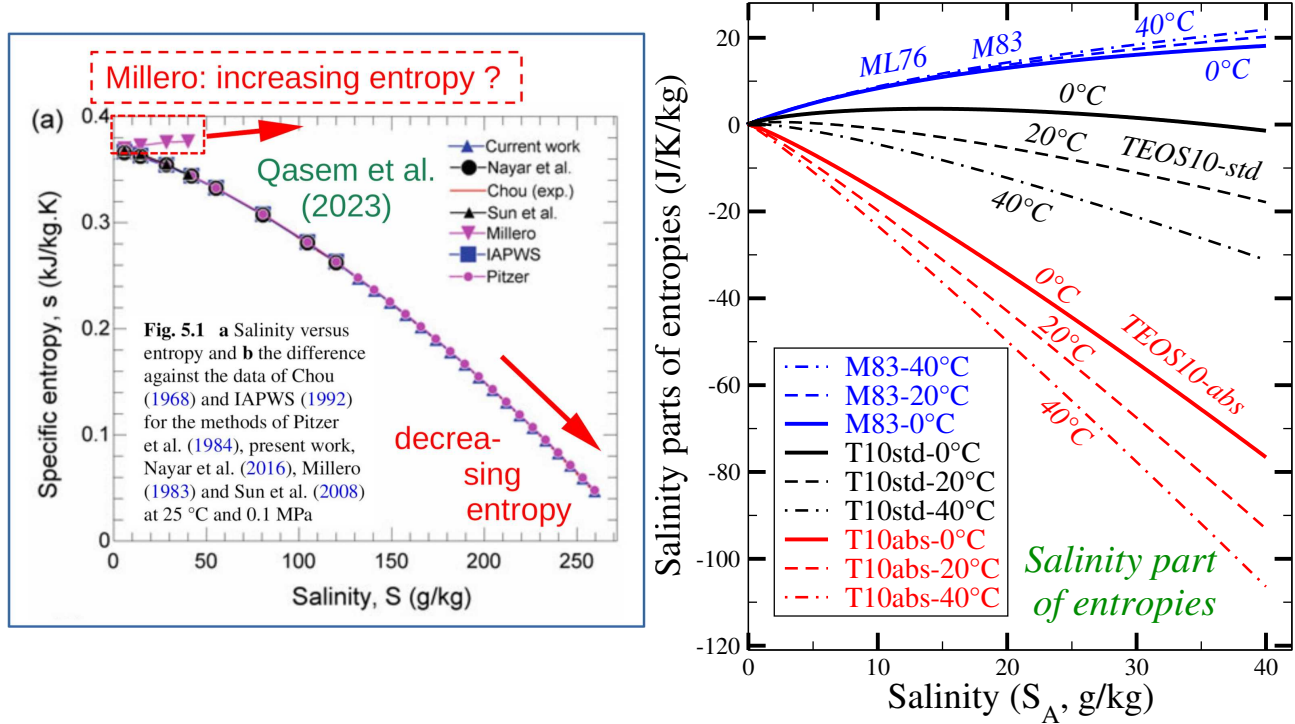
$$\eta_{\text{Millero}} \approx \eta_{\text{Teos10}} + 0.5 S_A + \text{constant} . \quad (16)$$

My positive coefficients  $+1.05$  (instead of  $-1.06$ ) and  $+0.5$  (instead of  $-0.5$ ) are close to the opposite of those derived by the referee (with however smaller values for smaller salinities, like 0.764 and 0.446



at 1 g/kg, respectively). My positive coefficients are also in agreement with the Millero (1976-1983) curves clearly located above the TEOS10 curves in the Figs. 1 and 3 recalled in the Fig. 9, where Qasem et al. (2023) independently confirmed that the Millero (1983) curves is clearly located above the IAPWS (pre-TEOS10) curves.

Figure 9: *The impacts on the seawater entropy of the change in salinity. On the left: the Fig. 5.1 of Qasem et al. (2023, p.125). On the right: The salinity parts of the Millero's (1976-1983/blue) and TEOS10's (standard/black and absolute/red) seawater entropies plotted against the absolute salinity for three selected temperatures (0, 20 and 40 °C).*



Therefore, in spite of the change of signs for these coefficients, I agree with the first remark of the referee and the important feature confirmed by Qasem et al. (2023) (recalled in the Figs. 9) that: “ (...) *the difference* (between Millero’s and TEOS10’s approaches) *is not simply a matter of improved values, but rather reflects a fundamental incompatibility between the approaches.*” Again, I agree that the only interesting feature brought by Millero in his 1976-1983 papers was the use of the (double) absolute entropy reference values for liquid water and sea salts, even if important issues were likely introduced in the next fitting to data processes.

