

Comment to Rainer Feistel's egosphere-2024-1243 paper about:
TEOS-10 and the Climatic Relevance of Ocean-Atmosphere Interaction

On the subject of: “absolute moist-air and seawater entropies”

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1 Reply-1 / General new Comments

“*CC1: 'Comment on egosphere-2024-1243', Pascal Marquet, 16 Jun 2024*”

“*AC3: 'Reply on CC1', Rainer Feistel, 17 Jun 2024*”

I disagree with almost all Rainer Feistel's answers to my Comments, and the next sections of the PDF are point-by-point Replies to the Reply of Rainer Feistel.

My aim will not to continue a too long exchange with Rainer Feistel, who will likely refuse to offer any other definition of his (equivalent) proxy values for the moist-air and seawater entropies. Nonetheless, my aim is to clearly show to the Editor (and to young and future generations reading the preprint and my Comment and Reply to Rainer Feistel) that the reference values have real impact on many kinds.

Moreover, since Rainer Feistel admits that vertical profiles, vertical sections and entropy diagrams are influenced by these arbitrary choices of reference entropies, he should at least offer as a possibility the calculations of the absolute moist-air and seawater entropies.

I want to recall that it is easy to add simple extra terms for computing draft versions of both the atmospheric and seawater absolute entropies ($\eta_s = \eta_e + \Delta_s \eta$) and the liquid-water proxy value ($\eta_l = \eta_e + \Delta_l \eta$) from the standard (TEOS10, equivalent) proxy formulations (η_e). However, it would be worthwhile redoing the TEOS10 settings/tunings without making arbitrary assumptions while imposing the absolute values of the reference entropies, going beyond the additional terms that I indicate and which are likely of the first order (especially for the ocean).

I recall in the Section 2 that the saturation-pressure relationship (1) derived by Nernst (1918), Planck (1921), Nernst (1921) and Nernst (1926) depends on the absolute value of the entropy for monatomic gases (used to set the translational part of the statistical entropy for all other polyatomic bodies). The same absolute entropies of bodies are also used to determine the equilibrium constants of all chemical reactions, which in turn determine the (measurable) concentrations of O₃ in the atmosphere and sea salts in the seawater, and therefore impact the vertical profile of the (measurable) temperature in the stratosphere, in particular.

I explain in the Section 3 that the constants arbitrarily specified by the 5th (1956) International Conference on Properties of Steam are unclear, presently unavailable, not reproduced elsewhere, and looks like a mere old-fashioned and arbitrary gentlemen agreement.

I explains in the Section 4 that the relativistic reference values have no impact on the computations of absolute values for the thermal energies and entropies (merely describing the variation of translational,

rotational and vibrational degrees of freedom for atoms and molecules), simply because present atmospheric and oceanic NWP models and GCMs are not designed to describe the thermodynamic impacts and physical processes of nuclear bombs or nuclear reactors in nuclear plants.

I explain in the Section 5 that there is no large uncertainty in the properties of H₂O Ice-Ih, with in particular the residual entropy at 0 K needed to make the Calorimetric and the Statistical methods coincide. I show in the Fig. 1 the values of the specific heat at constant pressure (c_p) plotted as a function of the absolute temperature from 0 K to $T = 273.15$ K, with the numerical values listed in the Table 2. It is with these numerical values that I have plotted the calorimetric curve in the Fig. 2, which show that the Statistical method and the Calorimetric method (including the residual entropy for Ice-Ih H₂O) lead to the same results for N₂, O₂, Ar, CO₂ and H₂O. If the uncertainty in the properties of Ice-Ih below 100 K was as important as suggested by Rainer Feistel, it would have been impossible to get the good agreement between the Statistical and Calorimetric methods (including the residual entropy at 0 K).

I explain in the Section 6 that the absolute reference values impacting the graphical representations may have physical meanings. I would like to stress, again, that the SCICEX'96 (cast 43) vertical profile (again shown in the Figs. 3) proves that the increasing entropy, decreasing entropy and isentropic features do depend on the absolute versions (or not) of the reference entropies. Since the (seawater) entropy is a state function, it cannot increase, decrease or be a constant depending on this or that arbitrary choices.

Moreover I show in the Section 6 unpublished zonal sections (Figs. 4), unpublished entropy changes at the Mauna Loa laboratory (Figs. 5), and unpublished Climate Change of entropies from NWP models, GCMs, Reanalyses and GIEC simulations (Figs. 6). All these unpublished results clearly show that the behaviour of the absolute version of the moist-air entropy is special and cannot be confused with other 'equivalent' versions of the 'entropies', which often produce results with opposite physical behaviour (vertical gradients and changes with time of different magnitudes, or even opposite signs).

I similarly show in the Section 7 that not only the surface of constant entropy (as shown in another example of zonal section in the Fig. 9), but also the isentropic trajectories, depend on the choice of the reference values. This was in particular the aim of the study of H₂O plumes (pathways) studied by Adriana Bailey (NCAR). I have shown with Adriana (see the Fig. 7 and Fig. 8) that these H₂O plumes preferentially follow the surface of absolute moist-air entropy, with clear difference with the other arbitrary-reference definitions like the equivalent-proxy one computed by the TEOS10 software (these differences are large in the moist and warmer boundary layers and within the Tropics).

I recall in the Section 8 that the reference values of the energy must have an impact on the computations of the value and flux of the moist-air energy, as already explained by Gibbs (1875-1878), as shown and recalled in the Fig. 10.

I explain in the Section 8.1 that the entropy flux of -1 W/m²/K mentioned in the preprint and suggested first by Ebeling-Feistel (1982) and then retained as such in Feistel-Ebeling (2011), as shown in the Figs. 11, is underestimated: it is more likely of about -1.18 to -1.28 W/m²/K. Rainer Feistel should update this value.

I show in the Section 8.2 how the reference values of the moist-air entropy (20) must impact most of the terms in the moist-air (absolute) entropy equation (19), including the turbulent fluxes of the moist-air (absolute) entropy, but with the notable exception of the current version of the moist-air (absolute) entropy production term.

I recall in the Section 8.3 that the turbulence are presently based in all NWP models and GCMs on flux-gradients relationships of the Betts (1973) variables, which must be generalized to the use of the moist-air absolute entropy itself, or even the associated moist-air absolute entropy potential temperature (according to Richardson, 1919, 1922). As a matter of fact, these turbulent terms are not managed by Rainer Feistel, nor the (absolute) entropy flux, nor the temporal change in (absolute) entropy. This may

be of a certain importance for several results shown in the preprint, and with a link with a questions asked by Trevor McDougall (RC1) about the Fig. A.16.1 of the TEOS-10 Manual and the “non-conservative production of entropy.” Rainer Feistel should more clearly explain which kind of moist-air (absolute) entropy equation he consider, and which terms are evaluated versus those discarded? In particular, I show in the Figs. 12 that it is needed to use the absolute moist-air variable (or the associated potential temperature) to arrive at the properties mentioned in the preprint by Rainer Feistel and the need to have turbulent ‘fluxes proportional to its driving force’ (in that fully justifying the suggestions of Richardson, 1919a,b, 1922, to use the absolute value of the moist-air entropy).

In the Section 9 I include some remaining developments to better explain why Rainer Feistel is wrong when he wrote that: ‘Measurable thermodynamic properties in geophysics must be independent of the choice of those conditions, otherwise those quantities are physically improperly specified.’ In particular I recalled that the need to define absolute reference entropies is related to the definition of the absolute scale of temperature (Fig. 13) and to the principle of unattainability of the absolute zero of the temperature (Fig. 14).

All Figures are placed in the last Section 10, located before the references.

2 Reply-2 / Measurable properties

“When an empirical thermodynamic potential for a certain substance is constructed from data sets of lab measurements, two of its adjustable coefficients always remain undetermined. These two coefficients represent the absolute energy and absolute entropy of that substance. In any thermodynamic lab experiments, only differences of energies or entropies can be measured, for example in the form of work applied or heat flux communicated to the sample under investigation.”

“In turn, consequently, whatever the values of those constants may be, they may not affect any measurable geophysical thermodynamic properties.”

The statements of Rainer Feistel disagree with the studies by Planck and Nernst about the “constant of integration” depending on the absolute entropies and measured via the saturation pressure, which is a measurable quantity.

Indeed, an important physical consequence of the third-law of thermodynamics was recalled by Planck (1921, p.221): “*The knowledge of the absolute entropy of a body permits the complete specification of the conditions of its thermal and chemical equilibrium in contact with other substances, whereas general thermodynamics must always leave an additive constant undetermined in the equilibrium formula.*”

By the way, this sentence is an answer of the need previously expressed by Le Chatelier (1888, p.182-184): “*Equilibrium equations (...) are integrable, but then they contain an arbitrary constant of integration that can be determined if the corresponding magnitudes of the various factors in a given state of equilibrium are known. It is quite likely that the constant of integration must, like the coefficients of the differential equation, be determined function of certain physical properties of the bodies involved. The determination of the nature of this function would lead to a complete knowledge of the laws of equilibrium. It would make it possible to determine a priori, independently of any new experimental data, the complete conditions of equilibrium corresponding to a given chemical reaction.*” (...) “*The exact nature of this constant has not yet been determined. It can only be shown, with the aid of the general law of equivalence which I have stated above, that there are certain precise relationships between the constants relating to the phenomena of simple dissociation and those relating to the more complex reactions of double substitution*

decomposition. These relationships would allow the latter of these constants to be calculated immediately if the former were known.”

Accordingly, Planck (1921, p.221-222) computed “As an example, (...) an application to the equilibrium of a monatomic vapor in contact with its condensate” (...) at very low temperature, with as a result “the pressure of the saturated vapor as a function of the temperature T ” given by the relationship (Eq. 476, p.222) valid in the vicinity of 0 K:

$$\ln(p_{sat}) = -\frac{\lambda_0}{kT} + \frac{5}{2} \ln(T) + \overbrace{\ln \left[\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right]}^{(i)}. \quad (1)$$

Here, λ_0 is the “heat of vaporization of an atom at the zero point of the temperature.”

This relationship (1) is similar to the formula derived in the Chapter X.2 of the German paper by Nernst (1918, Eq. 69, p.102), in the English translation by Nernst (1926, Eq. 69, p.124), and the one published in the Nobel lecture of Nernst (1921, p.361), but with the issue (negative sign before the λ_0 term) fixed according to Marquet (August 2023).

The term “(i)” in (1) is exactly the same as the “integration constant” independently computed by Sackur (1911), Tetrode (1912a,b), Sackur (1913a,b), Planck (1915, 1916, see the English translations I have uploaded in arXiv and Zenodo) and Sackur (1917). This special absolute-entropy value

$$i = S^0 = \ln \left[\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right] \quad (2)$$

was also recalled in Eq. 103 in the chapter XIII-1 of Nernst (1918, p.136) and Nernst (1926, p.166-167).

Therefore, as a consequence of (1) and (2), the absolute-entropy value for monatomic gases can be computed from the measurements of the heat of vaporization λ_0 , the absolute temperature T and the saturation pressure p_{sat} , according to:

$$S^0 = i = \ln(p_{sat}) + \frac{\lambda_0}{kT} - \frac{5}{2} \ln(T) = \ln \left[\frac{(2\pi m)^{3/2} k^{5/2}}{h^3} \right], \quad (3)$$

with the last theoretical value depending on (m, k, h) validated by all experiments recalled by Planck and Nernst.

Following, again, the need previously expressed by Le Chatelier (1888, p.182-184), but more recently than the results obtained by Nernst and Planck, in the last version of the series of JPL-NASA reports like DeMore et al. (1997) and Sander et al. (2003), in the section “Equilibrium Constants” in Burkholder et al. (2020, p.3-1/3-4) it is recalled that the Table 3-1 (p.3-3/3-4) (...) “lists the equilibrium constants

$$K_{eq}(T) / (\text{in } \text{cm}^3 \text{ molecule}^{-1}) = A \exp \left(\frac{B}{T} \right) \quad (\text{for } 200 < T < 300 \text{ K}) \quad (4)$$

for several (...) three-body reactions (... which ...) form products that are thermally unstable at atmospheric temperatures. In such cases the thermal decomposition reaction may compete with other loss processes, such as photo-dissociation or radical attack.”

For three-body reactions like $\text{H}_2\text{O} + \text{H}_2\text{O} \rightarrow (\text{H}_2\text{O})_2$ and $\text{Cl} + \text{O}_2 \rightarrow \text{ClOO}$ listed in this Table 3-1: “When values of the heats of formation and entropies of all species are known at the temperature T , we note that the equilibrium constant is given by the van’t Hoff equation:

$$\ln [K_{eq}(T) / (\text{in } \text{bar}^{-1})] = -\frac{\Delta G_T^0}{R_* T} = \frac{\Delta S_T^0}{R_*} - \frac{\Delta H_T^0}{R_* T}, \quad (5)$$

$$\ln [K_{eq}(T) / (\text{in } \text{cm}^{-3} \text{ molecule}^{-1})] = \frac{\Delta S_T^0}{R_*} - \frac{\Delta H_T^0}{R_* T} - \ln(T) + 50.36, \quad (6)$$

where the superscript “o” refers to a standard state of one bar. When the entropy is known (or can be calculated from molecular properties) as a function of temperature, experimental values of $K_{eq}(T)$ can be used to extract a value for ΔH_T^0 and $K_{eq}(T)$ can be calculated over a wide temperature range (Third law method).”

Therefore, for the aforementioned chemical reaction $\text{Cl} + \text{O}_2 \longrightarrow \text{ClOO}$ the value of ΔS_{298K}^0 can be computed from the (third law) absolute entropies listed in the Table 7-2 of Burkholder et al. (2020, p.7-3 to 7-22) given at 298 K and 1000 hPa: 165.190 J K⁻¹ mol⁻¹ for Cl, 205.152 J K⁻¹ mol⁻¹ for O₂ and 270.3 J K⁻¹ mol⁻¹ for ClOO, leading to $\Delta S_{298K}^0 = 270.3 - (165.190 + 205.152) = -100.042$ J K⁻¹ mol⁻¹.

Note that if any constant values, say S_1 , were added to the three entropies for Cl, O₂ and ClOO, ΔS_{298K}^0 would transform into $S_1 - 100.042$ J K⁻¹ mol⁻¹, with a change in equilibrium constant that cannot be arbitrary because it corresponds to the physical process associated with the preferred direct or indirect reaction $\text{Cl} + \text{O}_2 \longleftrightarrow \text{ClOO}$, depending on the temperature T .

I remember calculating the same equilibrium constants recalled in the general relationships (5) and (6), and also their variations with temperature as a function of the enthalpies of reaction on the one hand, and the absolute values of the entropies on the other, during my first thermochemistry studies when I was 20 in 1980, and after that during my postgraduate studies on the thermochemistry of ozone for the atmosphere, with Gérard Megie as my professor at the Paris-6 University.

This “*Third law method*” explicitly recalled and mentioned by DeMore et al. (1997), Sander et al. (2003) and Burkholder et al. (2020) contradicts what Rainer Feistel explains by saying that “*(...) whatever the values of those constants may be, they may not affect any measurable geophysical thermodynamic properties*” because the equilibrium constant $K_{eq}(T)$ can be calculated from (5) and (6) only if the absolute values of the entropies are known (for instance from the Tables in Lewis and Randall, 1961, cited by Rainer Feistel and forming one of the bases of the electrolyte part of the seawater Gibbs function computed by Rainer feistel and the TEOS10 software).

This means that there is a clear impacts of the absolute values of entropies in the analyses and prediction of the stability of all chemical reactions. Therefore, there is an impact of the absolute reference entropies on the (measurable) concentrations of O₃ that control the vertical structure of the (measurable) temperature in the stratosphere. The same impact of the absolute reference entropies exist on the seawater chemistry, and thus on the (measurable) concentrations of sea salts in the ocean.

3 Reply-3 / 5th International Conference on Properties of Steam

“*For pure water, those constants had arbitrarily been specified by the 5th International Conference on the Properties of Steam in London in 1956, by setting the internal energy and the entropy of liquid water to zero values at the common triple point. In TEOS-10, the SCOR/IAPSO Working Group 127 on Thermodynamics of Seawater followed that IAPWS definition for water and decided on similar reference-state conditions for sea salt and dry air.*”

I agree that the decision made at the “5th International Conference on the Properties of Steam in London in 1956” seems arbitrary ... To be honest, I have not been able to check the justification for this decision, simply because the proceeding of this Conference is not available nowadays. Moreover, no argument are given in other next Conference (like in the sixth Conference in New York City by Haywood, 1965). Therefore, I see no proof for this 1956 statement, which seems to be more an “arbitrary gentlemen agreement” than based on a scientific proof (if it existed, it would have been repeated in 1965, or in subsequent proceedings, which is not the case).

4 Reply-4 / Relativistic reference values

“Physical values for absolute energies can be derived from theory, such as the relativistic rest energy $E = m c^2$ of a given substance. This is a very large number, namely exactly 89 875 517 873 681 764 J/kg for water at the zero point. To properly represent practical changes of energy by some J/kg or much less, numbers with many digits are required. Water properties below 100 K are only poorly known; these uncertainties propagate inevitably into measured values at ambient conditions, such as at the triple point, if the zero point is used as the reference state where the absolute energy is exactly known. Such unnecessary uncertainties can be avoided in practice when instead the triple point is chosen where an exact energy value is specified.”

I can confirm that I have read all Rainer Feistel’s papers in detail, and in particular the one in which he already used the same arguments based on the relativistic rest energy, like “... energy could be fixed relativistically by mass measurements with more than 13 valid digits ...” in Feistel and Hagen (1995, p.268). Previously, Feistel (1993, p.105) used other arguments: “In order not to hide things behind a veil of mystery we will briefly explain our reference state in physical terms. In physics all energy definitions are relative to a certain reference state, e.g. the binding energy of an electron in an atom is just the energy needed to carry the electron from the given position to a location infinitely far from any other particle, where the electron then is at rest. Usually these reference states are so evident that they are not even mentioned in textbooks. For electrolyte solutions however the ‘best’ or ‘simplest’ reference state is more or less a matter of ‘scientific taste’ and depends on the kind of problem treated (...)” I really know all arguments used by Rainer Feistel, but none of them agree with the absolute reference values to be used in atmospheric and seawater thermodynamics.

In fact, Rainer Feistel is confusing the types of energy we are talking about and which are the subject of this Preprint + Comment + Reply. Indeed, the atmospheric and seawater entropies to be considered as output of the TEOS10 (SIA and GSW) software are the “thermal” version of the internal energy and entropy, which can be computed from the translational and possibly rotational and vibrational degrees of freedom of the atoms and molecules, with the corresponding thermodynamic relationships requiring the existence of a thermal equilibrium and a possible definition of an equilibrium value of the temperature (i.e. the zeroth law of thermodynamics).

If nuclear reactions were to be considered, with indeed the very large impact of the defect of mass and the large values of $\Delta m \times c^2$, we would deal with a totally different subject. In other words, atmospheric and oceanic NWP models and GCMs are not designed to describe the thermodynamic impacts and physical processes of nuclear bombs or nuclear reactors in nuclear plants, simply because the atmospheric and oceanic thermodynamics do not involve nor consider nuclear reactions. There is no need to involve the relativistic energy $m_0 c^2 \left[1/\sqrt{1 - v^2/c^2} \right] \approx m_0 c^2 + m_0 v^2/2 + \dots$, except for introducing in the right way the first-order variable kinetic energy term $m_0 v^2/2$.

I don’t want to be pedantic, but in the interests of precision, to go further and to be more precise on the subject of relativistic effects raised by Rainer Feistel, it should be remembered that the molecular weights of atoms and molecules, and therefore the corresponding molar masses, take into account the (relativistic) effects of the mass defect, which makes the mass of the atoms different from the sum of the mass of the nucleons forming the atoms. Therefore, the impact of the mass at rest of the particles are already somehow taken into account in the present atmospheric and oceanic thermodynamic, via the observed (non-arbitrary, without undetermined energies at rest) values of the molar masses for N_2 , O_2 , Ar, CO_2 , H_2O (vapour, liquid and ice) and sea salts.

5 Reply-5 / Uncertain reference values; Ice-XI; residual entropies

“Water properties below 100 K are only poorly known; these uncertainties propagate inevitably into measured values at ambient conditions, such as at the triple point, if the zero point is used as the reference state where the absolute energy is exactly known. Such unnecessary uncertainties can be avoided in practice when instead the triple point is chosen where an exact energy value is specified.”

In fact, there is no large uncertainty in the properties of solid H₂O (Ice-Ih), because I have used the numerical values of $c_p(T)$ shown in the Fig. 1 and the Table 2 to demonstrate that the Statistical and the Calorimetric methods (including the residual entropy for Ice-Ih H₂O) lead to the same results for N₂, O₂, Ar, CO₂ and H₂O. Indeed, the solid and dashed curves in the Fig. 2 almost superimpose, with in particular the need to use the residual entropy at 0 K for H₂O to obtain this result.

If the uncertainty in the properties of Ice-Ih below 100 K was as important as suggested by Rainer Feistel, it would have been impossible to arrive at this good agreement between the Statistical and Calorimetric methods (including the residual entropy at 0 K).

“Physical values for absolute entropies can be derived from theory, such as the statistical theory of Boltzmann, Planck and Pauling, $S = k \log(W)$. If a substance has a single configuration $W(0) = 1$ at the zero point, its residual entropy $S(0) = 0$ is zero, in agreement with the 3rd law of Nernst. If a substance has several zero-point configurations at 0 K, $W(0) > 1$, such as ice Ih, then this substance has a non-zero residual entropy. In the case of ice, however, the question is not yet ultimately decided whether ice Ih is really an equilibrium phase at 0 K, or whether it may possibly be a metastable state, while ice XI is the proper equilibrium state with zero residual entropy. Near the zero point, the extremely sluggish relaxation of ice to equilibrium makes experimental decisions of this problem difficult.”

Whatever may happen with the next studies of the metastable states, I have checked that the calorimetric method to compute the absolute entropy for H₂O must include the residual entropy at 0 K to agree with the statistical method. Consequently, the situation cannot be as serious as that indicated by Reiner Feistel.

Moreover, this near-coincidence between calorimetric and statistical values has been established for a very long time, as shown in the Table 1, and in particular by Gokcen and Reddy (1996, GR96).

I think that Rainer Feistel's criticisms are intended solely to avoid considering the absolute values of the entropies, which are nonetheless published in all the Thermodynamic Tables. These criticisms, which relate only to special (but known) properties of H₂O Ice-Ih, seem somewhat artificial.

“As with energies, if the zero point is the reference state, also entropies at ambient conditions suffer from large uncertainties due to the poorly known ice properties below 100 K. The triple point chosen as the reference state avoids this unnecessary complication. In the definition of the equation of state of ice Ih by Feistel and Wagner (2006: Tables 8 and 9 therein) and by IAPWS (2006), both the "absolute" and the "IAPWS-95" definitions of the reference state are offered and the resulting uncertainties are compared.”

I have indeed recalled previously in my Comment that Rainer Feistel published numerical values of the absolute entropy for H₂O, in particular in 2006. Therefore, why does Rainer Feistel continue to refuse to offer everyone the possibility of calculating (at least as an option) the absolute entropies for moist air and the seawater? Rainer Feistel may have used the values shown in the Table 1 for the other atmospheric gases, but in fact the dry-air value given by Lemmon et al. (2000) and the sea-salts value determined by Millero and Leung (1976) and Millero (1983).

However, it would be worthwhile redoing the TEOS10 settings/tunings without making arbitrary assumptions while imposing the absolute values of the reference entropies, going beyond the additional terms that I indicate and which are likely of the first order (especially for the ocean).

Table 1: Standard molar entropies in cal/K/mol (with 4.184 J/cal) at 1013.25 hPa (or 1000 hPa) and 298.15 K for the gases: Nitrogen (N_2), Oxygen (O_2), Argon (Ar), Carbon dioxide (CO_2) and Water vapour (H_2O). The suffix “/C” is for the calorimetric methods, whereas the suffix “/S” is for the statistical-physics methods. The column “ $\Delta(GR96)$ ” is the difference between the calorimetric method GR96/C compared to the (more accurate) statistical-physics formulation C98/S: namely $\Delta(GR96) = GR96/C - C98/S$.