However, I disagree with the second remark of the referee: “ *Given that the composition of seawater considered by Millero and Leung (1976) is not very different from that considered by TEOS10*” (...), since the Figs. 9 clearly show that the Millero’s entropy curves (increasing with the salinity) are at odds with all other curves, where entropy curves are mainly decreasing with the salinity.

Here are the reasons why I have clearly explained in the paper that I rely on the TEOS10 formulation for the non-linear dependence of the seawater with the temperature, salinity and pressure, but with  $a_4$  in the TEOS10’s arbitrarily modified linear term  $-a_2 - a_4 S_A$  set to the third-law absolute value, in a way almost similar to what is done in the Millero’s papers except with about half the reference values, and in fact with more recent and accurate values for these absolute values for these reference values.

- I finally disagree with the last remark of the referee: “ *Physically, it is generally expected that adding salt to pure water increases disorder, and thus absolute entropy, which is consistent with Millero’s result.*”

I have already explained at length in my reply to your “Point-6” that we are talking of different things when Millero’s (wrong) seawater entropy formulation increases with the salinity, whereas all other formulations (including the one for TEOS10) decrease with the salinity.

This (wrong) behaviour of the Millero’s formulation cannot be justified.

It seems that you are still considering in your present remark the impact of a brutal input of a crystal of NaCl into an existing seawater mixture, with indeed the processes of dissolution of oceanic salts increasing the disorder, and with an increase in entropy of the reaction  $\text{NaCl}_{cr} \rightarrow (\text{Na}^+)_{aq} + (\text{Cl}^-)_{aq}$  from 72.14 J/K/mol for a crystal of NaCl to the sum  $59.00 + 56.36 = 115.36$  J/K/mol for  $(\text{Na}^+)_{aq} + (\text{Cl}^-)_{aq}$ , with a difference +43.22 J/K/mol representing the impact on the entropy of the dissolution of the NaCl crystal into the separate ions  $(\text{Na}^+)_{aq}$  and  $(\text{Cl}^-)_{aq}$ .

The impact of salinity on the TEOS10 formulations, both standard and absolute, are of completely different nature, because the physical meaning of the absolute (third-law) negative coefficient  $-a_4 = (\eta_{s0} - \eta_{w0}) \approx 1633 - 3513 \approx -1880 \pm 17$  J/K/kg in the linear seawater entropy term  $-a_2 - a_4 S_A$  does not measure this “entropy of the dissolution” but rather the impact of an input of another type of seawater with a different salinity but with already dissolved salts. As a result, since the sea-salts value  $\eta_{s0} \approx 1633$  J/K/kg is smaller than the pure-water value  $\eta_{w0} \approx 3513$  J/K/kg, the input of a portion of saltier seawater and  $dS_A/dt > 0$  corresponds to a decrease in the specific seawater entropy, this logically explaining the negative coefficient  $-1880 \pm 17$  J/K/kg

Note, moreover, that this additional absolute (third-law) coefficient acts as a reinforcement of an effect already present in the standard formulation of TEOS10 (where  $a_4$  is almost cancelled out) which, through non-linear terms, already acts globally in the direction of a decrease in the entropy of seawater when salinity increases (as shown, again, in the black and red curved in the right part of the Figs. 9).

- As a conclusion of this Point-8, I think that I do not need to add nor modify sentences or Figures in my two-parts paper.

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9. Lines 291: “the present paper offers the possibility of correcting and generalising the current standard formulations of TEOS10 to calculate the seawater absolute entropy corresponding to the recommendations of the third law of thermodynamics”

*The TEOS-10 Gibbs function does not violate the third law of thermodynamics and does not require correction. The third law states that the absolute entropy of a pure crystal vanishes at absolute zero, but does not prescribe specific recommendations for seawater.*

- In the first part of your sentence, you correctly recalled the third law, which indeed must be applied to the most stable form of a pure crystal at 0 K.