	ST12/S	LG17/C	LR23/C	K32/C	GB32-34/S	GS36/C	R52	LR61
N_2		45.59	45.6	45.8 \pm 0.3			45.767	45.77
O_2		48.23	48	49.1			49.003	49.01
Ar	37.0	36.43	36.70	36.8 \pm 0.2			36.983	36.99
CO_2				50.0 \pm 2	51.14		51.061	51.08
H_2O				45.08 \pm 0.1 ⁽¹⁾	45.101	45.09 \pm 0.05 ⁽²⁾	45.106	45.10 ⁽³⁾

	W65	R78	GR96/C	GR96/S	$\Delta(GR96)$	C98/S	APxx	S1920
N_2	45.77	45.796 \pm 0.005	45.94 \pm 0.2	45.78	+0.144 (0.31%)	45.796 \pm 0.005	45.796	45.796
O_2	48.996	49.032 \pm 0.009	49.12 \pm 0.1	49.02	+0.089 (0.18%)	49.031 \pm 0.008	49.029	49.032
Ar	36.9822	37.008 \pm 0.005	36.96 \pm 0.2	37.00	-0.040 (0.11%)	37.000 \pm 0.001	37.008	--
CO_2	51.06	51.097 \pm 0.009	51.13 \pm 0.1	51.09	+0.032 (0.06%)	51.098 \pm 0.029	51.085	51.096
H_2O	45.104	45.105 \pm 0.009	45.11 ⁽⁴⁾	45.12	-0.022 (0.05%)	45.132 \pm 0.010	45.131	45.129

Datasets are from: ST12 (Sackur, 1911; Tetrode, 1912a,b; Sackur, 1913a,b; Tetrode, 1915; Sackur, 1917); LG17 (Lewis and Gibson, 1917); LR23 (Lewis and Randall, 1923) (from Lewis et al., 1922); K32 (Kelley, 1932); GB32-34 (Gordon and Barnes, 1932) and (Gordon, 1934); GS36 (Giauque and Stout, 1936), R52 (Rossini et al., 1952), LR61 (Lewis and Randall, 1961), W65 (Wagman et al., 1965), R78 (Robie et al., 1978), GR96 (Gokcen and Reddy, 1996, for both Statistical and Calorimetric values and the differences $\Delta(GR96)$), C98 (Chase, 1998, Statistical values), APxx (for either: Atkins and de Paula, 2006, 2010, 2014; Atkins et al., 2018, 2023), S1920 (Schmidt, 2019, 2022).

- ⁽¹⁾ The entropy 15.9 cal/K/mol given for the liquid water at the standard pressure 1013.25 hPa and temperature 298.15 K in K32 has served to compute the entropy for the water vapour (H_2O) at 1013.25 hPa and 298.15 K, including the impact $-R \ln(1013.25/6.11)$ due to the change from the saturation pressure at 273.15 K to the standard pressure (this impact is forgotten in the corresponding Table in Marquet (2019b)), leading to 44.27 cal/K/mol. The residual entropy for H_2O $R \ln(3/2) \approx 0.80574$ cal/K/mol (with $R = 1.98721$ cal/K/mol) computed by Pauling (1935) and Nagle (1966) is added to this K32 value to give 45.08 cal/K/mol.
- ⁽²⁾ In GS36 the water-vapour entropy 44.28 cal/K/mol is compared with the spectroscopic value 45.10 cal/K/mol, and the difference of 0.82 cal/K/mol is interpreted as due to the residual entropy calculated by Pauling of 0.806 cal/K/mol, which is thus added to give 45.09 cal/K/mol.
- ⁽³⁾ The liquid-water entropy in LR61 is 16.73 cal/K/mol and includes the residual entropy $16.73 - 15.9 = 0.83 \approx 0.80574$ cal/K/mol, leading to the water-vapour entropy 45.10 cal/K/mol.
- ⁽⁴⁾ The same residual entropy of 0.80574 cal/K/mol is added to the CR96/C value 44.31 cal/K/mol for H_2O , to give 45.11 cal/K/mol.

6 Reply-6 / Graphical representations: physical relevance

“When the reference state conditions of TEOS-10 are modified, such as those of water and of dry air, or of water and sea salt, graphical representations such as entropy-salinity diagrams will change. However, such changes have no physical relevance.”

Rainer Feistel cannot admit at the same time that the “*graphical representations such as entropy-salinity diagrams* (and vertical profiles) “*will change*” and largely depend on this or that definitions of the reference entropies, on the one hand, and say without any proof that “*such changes have no physical relevance,*” on the other hand.

We must not prejudge the future, and just because Rainer Feistel refuses on principle to define what he calls ‘entropy’ using the general recommendations of thermodynamics (third law), if only as a simple possibility open to everyone, does not mean that this should not and cannot be done, and that he must make people believe (without proof) that the large differences observed in these diagrams and vertical profiles cannot have a physical impact.

Rainer Feistel could at least clearly mention in all his papers that all these salinity diagrams and vertical profiles involving the seawater and moist-air entropy do depend on the arbitrary definitions of the reference entropies (as shown in my previous PDF file for the DYCOMS-II (RF01) Stratocumulus, the ASTEX Lagrangian experiment, the sea-air entropy-temperature diagrams, the SCICEX’96 cast 43 CTD vertical profiles).

It would be important to mention that the present arbitrary formulation of what Rainer Feistel called ‘entropy’ in the IAPWS and TEOS10 publications and software (in fact the ‘equivalent-proxy’ value of the entropy) may generate large differences for the vertical gradients in seawater and moist-air entropy of different sign when compared with the same vertical gradients computed with the ‘absolute’ values of the entropy.

I have shown in my previous PDF file such large differences for the DYCOMS-II (RF01) Stratocumulus, the ASTEX Lagrangian experiment, the sea-air entropy-temperature diagrams and the SCICEX’96 cast 43 CTD vertical profiles (again recalled in the Figs. 3).

I similarly show in the Figs. 4 several new (mean winter+summer) latitudes-pressure charts plotted with outputs from the French ARPEGE NWP model. The different (opposite-signs) gradients and slopes in the basic dry-air potential temperature θ and total water content q_t generates different isolines for the absolute entropy $s_{abs/M11}$ of Marquet (2011), on the one hand, and the equivalent-proxy ‘entropies’ $s_{e/P11}$ of Pauluis (2011) and $s_{e/E94}$ of Emanuel (1994), on the other hand. I also show a comparison of the isolignes of potential temperatures θ_s (red) and θ_e (blue), which correspond to $s_{abs/M11}$ and $s_{e/P11}$: the slopes of the isolines are especially different in the moist and warmer regions (boundary layer and tropical areas).

All these differences cannot “*have no physical relevance*” locally nor in the global studies of the atmospheric and the oceanic thermodynamics. Indeed, since the slopes of the isolines of $s_{abs/M11}$, $s_{e/P11}$ (and especially) $s_{e/E94}$ are so different, the absolute or ‘equivalent-proxy’ isentropic processes would correspond to different latitudes-pressure coordinates: this cannot be true (see also the next section), otherwise the moist-air entropy would cease to have any real physical meaning.

Moreover, different sign for these vertical gradients would generate different signs for the turbulent fluxes of the seawater and moist-air entropy, and thus in turn different signs for the evolution of the seawater and moist-air entropy. This cannot be true, because the entropy is a state function and it cannot increase or decrease depending on this or that arbitrary choices of the constants (in the same way as the stability of chemical reactions cannot depend on this or that definition of the entropies of reactants and products, this implying the use of the same absolute definition of the entropies as I have used to compute the moist-air and seawater entropies).

I show in the Figs. 5 unpublished results on the evolution between 1978 and 2019 of monthly mean (in red) and 12-months running average (in blue) values at the Mauna-Loa observatory computed from the hourly average values of: the basic properties $T(2m)$ (in °C), $q_v(2m)$ (in g/kg) and $p(2m)$ (in hPa), together with the change (with respect to 2019 values) in the absolute entropy (from Marquet, 2011, with $\Lambda_r \approx +6$) and the equivalent-proxy ‘entropy’ (from Pauluis, 2011, with $\Lambda_r \approx +9$).

Over this 1978-2019 period there is: an average increase in $T(2m)$ (+1.2°C); an average decrease in $p(2m)$ (−1 hPa); and an average increase in $q_v(2m)$ (+0.4 g/kg). As a result, the increase in the 12-months running average values of the equivalent-proxy ‘entropy’ overestimates the increase in the absolute entropy by a factor $(4 + 4.4)/(4 + 3.2) \approx 1.17 \approx +17\%$. Such a difference of +17% is too large to allow the possibility that, according to Rainer Feistel: “*When the reference state conditions of TEOS-10 are modified, such as those of water and of dry air, or of water and sea salt, graphical representations (...) will change. However, such changes have no physical relevance.*” The local Climate change in entropy computed from measurable quantities $T(2m)$, $p(2m)$ and $q_v(2m)$ cannot be arbitrary up to $\pm 17\%$: otherwise which is the interest of computing both the value of the entropy and the change in entropy caused by the physics of Climate Change?

I similarly show in the Figs. 6 other unpublished results showing another way to explain that it is not possible to call “*moist-air entropy*” any of the relationships computed with (more or less) arbitrary values for the reference entropies. I used datasets from two NWP models (IFS and ARPEGE), two NCEP reanalyses (1 and 2), three IFS-ERA reanalyses (Interim, 5 and 20CM-amip), and two CNRM-CM6 GIEC simulations (ARPEGE, amip and historical) to compute from the absolute temperature T , total water content q_t and other basic variables (p, q_l, q_i) the global mean (yearly and 10-years moving average) for the absolute moist-air entropy (from Marquet, 2011, with $\Lambda_r \approx +6$) and for other proxies called ‘entropies’ by Pauluis (2011, with $\Lambda_r \approx +9$) and by Emanuel (1994, with $\Lambda_r \approx +24.5$). I have also computed and plot another arbitrary definition of the moist-air ‘proxy-entropy’ based on $\Lambda_r = -25$.

Figs. 6 show that a consequence of the measurable global increase in T and q_t is a global increase in the absolute moist-air entropy $s_{abs/M11}$ computed with

$$\Lambda_r = \frac{s_v(T_r, e_r) - s_d(T_r, p_r - e_r)}{c_{pd}} \approx 5.875 \approx +6.$$

The increase is much larger for the ‘equivalent-proxy entropy’ $s_{e/P11}$ computed by Pauluis (2011) with $\Lambda_r \approx L_v(T_r)/(c_{pd} T_r) \approx +9$. The comparison of the labels in the vertical axes gives the ratio $(230 - 206)/(221 - 200) \approx 1.143$. The increases in the yearly and 10-years moving average values of the ‘equivalent-proxy entropy’ $s_{z/P11}$ are therefore 14% larger than those in the absolute values $s_{abs/M11}$.

The increase in the other ‘equivalent-proxy entropy’ $s_{e/E94}$ of Emanuel (1994) with $\Lambda_r \approx +24.5$ is even larger by a factor $(289 - 249)/(221 - 200) \approx 1.9$, and thus 90%, which is really very large! As for the last (lower-right) panel in the Figs. 6, it shows that for the other (almost reverse) arbitrary value $\Lambda_r \approx -25$ the resulting ‘proxy moist-air entropy’ would be almost constant (or even slightly decreasing) values!

To my mind, these results shown in the Figs. 5 and Figs. 6 are (other) proofs that it is not possible to arbitrary set the reference entropies for dry air and water species for the atmosphere (and the pure liquid water and the sea salts for the ocean) as done in the TEOS10 software, unless to modify at will and arbitrarily the climate change in entropy for the atmosphere, with even the possibility to reverse the

sign of the increase computed for the absolute definition of the moist-air entropy. This increase in the absolute moist-air entropy must have a physical meaning (otherwise which is the interest of computing both the value of the entropy and the change in entropy caused by the physics of Climate Change?) and disagrees with the sentence of Rainer Feistel: “*When the reference state conditions of TEOS-10 are modified, such as those of water and of dry air, or of water and sea salt, graphical representations (...) will change. However, such changes have no physical relevance.*”

7 Reply-7 / Isentropic trajectories

“*Similarly, when surfaces of constant entropy are considered in the atmosphere or in the ocean, those surfaces will be distorted by changes of the reference state conditions. What will remain unaltered, however, is the shape of isentropic trajectories, because the condition of equal entropy of different states does not depend and the value of the common absolute entropy.*”

The repeated mistake of Rainer Feistel for the seawater (and of Olivier Pauluis, for instance, for the atmosphere) is still to consider that “isentropic” processes automatically imply “adiabatic and closed-parcel processes.” Differently, “isentropic” processes only means “constant entropy” processes (as learned when I was a student, a long time ago), and thus possibly with varying total water content (q_t) in the atmosphere and varying sea-salts content and Salinity (S_A) in the oceans.

Of course, if q_t and S_A were a constant, then all proxy and absolute values would collapse in leading to the same properties called “isentropic” by Rainer Feistel (and Olivier Pauluis, among so many others), namely for the potential temperature θ_l , θ_s and θ_e (and the ‘entropies’ η_l , η_s and η_e) all constant at the same time (in fact up to the leading order approximations used to define these quantities). Differently, if q_t and S_A were not constant during the “isentropic” processes, then all these quantities may be different from each other.

As a example, I have plotted with Adriana Bailey (from NCAR) in the Fig. 7 and 8 the same Fig.1(e) of Bailey et al. (2019, p.7819-7827), but for both the “equivalent entropy” proxy potential temperature θ_e of Betts (1973, corresponding to the standard TEOS10-SIA “equivalent entropy” proxy value) and the (true) absolute entropy potential temperature (θ_s) computed from Marquet (2011, 2017) and Marquet and Stevens (2022).

The Fig. 7 and 8 clearly show that the “*shape of isentropic trajectories*” are completely different, with clearly a better agreement for the H₂O plumes following preferentially the (solid-line) absolute moist-air isentropes (θ_s) in the boundary layer and above, and not the (dashed) lines of equal values of the (TEOS10) “equivalent entropy-proxy” potential temperature (θ_e).

Similarly, I show in the Fig. 9 (with the plot of a south-hemisphere latitude-pressure mean winter+summer cross-section plotted with outputs from the French operational ARPEGE NWP model) that the three families of curves of equal values of θ_l , θ_s and θ_e are completely different in the boundary layer and in the whole tropical area. As a clear example, only the absolute entropy value θ_s exhibits an almost isentropic region within the Tropics (from the surface to about 550 hPa), whereas the liquid-water (and thus dry-air) proxy values ($\theta_l \approx \theta$) are almost horizontally stratified, and with vertical overturning for the equivalent proxy values (θ_e).

All these numerical results disagree with the assertion of Rainer Feistel explaining that “*however (...) the shape of isentropic trajectories (...) does not depend and the value of the common absolute entropy*” (i.e. when the reference entropies are arbitrarily set to this or that values at 0°C).

It is important to stress that the use of the absolute values for the moist-air and seawater entropies may reveal new non-trivial isentropic regions, where the existing gradients in sea-salts and total-water

contents may be balanced by existing gradients of opposite sign for the ‘equivalent-proxi entropy’ computed with the TEOS10 software. I consider that these isentropic (or not) regions cannot “*have no physical relevance*” and will be the source of a lot of studies in the future.

I therefore strongly disagree with the sentence of Rainer Feistel: “(*... the condition of equal entropy of different states does not depend (and?) on the value of the common absolute entropy.*)” This sentence is clearly contradicted at least by the two graphs I was able to draw (Figs. 7, 8 and 9 from the NCAR and ARPEGE NWP models), and no doubt by possible future sections plotted in polar parts of the oceans, with the same large impacts that must be related to the vertical profiles I was able to draw for the SCICEX’96 cast 43 (I again recalled in the Fig. 3).

8 Reply-8 / heat and energy (and entropy?) fluxes

“*Similar arguments apply to heat and energy fluxes.*”

I agree that the ‘latent-heat equation’ based on Eqs. (22)-(24) and to be computed with the subroutine `sea_air_enthalpy_evap_si()` in the TEOS-10 SIA library do not depend on the reference values for the enthalpies. Therefore, if the TEOS10 software can improve on the calculations currently performed in the NWP models and GCMs, then this is very welcome (if it is not too costly, of course).

However, this independence with the reference values is simply because the latent heats of evaporation, fusion and sublimation reflect changes of state of the same body (in this case between the vapour, liquid and ice phases of H₂O), and are just the difference in enthalpies between these different phases.

Differently, my reservations relate to another matter: the fact that the calculations of local values, vertical gradients and turbulent fluxes of (moist air and seawater) enthalpy and entropy depend on the reference values of these enthalpy and entropy.

This is due to the fact that the moist-air and seawater internal energies (e_i) and enthalpies ($h = e_i + p/\rho$) depend on weighted sums of the reference values and of concentrations. Indeed, for a mixture ($k = 1, 2, \dots, n$) of variable composition, Gibbs (1875-1878) himself already shown that, with modern notations:

$$\text{for the internal energy: } e_i = \sum_k c_{vk} q_k (T - T_0) + \boxed{\sum_k e_{ik0} q_k} = \sum_k c_{vk} q_k T + E, \quad (7)$$

$$\text{where } E = \boxed{\sum_k e_{ik0} q_k} - \sum_k c_{vk} q_k T_0, \quad (8)$$

$$\text{and similtaly for the enthalpy: } h = \sum_k c_{pk} q_k (T - T_0) + \boxed{\sum_k h_{k0} q_k}. \quad (9)$$

The boxed terms depends on the reference values e_{ik0} for the internal energy and h_{k0} for the enthalpies, and as recalled in the Fig. 10 Gibbs (1875-1878, p.211) already explained that for a mixture of variable composition “*the constants for E (...) cannot in general (...) be treated as arbitrary.*”

This can be easily understood by computing the differential of E given by (8):

$$dE = \sum_k (e_{ik0} - c_{vk} T_0) dq_k, \quad (10)$$

$$\text{and thus for the vertical gradient a term: } \frac{\partial \bar{E}}{\partial z} = \sum_k (e_{ik0} - c_{vk} T_0) \frac{\partial \bar{q}_k}{\partial z}, \quad (11)$$

$$\text{and thus for the vertical fluxes a term: } \overline{w' E'} = \sum_k (e_{ik0} - c_{vk} T_0) \overline{w' q'_k}. \quad (12)$$

The last result (12) clearly show that, for a mixture of variable composition (like the moist-air and the seawater), the flux of energy $\overline{w' e_i}$ must depend via the term $\overline{w' E'}$ on the reference values e_{ik0} , this contradicting the sentence of Rainer Feistel: “(...) *the condition of equal entropy of different states does not depend (and?) on the value of the common absolute entropy. Similar arguments apply to heat and energy fluxes.*”

Since Rainer Feistel computed several kinds of changes in entropy in the preprint, I would like to go beyond the “*heat and energy fluxes*” mentioned in the reply, and to explain how the entropy equation is impacted by the values of the reference entropies via the gradients and turbulent fluxes of the moist-air and seawater entropies.

Indeed, the concepts of entropy fluxes and entropy production are mentioned at several places in the preprint:

- (lines 147-151) “*The roles of enthalpy, chemical potential and entropy are explained by means of explicit theoretical descriptions of three simplified tutorial examples (...) and (iii) for the entropy production of irreversible evaporation*;”
- (lines 568-570) “*The climate system functions far from thermodynamic equilibrium, permanently producing and exporting entropy at an average rate of $1 \text{ W m}^{-2} \text{ K}^{-1}$ per global surface area (Ebeling and Feistel, 1982; Feistel and Ebeling, 2011)*;”
- (lines 622-623) “*The irreversible production of entropy is an internal conversion or redistribution of energy rather than a change of it*;”
- (lines 629-630) “*Entropy production appears wherever a flux is passing its driving gradient. Near equilibrium, this flux is proportional to its driving force (...)*;”
- (lines 635-639) “*The associated entropy production, eq. (44), obeys the 2nd law of thermodynamics by the inequality $(\sigma) = C (\Delta\mu)^2 \geq 0$ (48) while the total entropy change, eq. (42) may possess any sign. In other words, the 2nd law forbids that Onsager fluxes may be directed against their causing Onsager forces*;”
- (lines 645-647) “*Under typical marine circumstances, the entropy production density of ocean evaporation can be estimated to about $4 \text{ mW m}^{-2} \text{ K}^{-1}$, contributing roughly 0.4% to the global entropy production (Feistel and Ebeling, 2011; Feistel and Hellmuth, 2024)*;”
- (lines 831-834) “*This paper explains some tutorial examples for the application of TEOS-10 to selected current climate problems. There is (i) the two-phase conceptual model of "sea air" which provides rigorous equations for (...) the irreversible production of entropy by evaporation into the marine troposphere.*”

8.1 Reply-8-1 / What about the value of $-1 \text{ W m}^{-2} \text{ K}^{-1}$?

The entropy flux of about $-1 \text{ W m}^{-2} \text{ K}^{-1}$ at the top of the atmosphere recalled by Rainer Feistel (see the Fig. 11) was defined in Ebeling and Feistel (1982), and then retained as such without any upgrade in Feistel and Ebeling (2011), by the simple relationship:

$$\frac{d_e S}{dt} = \frac{4}{3} \left(\frac{230 \text{ W m}^{-2}}{6000 \text{ K}} - \frac{230 \text{ W m}^{-2}}{300 \text{ K}} \right) \approx 0.97 \text{ W m}^{-2} \text{ K}^{-1} \approx \boxed{-1 \text{ W m}^{-2} \text{ K}^{-1}}. \quad (13)$$

This value can however be compared with other (larger) evaluations made in well-known atmospheric studies.

Peixoto et al. (1991, p.10,985) evaluated the production of entropy at the top of the atmosphere as a sum of several ratios \vec{F}_k/T_k of energy fluxes (\vec{F}_k) divided by absolute temperatures (T_k), with the energy flux 238 W m^{-2} for the solar radiation from the Sun at 5760 K, -129.2 W m^{-2} from the atmosphere at 252 K, -88.4 W m^{-2} from the clouds at 259 K and -20.4 W m^{-2} from the surface at 288 K. These contributions lead to the sum $238/5760 - 129.2/252 - 88.4/259 - 20.4/288 \approx -0.8835 \text{ W m}^{-2} \text{ K}^{-1}$ without the Planck's factor $4/3$, and thus corresponding to $(4/3) \times 0.8835 \approx \boxed{-1.18 \text{ W m}^{-2} \text{ K}^{-1}}$, which is larger in magnitude than the value $-1 \text{ W m}^{-2} \text{ K}^{-1}$ given by (13).

In another study, Stephens and O'Brien (1993, p.135 and p.143) computed the global entropy budget of the planet based in part on the analysis of the ERBE and including the Planck's factor $4/3$. They obtained the globally averaged values of the entropy flux $-1.27 \text{ W m}^{-2} \text{ K}^{-1}$ for the DJF season and $-1.25 \text{ W m}^{-2} \text{ K}^{-1}$ for the JJA season, with the average of the DJF and JJA long-wave and short-wave entropy flux densities at the top of the atmosphere $-1.23 \text{ W m}^{-2} \text{ K}^{-1}$ and $-0.02 \text{ W m}^{-2} \text{ K}^{-1}$, respectively, giving a net flux of $\boxed{-1.25 \text{ W m}^{-2} \text{ K}^{-1}}$, which is even higher in magnitude than the values $-1.18 \text{ W m}^{-2} \text{ K}^{-1}$ derived by Peixoto et al. (1991, p.10,985).

Another example is the more recent study by Bannon (2015, p.3275), who arrived at the even larger global entropy flux of about $\boxed{-1.28 \text{ W m}^{-2} \text{ K}^{-1}}$.

Note that both Stephens and O'Brien (1993) and Bannon (2015) defined the (solar) entropy fluxes received from the Sun and those re-emitted by the Earth differently than the simple formulation (13) considered both in Ebeling and Feistel (1982) and Feistel and Ebeling (2011). Stephens and O'Brien (1993, Eq. 15, p.126) explained that, if the Planck's black-body entropy flux density is still given by $J = (4/3) \sigma T^3$, the incident solar entropy flux density is computed via

$$J_0 = \frac{4}{3} \sigma T_{sun}^3 \cos(\theta) \frac{\Omega_0}{\pi}, \quad (14)$$

where Ω_0 is the solid angle subtended by the sun at a point on this surface and θ is the zenith angle of the sun. As for the broad-band, solar entropy flux density reflected from the surface with albedo α_v , Stephens and O'Brien (1993, Eq. 18, p.126) arrived at the relationship

$$J = \frac{4}{3} \sigma T_{sun}^3 \chi(u), \quad (15)$$

where $u = \alpha \cos(\theta) (\Omega_0/\pi)$ and where (Eq. 19, p.126):

$$\chi(u) \approx u [p \ln(u) + q] \quad (16)$$

with $p \approx -0.2777$ and $q \approx 0.9652$. Then Stephens and O'Brien (1993, Eq. 30, p.134) computed the net solar entropy flux density as the difference $J - J_0$ of (15) and (14), leading to the total solar entropy flux:

$$J_s = \frac{4}{3} \sigma T_{sun}^3 \left[\chi(u) - \cos(\theta) \frac{\Omega_0}{\pi} \right]. \quad (17)$$

It is however true that the solar part of (13) is a small term, with $(4/3)(230/6000) \approx +0.05 \text{ W m}^{-2} \text{ K}^{-1}$, whereas the long-wave part is the larger contribution $-(4/3)(230/300) \approx -1.02 \text{ W m}^{-2} \text{ K}^{-1}$. The correction term $\chi(u)$ in (17) thus only impact the much smaller part of $d_e S/dt$, and the explanation leading to the larger values of -1.18 , -1.25 and $-1.28 \text{ W m}^{-2} \text{ K}^{-1}$ are due to more accurate impacts of the long-wave radiation fluxes (which is too simplified by Rainer Feistel and Werner Ebeling).