This means, in particular, that it cannot (and must not) be applied to a mixture such as the moist air (a mixture of dry air and water) or the seawater (a mixture of water and sea salts): this contradicts the second part of your proposal.

Indeed, the second part of your sentence is partly correct, and partly incorrect: it is true that the third law does not apply to a crystal of seawater at 0 K, but differently it is not only possible, but also needed (otherwise: why Nernst, Sackur, Tetrad, Planck and others have invented and validated the third-law of thermodynamics, as previously recalled?) to compute the third-law seawater entropy from the absolute value of the entropy of the seawater components (i.e. for the pure liquid water and sea salts) at ambient temperature (such as 0°C or 25°C).

In fact, I have already had to respond to this type of criticism in the past years when I continued the work of Hauf and Höller (1987) to calculate the absolute moist-air entropy (see Marquet, 2011, and the numerous papers that followed until 2022). In this context, I would like to point out that not only



absolute entropy, and  $q_v$  and  $s_{v0}$  are the water-vapour content and absolute entropy, respectively. Here is how “*the third law* (indeed) *prescribe specific recommendations*” for computing the moist-air absolute entropy.

Similarly, I recall in the present paper that the seawater is made of a mixture of liquid water and solved anions and cations, and that the reference entropy of the seawater is therefore a weighted sum of the reference entropies of all the components (leading in particular to the linear terms  $-a_2 - a_4 S_A$ ), with all reference entropies of these components available in the general thermodynamic Tables (like Lewis and Randall, 1961, at the bases of TEOS10). There is therefore no inconsistency (nor freedom) in the absolute (third-law) definition of the entropy of seawater.

In this sense, I maintain that the value currently provided by TEOS10 is contrary to the third law of thermodynamics. This is not a gratuitous assertion, because this is a mere scientific fact, and I believe I have recalled in the preceding lines (and sections) the physical motivations, validations and detailed explanations. People can decide to disregard the third law of thermodynamics, but then they must clearly accept this position and its consequences.

- However, even though it costs me a lot, but in order to avoid being too critical of TEOS10’s use of arbitrary definitions of reference entropies: I have chosen to refer throughout the revised version of the two-part paper to “conventional” values for TEOS10, without further stating that they disagree with the third law.

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*10. Lines 298-301: “I show in the second part of the paper several examples from observations and analysed datasets, where new isentropic features are revealed only with the absolute entropy of seawater, with therefore a hitherto hidden physical meaning that the standard TEOS10 version of seawater entropy is not able to perceive.”*

*Given the concerns raised above about the validity of the proposed definition of absolute entropy, it is difficult to assess the physical significance of these new features.*

- I recall in the present two-parts paper that: (...) Millero (2010, p.19) explained that “ (...) *new TEOS-10 (...) will be very useful to modelers examining the entropy and enthalpy of seawater*” (...)

If the values of the reference entropies of liquid water and sea salts are truly arbitrary, then Millero’s sentence must apply whatever these values are, and therefore both for the “conventional” entropy (calculated by IAPWS or TEOS10) and for the seawater entropy using the “absolute” reference values that I defined in the present two-parts paper.

I could have been much more dogmatic and refused to calculate and study the current version of TEOS10. Differently, I believe I took a scientific approach when I wanted to conduct a mere “*impact study*” of the change in the seawater entropy constants in the TEOS10 software.

- However, in order not to offend anyone, I have clearly mention in the first part of the paper that: “*The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater itself, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.*”

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*11. Lines 318: “It should be noted that the absolute definition of the seawater entropy, as described by Franck Millero and in the current paper, is currently rejected by the ocean community. [...] It is within this last framework that the present paper is situated.”*

*This misrepresents the situation. The prevailing view in the oceanographic community is that the choice of the linear function of salinity  $a_2 + a_4 S$  entering the definition of entropy has no practical*

*impact on any known oceanographic applications, and how one chooses to fix  $a_2$  and  $a_4$  is a matter of convention. Both the Millero and TEOS10 approaches are considered valid; there is no widespread rejection of either. The paper could better reflect this consensus and avoid framing the issue as a conflict.*

- I hope the new wording of the sentence in the Introduction will be more acceptable to the referee: “*The fact that the values of the reference entropies have no impact in most oceanographic applications, unless one wants to calculate and study the entropy of seawater itself, is a key reason for the dominant approach where these reference entropies are defined arbitrarily as in TEOS10.*”

- I have also added the following sentence in the Conclusion: “*Since Fofonoff (1962, p.8), the prevailing view in the oceanographic community is that the choice of the linear salinity function  $-a_2 - a_4 S$  entering into the TEOS10 definition of the seawater entropy has no practical impact on known oceanographic applications, and that the choice of fixing  $-a_2$  and  $-a_4$  is a matter of convention. However, some people think that the Millero and TEOS10 approaches may be considered valid, and that neither should be subject to general rejection. It is within this last absolute-entropy framework that the present and Millero’s papers are situated.*”

I was indeed able to verify, by rereading so many old articles and books, that this idea that the seawater entropy could be “*defined up to an linear function of salinity*” seems to have first appeared in the Chapter 1 (p.3-30) written by Fofonoff (1962) in the book “*THE SEA*” about “*Ideas and observations on progress in the study of the Seas.*”

This fact is explicitly mentioned in the TEOS10 manual McDougall et al. (2010) close to Eq. 2.6.2 and about the idea that: “*The Gibbs function contains four arbitrary constants that cannot be determined by any set of thermodynamic measurements. These arbitrary constants mean that the Gibbs function ( $g$ ) is unknown and unknowable up to the arbitrary function of temperature and Absolute salinity*”

$$[a_1 + a_2 (T_0 + t)] + [a_3 + a_4 (T_0 + t)] S_A$$

noted  $(d + aT) + (c + bT)S$  by Fofonoff (1962, p.8). This lowest-order part of the Gibbs function implies that the specific entropy  $\eta = -\partial g / \partial T$  depends on the lowest-order “*arbitrary function*”  $-a_2 - a_4 S_A$ .

As a matter of fact the aspect “*unknowable*” of  $a_2$  and  $a_4$  is in contradiction with the third-law of thermodynamics, which (“*without framing the issue as a conflict*”) allows the determination of the absolute entropies for pure water and sea salts since Lewis and Randall (1961) at least, as recalled in Millero and the present paper where the constant term  $-a_4 = (\eta_{s0} - \eta_{w0}) \approx 1633 - 3513 \approx -1880 \pm 17$  J/K/kg can indeed precisely be known (and thus is not “*unknowable*” by definition).

- I am fully aware that almost the entire oceanic community that I have been in contact with is completely opposed to the idea of adding, even as an option, the calculation of the absolute version of seawater entropy. I know, in particular that both the Millero and TEOS10 approaches are not considered valid, and that there is a clear widespread rejection of the Millero’s approach and my approach as well (for me since about 2014, when I first contacted Rainer Feistel).

- It is likely that the paper by Fofonoff (1962) has strongly and lastingly influenced all subsequent studies, with the present habit to consider the same referee’s assumption that “*the choice of fixing  $-a_2$  and  $-a_4$  is a matter of convention*” for defining the seawater entropy.

However, Fofonoff (1962) also added in a footnote (still p.8) that: “*An alternative interpretation of the arbitrary linear function of salinity in the definition of  $\eta$  is obtained by introducing a combined partial entropy of the salts,  $\eta_s = -\partial \mu_s / \partial T$ . Then, the specific entropy,  $\eta$ , is given by  $s \eta_s + (1 - s) \eta_w$* ” (with a typo corrected). This is precisely the method used by Millero and myself to define the seawater entropy. However, Fofonoff (1962) immediately added in this footnote, without proof, that: “*The partial entropies,  $\eta_s$ ,  $\eta_w$ , contain arbitrary constants giving rise to an arbitrary linear function of salinity in  $\eta$* ” (the seawater entropy).

It should be noted that Fofonoff (1962, p.4) also explained that he wrote the Gibbs equation in agreement with the equations previously written in several steps by Guggenheim (1950), as Eq. 1.33.1 (p.21) for a single-component system, and then as Eq. 11.03.3 (p.356) for a multi-component system, with  $U = \sum_i n_i U_i$  (for the internal energy) and  $S = \sum_i n_i S_i$  (for the entropy).

• However, Fofonoff (1962) did not recalled that Guggenheim (1950) do believed in the third law of thermodynamics and wrote the sections:

- 1.63 about the “Third Principle” (p.46-47);
- 2.17 about the “Third Principle of Thermodynamics” (p.65-67);
- 4.60 about the “Zero-entropies of Crystals” (p.150-151);
- 4.66 about the “Third Principle of Thermodynamics and Nernst’s Heat Theorem” (p.158-160);
- 4.68 about the “Unattainability of Absolute Zero” (p.161-163).