Therefore, Rainer Feistel may use a more recent and more accurate (and larger) value than the one of about $-1 \text{ W m}^{-2} \text{ K}^{-1}$ derived from likely too simple arguments by Ebeling and Feistel (1982).

8.2 Reply-8-2 / Impact of reference values on the entropy equation

It may be useful to recall that the entropy equation have been tackled long before the 1982-2011 books of Rainer Feistel and Werner Ebeling.

Indeed, after the pioneering works of Jaumann (1911, 1918) and Lohr (1917), the general entropy equation has next been published and studied by Onsager (1931), von Meixner (1939, 1941, 1942, 1943a,b), Eckart (1940a,b), Prigogine (1947, 1949), de Groot (1951), von Haase (1951a,b, 1953), de Groot (1959), de Groot and Mazur (1962), Prigogine (1967), Glansdorff and Prigogine (1971a,b), Dufour and van Mieghem (1975), Herbert (1975), all published before the books by Ebeling and Feistel (1982). Other next important contributions are by de Groot and Mazur (1984), Landau and Lifshitz (1987) ... up to Zdunkowski and Bott (2004, for the atmosphere), among so many others.

According to the continuity equation $\partial\rho/\partial t + \nabla \cdot (\rho \vec{v}) = 0$, the material derivative of the local (microscopic) specific entropy can be written as:

$$\rho \frac{ds}{dt} = \rho \frac{\partial s}{\partial t} + \rho \vec{v} \cdot \vec{\nabla} s = \frac{\partial(\rho s)}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v}) = \frac{\dot{q}}{T} = -\vec{\nabla} \cdot \vec{J}_s + \sigma_s, \quad (18)$$

where $\rho s \vec{v}$ is the advective entropy flux, \dot{q} the diabatic sources/sinks terms of energy, \vec{J}_s the non-advective entropy flux and σ_s the positive entropy-production term. This entropy equation is valid for the microscopic scale only (namely a few millimetres), and is not valid for the larger scales involved in our oceanic and atmospheric NWP models and GCMs.

It is then possible to start with the local entropy equation (18) and to derived (like first done by Herbert, 1975, Eq. I-6, p.7) the associated turbulent entropy equation that can be written as:

$$\bar{\rho} \frac{d\hat{s}}{dt} = \frac{\partial(\bar{\rho} \hat{s})}{\partial t} + \vec{\nabla} \cdot (\bar{\rho} \hat{s} \hat{v} + \overline{\rho s'' \vec{v}''}) = \overline{\left(\frac{\dot{q}}{T} \right)} = -\vec{\nabla} \cdot (\overline{\vec{J}_s}) + \overline{\sigma_s}, \quad (19)$$

where $\overline{\rho s'' \vec{v}''}$ is the turbulent flux of entropy. This is the entropy equation that must be used to study the atmospheric NWP models and GCMs, and in the oceanic models as well. The diabatic sources/sinks terms are summarized into the term $\dot{q} = -\vec{\nabla} \cdot \vec{F}$, where \vec{F} represents all the diabatic energy fluxes (and somehow including the impacts of the radiation fluxes).

This means that the moist-air and seawater entropies s , for which the reference values generate the Gibbs weighted sum

$$S_0 = \sum_k s_{k0} q_k, \quad (20)$$

lead to existing impacts in all terms of (19), except the present formulations of the positive production entropy terms $\overline{\sigma_s}$. This weighted sum was noted $\sum_1 m_1 H_1$ by (Gibbs, 1875-1878, Eq. 278, p.217) as recalled in the Fig. 10.

Indeed, computations of the quantity $\partial(\bar{\rho} \hat{s})/\partial t$ lead to an impact $\sum_k s_{k0} \partial(\bar{\rho} \hat{q}_k)/\partial t$, which is not equal to zero for the (non-arbitrary) absolute values of the s_{k0} .

The same is true for the convective term $\bar{\rho} \hat{s} \hat{v}$, which generate the terms $\sum_k s_{k0} \bar{\rho} \hat{q}_k \hat{v}$, which is not equal to zero for the (non-arbitrary) absolute values of the s_{k0} .

The same is true for the turbulent fluxes of the kind $\overline{\rho s'' \vec{v}''}$, which generate the terms $\sum_k s_{k0} \overline{\rho q_k'' \vec{v}''}$, which is not equal to zero for the (non-arbitrary) absolute values of the s_{k0} .

This is also true for the entropy-flux term \vec{J}_s in the divergence term in the r-h-s of (19), which usually depends on the flux $-\sum_k (\mu_k/T) \vec{J}_k$ with $\mu_k = h_k - T s_k$ the chemical potentials and \vec{J}_k the diffusion flow of the substances k , thus generating the sum $\sum_k s_{k0} \vec{J}_k$. Again, this is not equal to zero for the (non-arbitrary) absolute values of the s_{k0} .

Therefore, when Feistel (2024, lines 622-623) explains in the preprint that: “*The irreversible production of entropy is an internal conversion or redistribution of energy rather than a change of it*” this corresponds to the study of the sole entropy-production term $\overline{\sigma_s}$ in (19), with all other terms discarded.

Differently, what must likely be studied in atmospheric and oceanic sciences should be the whole entropy equation (19) written as:

$$\frac{\partial(\overline{\rho} \hat{s})}{\partial t} + \overline{\nabla} \cdot (\overline{\rho} \hat{s} \hat{v}) = -\overline{\nabla} \cdot \left(\overline{J_s} + \overline{\rho s'' \vec{v}''} \right) + \overline{\sigma_s}, \quad (21)$$

where the turbulent flux of entropy is put in the r-h-s of this turbulent-entropy budget equation (as usually done in all NWP models and GCMs).

Therefore, since all terms except the sole entropy-production term $\overline{\sigma_s}$ (see the section 8.3) depend on the reference entropies values, in order to study the full entropy equation (21) *it would be highly desirable that the TEOS10 software could provide the absolute value of the entropy for both the atmosphere and the seawater.*

In fact, Rainer Feistel only considers the impact of the entropy production term, and thus the different entropy equation:

$$\overline{\sigma_s} = \frac{\partial(\overline{\rho} \hat{s})}{\partial t} + \overline{\nabla} \cdot (\overline{\rho} \hat{s} \hat{v}) + \overline{\nabla} \cdot \left(\overline{J_s} \right) + \overline{\nabla} \cdot \left(\overline{\rho s'' \vec{v}''} \right). \quad (22)$$

However, rewriting as this, even though $\overline{\sigma_s}$ may be known and even if possibly $\overline{\sigma_s} \geq 0$, this does not mean that we can deduce from the whole terms in the r-h-s of (22) that the entropy is increasing, decreasing or remains a constant.

In all honesty and transparency, I would like to add that these reference entropy terms can be grouped like in the term Λ_r considered since Marquet (2011), with an additional entropy term of the form $c_{pd} \Lambda_r q_t$, where $q_t = q_v + q_l + q_i$ is the total water content. Therefore, in order to study this budget equation (21) the impact of the reference entropy values depends (for instance) on the turbulent flux $c_{pd} \Lambda_r \overline{w' q'_t}$, which is proportional to the turbulent flux of total water content q_t .

It is thus true that for a (very) global study of a stationary atmosphere and/or ocean, and if the (very) global flux of water is exactly zero at the interface, then this additional flux $c_{pd} \Lambda_r \overline{w' q'_t}$ might be discarded if the evaporation and precipitation flux exactly cancel each others with $E - P = 0$.

However, this result is no longer true for any other kind of studies, like for instance for more regional studies (tropical, extra-tropical, polar, hemispheric; ...), or for hourly, diurnal, monthly or seasonal sub-annual range, or for the study of the climate change with an increase in average in both global temperature and total-water content, where therefore $E - P \neq 0$ in order to make q_t increase... For all these cases where $E - P \neq 0$ and q_t is not a constant: *it would be highly desirable that the TEOS10 software could provide the absolute value of the entropy for both the atmosphere and the seawater.* This is true both locally (see the Figs. 5 plotted from the Mauna Loa hourly data set) and globally (see the Figs. 6 plotted from NWP models, Reanalyses and GIEC simulations).

8.3 Reply-8-3 / Which terms in the entropy-production terms?

When Feistel (2024, lines 629-630) explains in the preprint that: “*Entropy production appears wherever a flux is passing its driving gradient. Near equilibrium, this flux is proportional to its driving force (...)*” it is unclear if these fluxes and driving gradients can be extended to the case of the moist-air atmosphere?

The paradigm of the positivity of the entropy-production term $\sigma_s \geq 0$ is the case of the (simple) Fourier flux of heat for the microscopic scale for which $\vec{F}_T = -a \overline{\nabla} T$ (with $a > 0$). In this case, the

term \dot{q}/T in the entropy equation (18) can be written as:

$$\rho \left. \frac{ds}{dt} \right|_{cond.} = \frac{\dot{q}|_T}{T} = \frac{-\vec{\nabla} \cdot \vec{F}_T}{T} = -\vec{\nabla} \cdot \left(\frac{\vec{F}_T}{T} \right) + \vec{F}_T \cdot \vec{\nabla} \left(\frac{1}{T} \right) = \overbrace{-\vec{\nabla} \cdot \left(\frac{\vec{F}_T}{T} \right)}^{(-\vec{\nabla} \cdot \vec{J}_s)} + \overbrace{a \frac{[\vec{\nabla}(T)]^2}{T^2}}^{(+\sigma_s \geq 0)}, \quad (23)$$

where the last two terms in (23) are just another way of writing $-(\vec{\nabla} \cdot \vec{F}_T)/T$ by using the product rule for the divergence. For this case, the flux term \vec{F}_T/T can then be considered as a contribution to the entropy-flux term \vec{J}_s , while $\vec{F}_T \cdot \vec{\nabla}(1/T) = +a [\vec{\nabla}(T)]^2/T^2$ may be considered as a contribution to the entropy-production term σ_s , because it is positive for this Fourier's law $\vec{F}_T = -a \vec{\nabla}T$ (with $a > 0$) that operates in counter-gradients with the gradients of absolute temperature.

However, in the the moist-air atmosphere the Fourier's flux of heat only concern the very first millimetres or centimetres above the ground. Differently, the heat and moisture fluxes are usually computed in the NWP models and GCMs via bulk-formula and/or K -gradient theories. Moreover, these moist-air bulk-formula and K -gradient theories are not based on the gradients of the absolute temperature, but rather on the Betts (1973) 'conservative' variable (i.e. the liquid-water potential temperature θ_l and the total water content q_t).

This has been already described by Gassmann and Herzog (2015, p.858-860), where it is recalled that the “*For the sensible heat flux we have to choose a K -ansatz with the temperature gradient*” that may be rewritten (to agree with the previous notations) as:

$$\vec{F}_T = -\rho c_{pd} \vec{K}_h \cdot \vec{\nabla}T.$$

“*Here, \vec{K}_h is a tensor with only diagonal elements. Different horizontal and vertical coefficients are distinguished. A different approach for the sensible heat flux is often used in numerical models of the atmosphere, namely*

$$\vec{F}_\theta = -\rho c_{pd} \pi \vec{K}_\theta \cdot \vec{\nabla}\theta,$$

where θ and $\pi = T/\theta = (p/p_0)^\kappa$ are the potential temperature and the Exner pressure, respectively. (...) it can be verified (that this flux does not) conform with the second law, because it cannot be guaranteed that the gradients of temperature and potential temperature have the same direction. This discrepancy has already been noted by Goody (2000). Romps (2008) therefore encourages “further research to assess existing turbulence schemes for their ability to produce entropy sources of the correct sign and magnitude”

In fact, the answer to the question asked by Gassmann and Herzog (2015) has been given long ago by Richardson (1919a,b, 1922), who explicitly explained that the moist-air turbulence must be applied to the total water content ($q_t = q_v + q_l + q_i$) and the absolute (Nernst, Lindemann, Koref and others) moist-air entropy s (or the associated potential temperature θ_s I have defined in Marquet, 2011).