• Moreover, I recall in the section 12.16 of the SM entitled “Validations and physical meaning of absolute entropies / General physics?” that in the last section entitled “So-called Absolute Entropies” of a previous book, Guggenheim (1933, p.198) wrote: “In our discussion we have followed Fowler (1929) in referring only to the difference in entropy or partial molar entropy between two states, never to the absolute value of either in a given state. The value that can be assigned to the latter is arbitrary. Some authors, in particular Planck, G. N. Lewis and Giaugue, adopt the convention that the entropy of each element in a perfect crystalline state at the absolute zero is zero, and they call the entropy referred to this zero “absolute entropy”.”

... this is precisely the program followed by Millero and myself for defining the seawater absolute entropy...

Note that Fowler (1929) wrote the whole Chapter VIII (p.144-163) about the “Nernst’s Heat Theorem and the chemical constants” with in particular the Table II (p.156) where the theoretical (third-law) Sackur-Tetrode statistical value of the chemical constants (Eq. 443, p.146)

$$i_0 = i - \frac{3}{2} \log(M) \log \left[ \frac{(2\pi)^{3/2} k^{5/2}}{h^3 N^{3/2}} \right]$$

is compared to observed values for several monatomic vapours. Fowler (1929, p.157) explained that: “*These values are extremely interesting and suggestive. They indicate, firstly, that the theoretical value ( $i_0$ ) is correct for the first group, and no doubt for the other inert gases as well. That is to say, for these vapours the chemical constant is correctly given by (443) and the assumption of equal (unit) weights for the atom in the solid and vapour phase is justified. (...) As a general summary of this discussion we may conclude that the foregoing results, so far as present accuracy goes, are in full accord with the theory, taking atomic structure into account, if the proper weights of Chapter XIV are assigned to the states of the free atoms and the weights of the atoms in the solid form near the absolute zero remain unity.*”

However, Guggenheim (1933, p.198) added that: “There is no objection to this conventional choice of zero entropy, but there is nothing “absolute” about it.”

... the third law would therefore be physically grounded, but it would just be the “*absolute*” designation that poses a problem?

Guggenheim (1933, p.198) provided the following details: “*If an element consists of several isotopes its entropy at the absolute zero will be greater than that of a crystal consisting of a pure isotope. To determine this difference it is not sufficient to know the proportions of isotopes of each atomic mass, because there is the possibility of several isotopes with equal atomic mass (isobaric isotopes). Knowledge on this point is usually not available. A second objection is that since transmutation of elements is now known to be possible the entropies of the various elements are not independent of one another. The only rational system of absolute entropies would be referred to certain standard states of nuclei and protons. It is hardly necessary to state that the use of such a system is not feasible owing to lack of data on*

*the entropy changes in transmutation. Even is feasible, it is doubtful whether it would serve any useful purpose.*”

It is true that Nernst, Planck and others never considered the nuclear processes (unknown to them!) and rather simply considered the entropy corresponding to the translational, rotational, vibrational and electronic degrees of freedom of atoms and molecules. Therefore, the possibility and the need to define the absolute definition of the entropies are distinct from all possible transmutation and changes in states of nuclei and protons.

This rather corresponds to an absolute definition of the thermodynamic thermal entropy, namely by setting the unknown thermodynamic integration entropy constants to relevant theoretical values, without any attempt to take into account the impact of nuclear physics phenomena: here is the way Millero and myself have taken into account the absolute entropy of pure liquid water, on the one hand, and of the sea salts, on the other hand.

• In line with this previous book by Guggenheim (1933, p.198), Guggenheim (1950) still considered that: “*Planck, G. N. Lewis and Giauque, adopt the convention that the entropy of each element in a perfect crystalline state at the absolute zero is zero, and they call the entropy referred to this zero “absolute entropy”. There is no objection to this conventional choice of zero entropy, but there is nothing “absolute” about it.*”

Therefore, there would be only a semantic disagreement between Guggenheim with Planck, Lewis and Giauque, and Guggenheim (1950) equally admitted the validity and universality of the Sackur-Tetrode constant he wrote (Eqs. 4.56.3 and 4.58.1, p.147-148, with  $p^\dagger = 1$  and  $m = N m$ ) as

$$i_0 = \frac{p^\dagger}{(\Theta^\dagger)^{5/2} M^{3/2}} = \ln \left[ \frac{(2\pi)^{3/2} k^{5/2}}{N^{3/2} h^3} \right] \approx 18.22285,$$

which Guggenheim only refuses to qualify as “absolute” insofar as, for him, an “absolute” entropy should include all the effects linked in particular to the transmutation of elements and to nuclear reactions of formation of atoms from neutrons, protons and electrons...

Guggenheim (1950) never explained that the reference entropy may be set to any arbitrary values when he wrote the equation for the entropy for “*Systems of several non-reacting components*” of variable composition (Chapter VI, p.230-257), and in particular in the section 6.20 about “*Ideal Solutions*.”

Fofonoff (1962) should have recalled that Guggenheim (1950, p.147) clearly explained that: “*These formulae correspond to the following conventional definition of zero entropy. The entropy of a monatomic substance is conventionally defined to be zero in a state such that:*

- (a) *the contributions to the entropy from the translational and electronic degrees of freedom are zero;*
- (b) *the contributions due to any intranuclear degrees including spin are ignored, this being allowable only because the contributions are, under terrestrial conditions, independent of temperature and the state of the substance.*

*This “conventional choice of zero entropy” has proved convenient and is widely used. Unfortunately some authors use the expression “absolute” to denote the value of the entropy according  $S_m^\circ(T = 0) = R \ln(o) = 0$  with  $o = 1$  (see p.145-147), or some closely related “convention”. Such terminology is misleading and (...) should be avoided. (...) To recapitulate, the convention  $S_m^\circ = 0$  is, at least for terrestrial conditions, the most “convenient”, but it is in no sense “absolute”. We shall accordingly refer to the entropy values conforming to the convention as the “conventional” entropy values.*”

We can recognise with these words of Guggenheim (1950) several of the criticism retained in IAPWS and TEOS10 documents against the use in oceanic studies of the (third-law) absolute values of entropies published in all Thermodynamic Tables, in the name of this pseudo-problem of the impact of the effects of nuclear transmutation... In fact, whatever name we give it, in the approaches of Millero and mine

it is a matter of taking into account, in order to define the seawater entropy, the values published in these Tables, whether we call them “*absolute*” or “*conventional*” matters little, as long as they take into account all the degrees of freedom of atoms and molecules (translational, rotational, vibrational and electrical), and of course without any desire to be interested in nuclear effects.

Accordingly, Guggenheim (1950, Eq. 6.10.2, p.234) wrote the entropy of a “*Perfect Gaseous Mixture*” as

$$S = - \sum_i n_i \left[ \frac{d\mu_i^\dagger}{dT} + R \ln \left( \frac{n_i p_i}{p^\dagger} \right) \right],$$

where  $p^\dagger$  denotes a standard pressure and  $\mu_i^\dagger$  is the value of  $\mu_i$  of the pure gas  $i$  at the pressure  $p^\dagger$ . Similarly, Guggenheim (1950, Eq. 6.20.7, p.238) expressed the entropy for an “*Ideal Solution*” as

$$S_m = - \sum_i x_i S_i^\circ - R \sum_i x_i \ln(x_i),$$

where  $S_i^\circ = -d\mu_i^\circ/dT$  refers to the pure liquid entropy.

Guggenheim (1950, Eq. 4.58.4, p.148) had no doubt when he derived and trusted the “conventional (absolute)” entropy of a perfect gas, with exactly the same Sackur-Tetrode value

$$S = R \left[ \frac{5}{2} + \frac{5}{2} \ln(T) - \ln(p) + \frac{3}{2} \ln(M) + i_0 \right].$$

Guggenheim (1950, §4.59, p.149-150) also explained that the “*Entropy Constants of Diatomic and Polyatomic Substances*” can be computed starting from the translational value  $i_0$  and by adding the impact on the entropy of the rotational, vibrational and electronic degrees of freedom. In particular, Guggenheim (1950, §4-61/4.65, p.151-158) showed examples of entropy formulas for CO, N<sub>2</sub>O, H<sub>2</sub>O, H<sub>2</sub>, Cl<sub>2</sub>... (including p.152 the possible residual entropies at 0 K and the factor 3/2 of Pauling for H<sub>2</sub>O)

All these facts have not been recalled in Fofonoff, IAPWS and TEOS10 papers, documents and manuels.