Accordingly, if the aim would be to arrive (as expected by Rainer Feistel) to the property that “*(...) Near equilibrium, this flux is proportional to its driving force (...)*” this requirement could be a way to distinguish which is the relevant variable to be used in the entropy equation to express the ‘heat and entropy fluxes’?

To do so, I have plotted in the (unpublished) Figs. 12 the vertical profiles of LES outputs from digitized datasets for the BOMEX case (last 3 hours) published in Siebesma et al. (2003), for:

- (a) the Betts (1973) liquid-water variable θ_l ;
- (b) the water contents variables ($q_v, q_l, q_t = q_v + q_l$);

- (c) the absolute-entropy potential temperature $\theta_s = T_0 \exp[(s - s_{d0})/c_{pd}]$ and its (very close) first-order θ_{s1} and second-order approximations and θ_{s2} (from Marquet, 2011, 2015, 2019a);
- (d) the vertical gradients $(\partial\bar{X}/\partial z)$ for $X = \theta_l, q_t, \theta_{s1}$ and θ_{s2} ;
- (e) the vertical turbulent fluxes $(\overline{w'X'})$ for $X = \theta_l, q_t, \theta_{s2}, \theta_{s1}$ and q_t ;
- (f) the exchange coefficients $(K_h, K_w, K_{s1}, K_{s2})$ defined by $K_X = -\overline{w'X'}/(\partial\bar{X}/\partial z)$ for the variables $X = \theta_l, X = q_t, X = \theta_{s1}$ and $X = \theta_{s2}$, respectively;
- (g) the value $K_h = K(\phi = \theta_l)$ and $K_w = K(\phi = q_t)$ published in Siebesma et al. (2003); and
- (h) the Lewis functions (ratios of exchange coefficients) $Le_t = K_h/K_w$ for θ_l , $Le_{ts1} = K_{s1}/K_w$ for θ_{s1} and $Le_{ts2} = K_{s2}/K_w$ for θ_{s2} .

The Fig. 12 (f) shows that the coefficient K_w (in blue) for the total water content q_t is positive and well-founded.

Differently, the Betts liquid-water variable θ_l (in black) leads to physically unfounded (negative) exchange coefficient K_h in the middle of the boundary layer between about 100 m and 190 m, where the thin curve for $K(\phi = \theta_l)$ was interrupted in (g) by Siebesma et al. (2003).

This issue is solved by using the suggestion of Richardson (1919a,b, 1922) to base the moist-air turbulence on the absolute entropy variables (s or $\theta_s \approx \theta_{s2} \approx \theta_{s1}$). Indeed, the red (superimposed) curves in the Fig. 12 (f) show that the values of both K_{s1} and K_{s2} are positive from the surface up to the 1900 m.

The same results are also valid for AROME-LES outputs and for several cases (BOMEX, RICO, ARM-Cu, ATEX), where the exchange coefficients K_h (defined with the Betts θ_l variable) are physically unfounded (negative) in the middle of the boundary layer, whereas the exchange coefficients K_w (for q_t) and K_{s1} or K_{s2} (for θ_{s2} or θ_{s1}) are all positive and physically relevant.

As a conclusion, all these results prevent the definition of turbulent fluxes proportional to its driving force if one uses the Betts (1973) liquid-water variable θ_l (as done in all NWP models and GCMs), and it is needed to use instead the absolute moist-air variable s (or the potential temperatures θ_s or θ_{s2} or θ_{s1}) to arrive at the properties mentioned in the preprint by Rainer Feistel (turbulent fluxes proportional to its driving force).

Therefore, for this reason to be able to rely on well-founded positive exchange coefficients, *it would be highly desirable that the TEOS10 software could provide the absolute value of the entropy for both the atmosphere and the seawater.*

Indeed, due to the definition $s = c_{pd} \ln(\theta_s/T_0) + s_{d0}$, where c_{pd} , T_0 and s_{d0} are all constant, the differential, vertical gradients and vertical turbulent fluxes are exactly proportional, according to:

$$ds = \left(\frac{c_{pd}}{\theta_s}\right) d\theta_s, \quad \frac{\partial\bar{s}}{\partial z} \approx \left(\frac{c_{pd}}{\theta_s}\right) \frac{\partial\bar{\theta}_s}{\partial z}, \quad \overline{w's'} \approx \left(\frac{c_{pd}}{\theta_s}\right) \overline{w'\theta'_s}. \quad (24)$$

Therefore, if the fluid is well mixed in terms of the entropy (s) it is well mixed in terms of the associated potential temperature (θ_s), simply because all the vertical gradients and vertical fluxes cancel out at the same time.

9 Reply-9 / The remaining credo or dogma?

“There is no need to distrust the TEOS-10 equations of state with respect to the definition of reference state conditions. Measurable thermodynamic properties in geophysics must be independent of the choice of those conditions, otherwise those quantities are physically improperly specified.”

This is simply an unproven assertion that is contradicted by the facts.

Indeed, I have previously explained that the (measurable) saturation vapour pressures may depend on absolute entropy values (thanks to the works of Planck and Nernst), with chemical reaction constants also depending on these absolute entropy values (in that justifying the publication of the absolute entropies in all thermodynamic Tables), and therefore with measurable impacts on the concentration of sea-salts in the oceans and the concentration of ozone in the atmosphere, and therefore with (measurable) impacts on the temperature profile in the stratosphere.

Rainer Feistel end his reply by the sentence: “*Measurable thermodynamic properties in geophysics must be independent of the choice of those conditions, otherwise those quantities are physically improperly specified.*”

It seems to me that entropy, even if it cannot be “measured” (in the sense of a thermometer for temperature or an anemometer for the wind), is a fundamental quantity in thermodynamics, and is even a “state function” (one of the most important properties in thermodynamics).

The dogma defended by Rainer Feistel cannot be used as a reason not to properly calculate the entropies of the atmosphere and the ocean, especially as the solution has existed since the work of Nernst (1906) and then Planck (1911). I do not consider these people to be insignificant, quite the contrary, and my work on these subjects since 1989 has followed on the works of Hauf and Höller (1987) and the previous advices of Richardson (1919a,b, 1922, who was not insignificant either).

Moreover, if the same dogma had been applied to the concept of temperature (namely to only rely on the measurable differences in Celsius temperatures), we would still continue to simply add an arbitrary constant (approximately linked to the compressibility of fluids), as initially published by Carnot (1824), and then translated by Clapeyron (1834, 1837, 1843a,b), to write the equation of state of a gas in the form $p v = R (266 + t)$, thus without having the next idea of W. Thomson (Lord Kelvin, 1848) of defining the absolute temperature scale as $T = 273 + t$.

More precisely, W. Thomson (Lord Kelvin, 1848) explained (p.102) that: “*Although we have thus a strict principle for constructing a definite system for the estimation of temperature, yet as reference is essentially made to a specific body as the standard thermometric substance, we cannot consider that we have arrived at an absolute scale, and we can only regard, in strictness, the scale actually adopted as an arbitrary series of numbered points of reference sufficiently close for, the requirements of practical thermometry. In the present state of physical science, therefore, a question of extreme interest arises: Is there any principle on which an absolute thermometric scale can be founded? It appears to me that Carnot’s theory of the motive power of heat enables us to give an affirmative answer.*”

The relation between motive power and heat, as established by Carnot, is such that quantities of heat, and intervals of temperature, are involved as the sole elements in the expression for the amount of mechanical effect (...) we are thus furnished with a measure for intervals according to which absolute differences of temperature may be estimated.”

Next W. Thomson (Lord Kelvin, 1848) explained (in the footnote, p.104): “*(...) that infinite cold must correspond to a finite number of degrees of air-thermometer below zero (centigrade); since, if we push the strict principle of graduation, stated above, sufficiently far, we should arrive at a point corresponding to the volume of air being reduced to nothing, which would be marked as -273° of the scale ($-100/0.366 \approx 273.2$, if 0.366 be the coefficient of expansion); and, therefore, -273° of the air-thermometer is a point which cannot be reached at any finite temperature, however low*” (see the Fig. 13 published as the Fig. 1 in Marquet, 2019b).

We recognize here another great principle of thermodynamic suggested by Nernst (1912), and then studied by Simon (1927), a principle which is associated with, but not strictly equivalent to the third-law of thermodynamics: the alternative principle of unattainability of $T = 0$ K (“*Unerreichbarkeit des*

absoluten Nullpunktes”), namely that absolute zero temperature cannot be reached in a finite time interval and in a finite number of steps. A proof for this second way to express the third law of thermodynamics is given in the recent paper Masanes and Oppenheim (2017).

If the dogma of Rainer Feistel (to arbitrarily set the reference values at 0°C) was valid, then the reference entropy could be different for this or that state of matter, with $S_{01} \neq S_{02}$ in the Fig. 14 (published as the Fig. 3 in Marquet, 2019b), and then the principle of unattainability of $T = 0$ K would be violated, as shown in the left part of the Fig. 14. For this reason we must set $S_{01} = S_{02} = S_0$, and then S_0 must be a universal value, which can be explicitly set to zero according to Planck (1917). Note that this principle of unattainability of $T = 0$ K have been amply verified by experiments from the 1920’s up to 2024 (in particular by quasi-static adiabatic processes) and down to mK or even μ K.

The dogma of Rainer Feistel (to arbitrarily set the reference values at 0°C) would amount to deny any physical meaning of the constant 273.15 in the Kelvin scale, because *only differences in temperature are measured in the laboratories?* Differently, just like the indirect but existing physical impact of the absolute entropies S_0 on the saturation pressure via (1) and (2), the absolute constant 273.15 only have indirect physical impact, first via the state equation of state $p v = R T$ and then in the Boltzmann statistic-physics distribution law $\exp[-u_i/(k T)]$. However, even if there is no direct measurement of this constant α in $T = t + \alpha$, it can be calculated via the reverse relationship $\alpha(p, v, t) = p v / R - t \approx 273.15$ K, in the same way as the absolute (translation) entropy S_0 can be calculated via (3).

Similarly to what I have recalled about the absolute scale of temperature (by Thomson, 1848), the heat theorem (by Nernst, 1906), the third law of thermodynamics (by Planck, 1911, 1917) and the principle of unattainability of $T = 0$ K (by Nernst, 1912; Simon, 1927), I want to recall that the need to avoid arbitrary definitions for reference values (E) for the internal energy and (H) for the entropy was previously studied by Gibbs (1875-1878) himself, who already explained that: “*the constants for E and H cannot in general (...) be treated as arbitrary*” for a mixture of variable composition, as shown in the Fig. 10 and due to the last term $\sum_k q_k s_{0k}(T_0, p_0)$ in the relationship (25) for “*the entropy of the gas-mixture (...) in which the proportion of the components shall be variable.*”

Gibbs (1875-1878) already explained that, if the constants for E and H cannot in general (...) be treated as arbitrary, the method to set these constants would be: “*we may have determined the states of the substance of the gas for which ($u =$) $\varepsilon = 0$ and ($s =$) $\eta = 0$ with reference to some other form in which the substance appears, or, if the substance is compound, the states of its components for which ($u =$) $\varepsilon = 0$ and ($s =$) $\eta = 0$ may be already determined.*” This is precisely the method presently used to set the absolute version of the entropy by using the third law of thermodynamic via the calorimetric method (including the residual entropy for H₂O) or equivalently by using the statistical method, with the translational, rotational and vibrational degrees of freedom (the absolute part of the entropy been included into the translational part, including the residual entropy for H₂O). The equivalence of these two methods for the main atmospheric species is shown in the Fig. 2.

Accordingly, nowadays all thermodynamic definitions of the entropies in variable composition systems rely on the absolute (third-law) definition of the entropies, except however for most of present atmospheric and oceanographic thermodynamic applications... In this sense, the atmospheric and oceanographic thermodynamics are especially unusual, for historical reason and due in particular to the dogma imposed by Kerry Emanuel, Olivier Pauluis, Rémi Tailleux (the second referee RC2) and Rainer Feistel, among so many others.