- These facts means that Guggenheim (1950) agreed that the entropies for the pure liquid water can be computed in a “conventional (absolute)” way from the value of the perfect gas depending on  $i_0$ , simply by removing the impact of the change of phases (vaporization) and of pressure (from standard to saturation values).

This means that Fofonoff (1962) could have recalled this fact and avoided an arbitrary definition for the liquid-water reference entropy, at least.

Similarly, Fofonoff (1962) could also have recalled that the “conventional (absolute)” entropies of seawater anions and cations were available since the works of Born (1920), Latimer (1921, 1926), Latimer and Buffington (1926), Latimer and Kasper (1929), Latimer et al. (1934), Latimer (1936), Latimer et al. (1938, 1939), Latimer (1951), Powell and Latimer (1951), Latimer (1952) and Rossini et al. (1952, NBS-500).

- This means that the linear function of salinity  $-a_2 - a_4 S$  entering the seawater entropy formulation mentioned by the referee, with  $-a_4$  depending on the difference in the reference entropies of pure liquid water and sea salts, can be determined by the “conventional (absolute)” reference entropies for pure liquid water and sea salts since at least the NBS-500 Tables of Rossini et al. (1952), and thus before Fofonoff (1962) and TEOS10, as already recalled in the Millero’s 1976-1983 papers based on the relationships and Tables published in the book of Lewis and Randall (1961).

I have recalled above the content of relevant old papers and books that may justify the possibility to use the “conventional (absolute)” reference entropies for pure liquid water and sea salts, and that the arbitrary choice to discard this possibility in the domain of oceanography can be likely traced back to



Fofonoff (1962), and thus far before the IAPWS, and TEOS10 documents and software. However I have shown that Fofonoff (1962) did not properly justified the reason why we might discarded the possibility to use the “conventional (absolute)” values of the reference entropies to set the linear function  $-a_2 - a_4 S$ , and he even did not mentioned this possibility.

- [Note that I have also included additional sentences about the two recommendations adopted at the \(1956\) 5th International Conference on the Properties of Steam](#) (see the section 12.5 of the SM entitled “*Validations and physical meaning of absolute entropies / 1956 ICPS conf. ?*”), [with the need to understand that even in this 1956 meeting was expressed in a second resolution the need to provide the absolute version of the entropy of water in all next studies](#), in addition to the first resolution (the sole part mentioned in IAPWS and TEOS10 documents) where the standard value of the entropy of steam has been arbitrarily set to 0 at 0.01°C, but this only for a pure steam of water, and not at all for a mixture like the seawater:

*“Accordingly, other contributions than TEOS10 have admitted the possibility of at least considering as an option the absolute entropies for liquid water and dry air (Millero and Leung, 1976; Millero, 1983; Feistel and Hagen, 1995; Lemmon et al., 2000; Feistel and Wagner, 2006). However, it is often still considered that the TEOS10’s choice is consistent with the first conclusion of the 5th International Conference on the Properties of Steam in London (5th-ICPS et al., 1956), which recommended (p.1/30-1/32 and 3/34) that the specific internal energy and the specific entropy of the liquid water should been set equal to zero at the triple point temperature of 0.01°C, instead of 0.00°C, without affecting any measurable thermodynamic properties of the climate system. However, I show in the section 12.5 and Fig. 32 of the SM that this first 1956 recommendation (p.3/34) was only valid for the case of a pure liquid-water steam system, and not for a mixture involving other species like in the moist-air atmosphere and the seawater. Moreover, it was decided at the same time (5th-ICPS et al., 1956, p.3/35-3/37) that the absolute values for the entropy of liquid water (computed from hypotheses made at 0 K) should also be mentioned in all subsequent studies. This is precisely what I have achieved in the present study by defining both  $\eta_{\text{abs}}$  and  $\theta_\eta$  for seawater, including the impacts of absolute and non-arbitrary definitions for both pure liquid-water and sea-salt reference entropies.”*

... and next ...

*“For my part, I have complete confidence in these thermodynamic tables, rather than continuing to apply only the first pure-liquid water arbitrary recommendations expressed (p.3/34) in 1956, and not the following one (p.3/35-37) about the need to compute the absolute version of the entropy, and in particular for the more general case of a mixture of variable composition like the seawater as shown in this study.”*

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