Note that I am not so alone (as Rémi Tailleux so often suggests) because I worked and published on the subject of moist-air absolute entropy with late Jean-François Geleyn (between 1989 and 2015), I have then studied and published several applications of the moist-air entropy with S. Belamari, Th. Dauhut, G. Canut, W. Maurel, R. Honnert, A. Bailey, P. Martinet, J.-F. Mahfouf, including an operational application in 2021 in the IFS NWP model by P. Bechtold, and even more recently I have published with Bjorn Stevens a paper where he explicitly added at the end of Marquet and Stevens (2022): “ θ_l and θ_e are poor measures of entropy (...) In contrast, θ_s measures the entropy of moist air” (following the Chapter written by Stevens and Siebesma, 2020, where the absolute reference entropies for dry air and water vapour were published there in the Table 2.3). Moreover, I have only followed the existing studied previously published by Hauf and Höller (1987) for the moist-air atmosphere, and Millero and Leung (1976) and Millero (1982) for the sea-salts water, where the absolute values of the entropy were fully considered for the dry air, water vapour, liquid water and sea salts.

10 Additional Figures and Table

Table 2: *The specific heat (at constant pressure) for the solid (ice-Ih) state of H_2O from $T = 0$ K to 273 K. Data were obtained from Table 13 of Feistel and Wagner (2006) for 10 K, 20 K and above 30 K. Other data below 28 K are from interpolated and smoothed measured values given in Table I of Flubacher et al. (1960), according to the top of Fig. 1. Units are K for T and $J K^{-1} kg^{-1}$ for c_p (with $4.184 J cal^{-1}$ and a molar mass of $0.01801528 kg mol^{-1}$ to transform values of Flubacher et al. (1960) into unit of $J K^{-1} kg^{-1}$). The value at 273.15 K (2096.70) is linearly extrapolated from those at 270 and 273 K.*

$c_p(T)$ for H_2O (ice-Ih) - Unit of $J K^{-1} kg^{-1}$

T	c_p	T	c_p	T	c_p
0	0	28	208.54	160	1293.51
2	0.0784	30	230.66	170	1361.21
4	0.6624	40	337.89	180	1429.53
6	2.506	50	437.49	190	1498.57
8	6.917	60	532.56	200	1568.35
10	14.80	70	623.92	210	1638.86
12	27.42	80	711.48	220	1710.03
14	44.32	90	794.93	230	1781.79
16	64.72	100	874.14	240	1854.08
18	87.01	110	949.38	250	1926.83
20	111.43	120	1021.30	260	1999.98
22	135.34	130	1090.80	270	2073.48
24	160.36	140	1158.82	273	2095.59
26	185.43	150	1226.18	(273.15)	(2096.70)

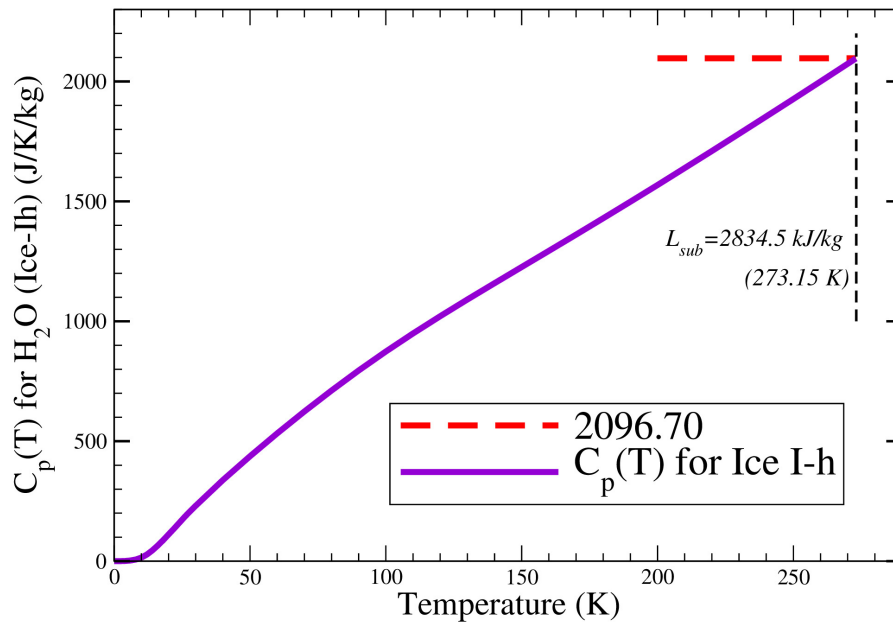
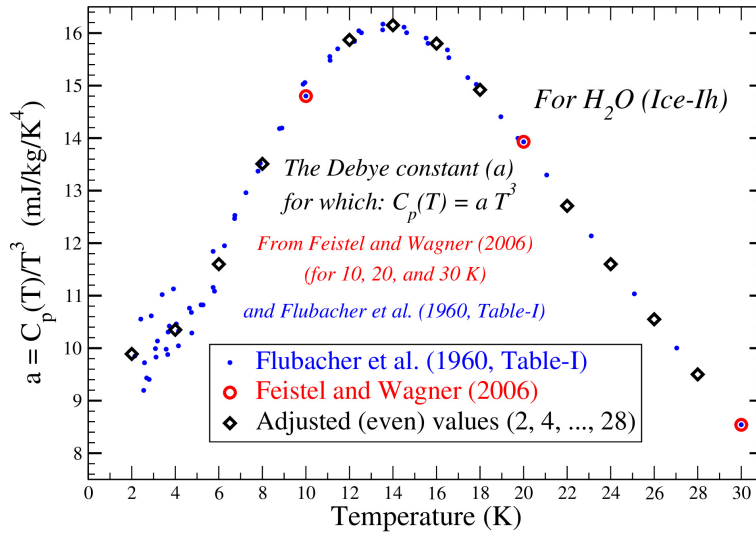


Figure 1: Top: the Debye's constant for H_2O . Bottom: the specific heat at constant pressure $c_p(T)$ (in $J/K/kg$) for H_2O (Ice-Ih) and corresponding to the Table 2.

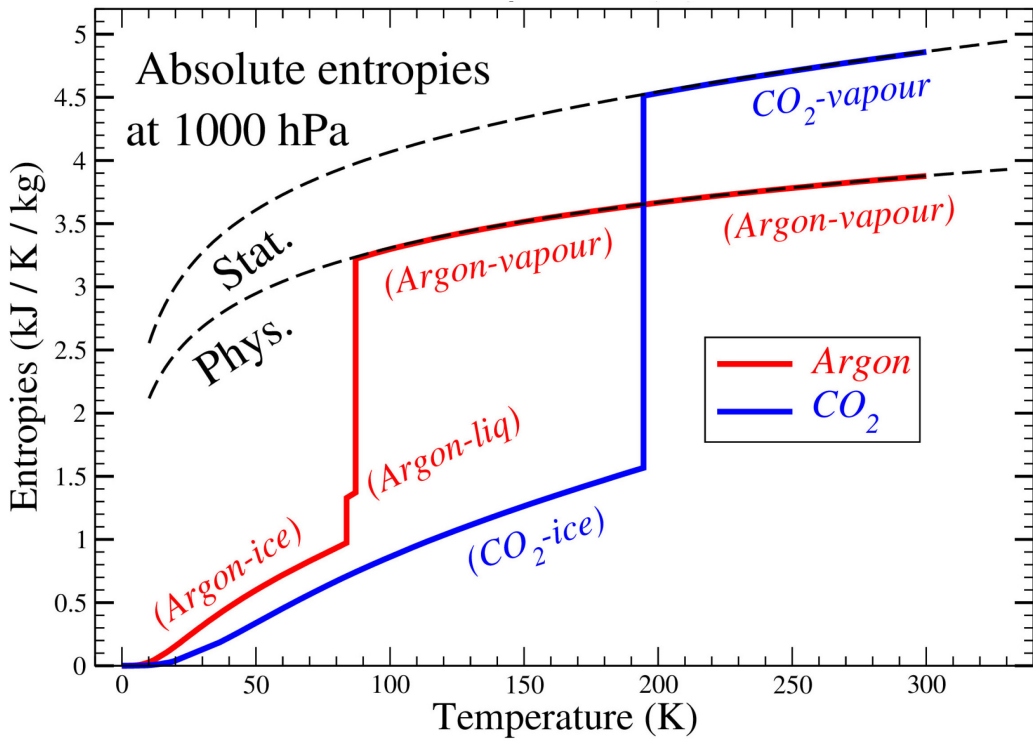
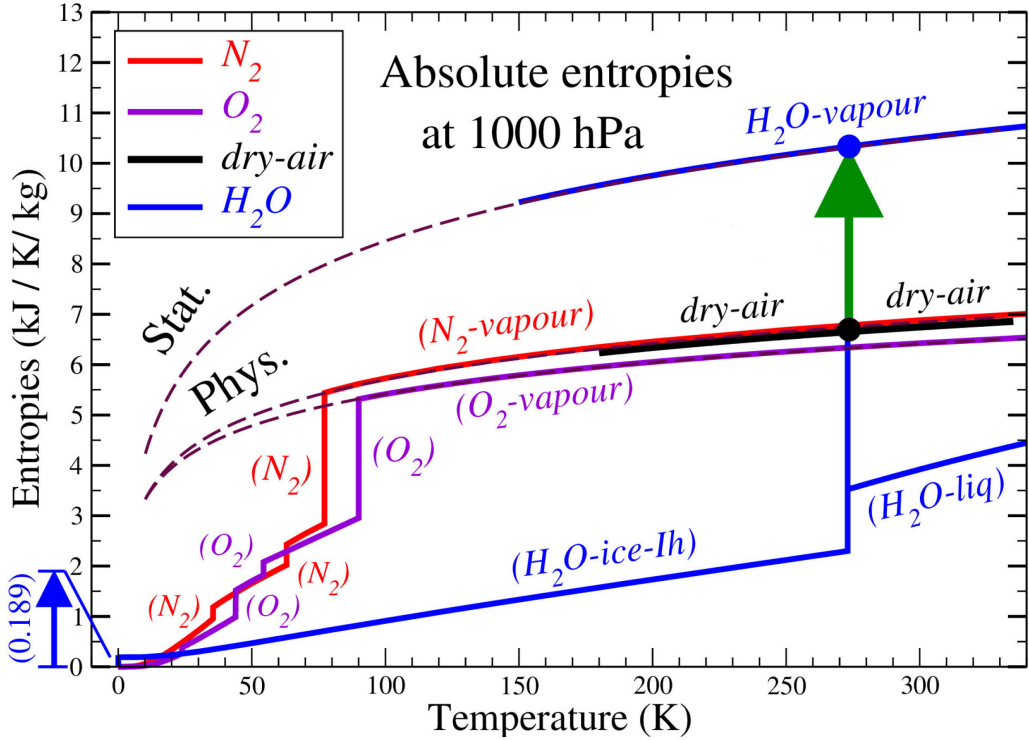
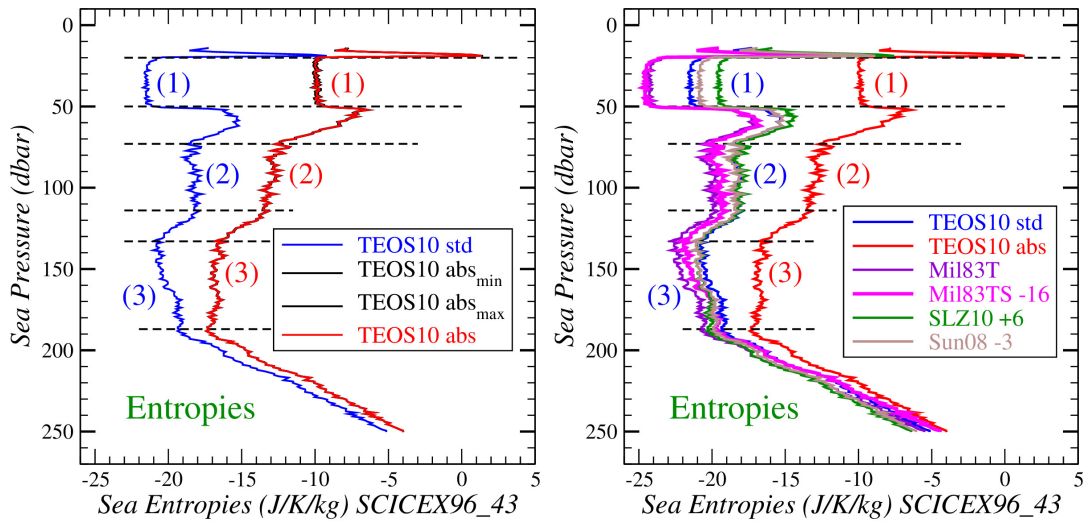
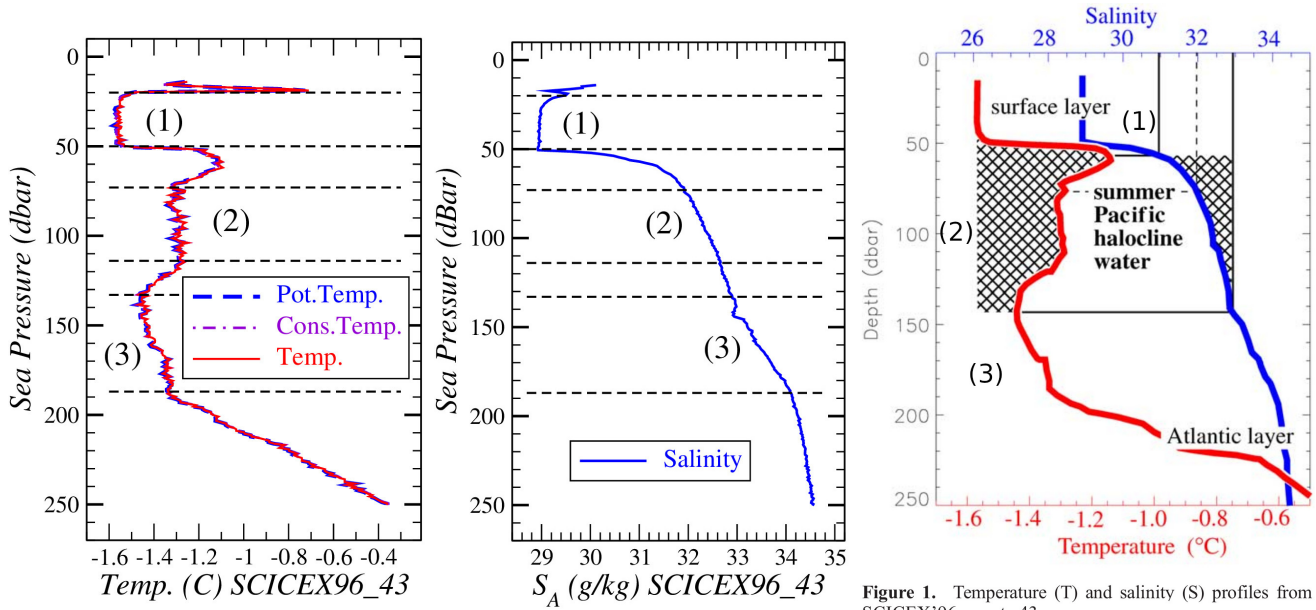


Figure 2: Entropies for dry-air (N_2 , O_2 , Ar, CO_2 and water H_2O) species plotted against the absolute temperature and computed at 1000 hPa. The calorimetric method $\left(\int_0^T c_p(T') d\ln(T') + \sum_j L(T_j)/T_j\right)$ corresponds to the coloured solid lines. The third-law hypothesis is applied at 0 K with zero entropies for all the solid phases, but with the residual entropy of $189 \text{ J kg}^{-1} \text{ K}^{-1}$ for ice-Ih. The vertical jumps correspond to phase changes at T_j with the phase-change enthalpies $L(T_j)$ between solids phases (for N_2 and O_2), then from solid to liquid phases, then from liquid to vapour phases. The statistical-physic values (black dashed lines) are computed from $S = k \ln(W)$ and $F = -kT \ln(Z)$ for the vapour phases according to the method described in Chase (1998) for translational, rotational, vibrational and electronic partition functions (Z).



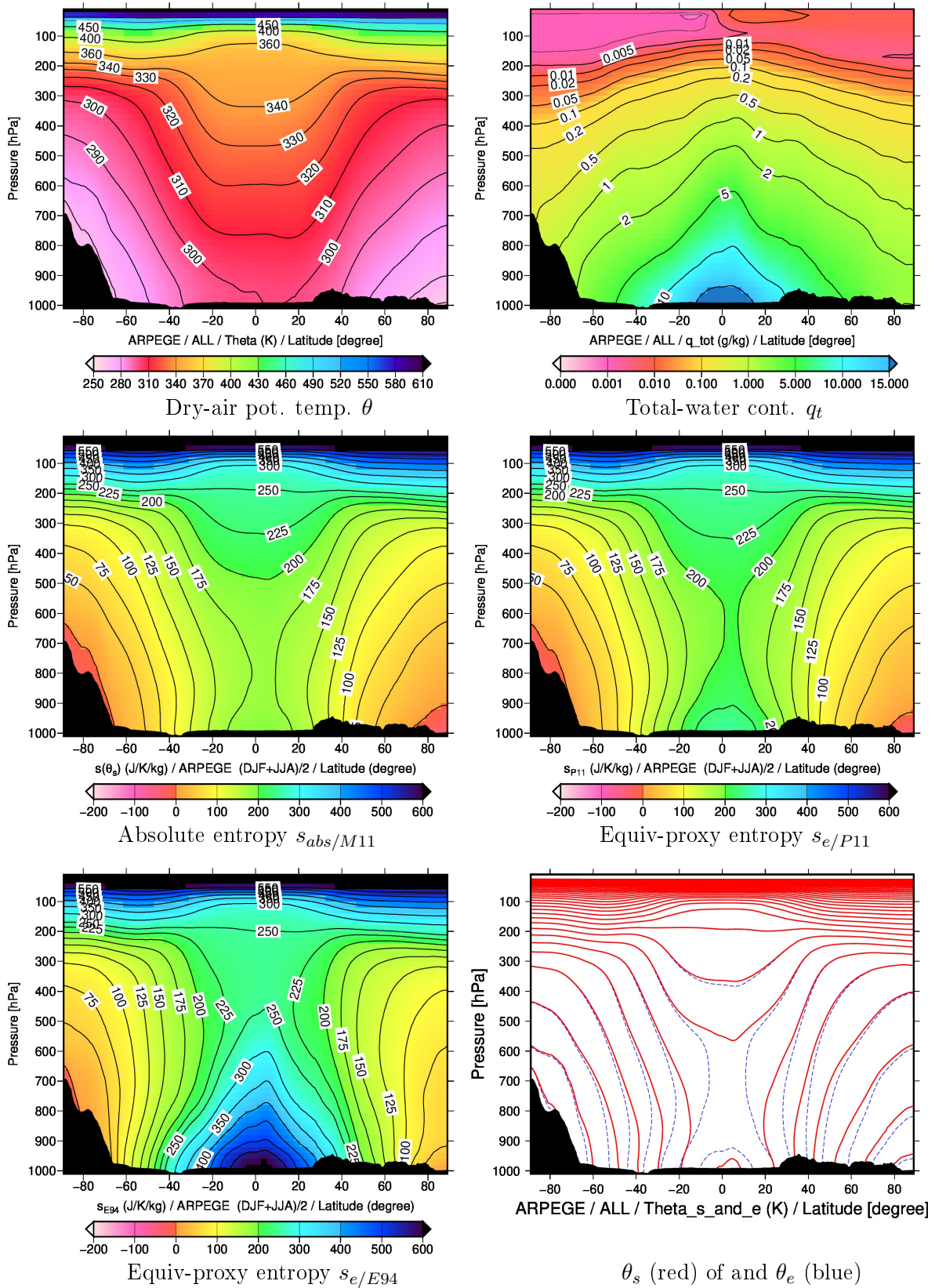


Figure 4: The mean winter+summer latitudes-pressure charts for: **Top:** the dry-air potential temperature (θ) and total water content (q_t); **Middle:** the absolute entropy ($s_{abs}/M11$) of Marquet (2011) and equivalent-proxy 'entropy' ($s_e/P11$) of Pauluis (2011); **Bottom:** the equivalent-proxy 'entropy' ($s_e/E94$) of Emanuel (1994) and a comparison of the absolute θ_s (in red) and equivalent-proxy θ_e (in blue) potential temperatures.

Moist-air entropy at the Mauna Loa laboratory

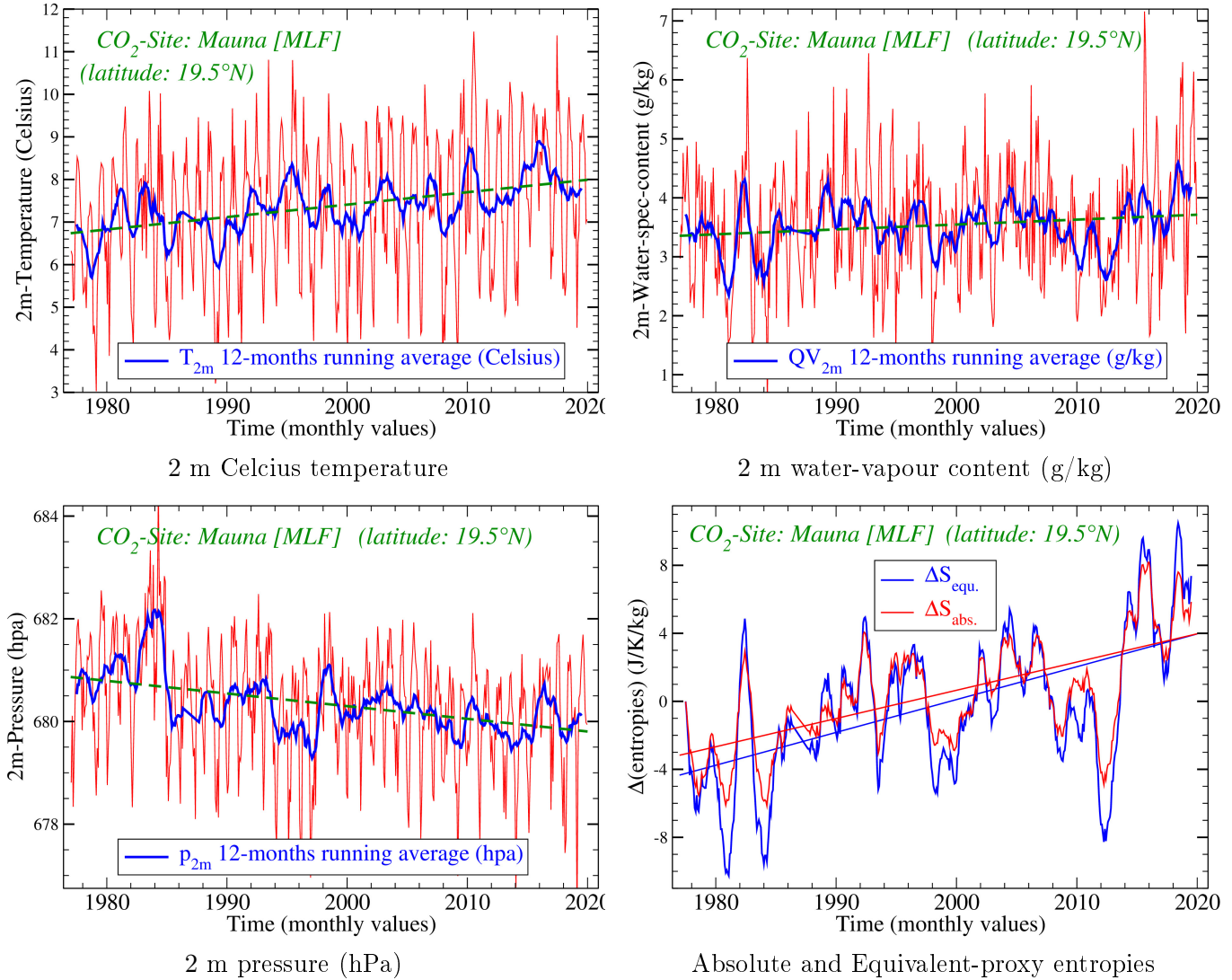


Figure 5: Evolution between 1978 and 2019 of monthly mean (in red) and 12-months running average (in blue) values at the Mauna-Loa observatory computed from the hourly average values of: the basic properties $T(2m)$ (in °C), $q_v(2m)$ (in g/kg) and $p(2m)$ (in hPa), together with the change (with respect to 2019 values) in the absolute entropy (from Marquet, 2011, with $\Lambda_r \approx +6$) and the equivalent-proxy ‘entropy’ (from Pauluis, 2011, with $\Lambda_r \approx +9$).

Climate Change of the moist-air entropy

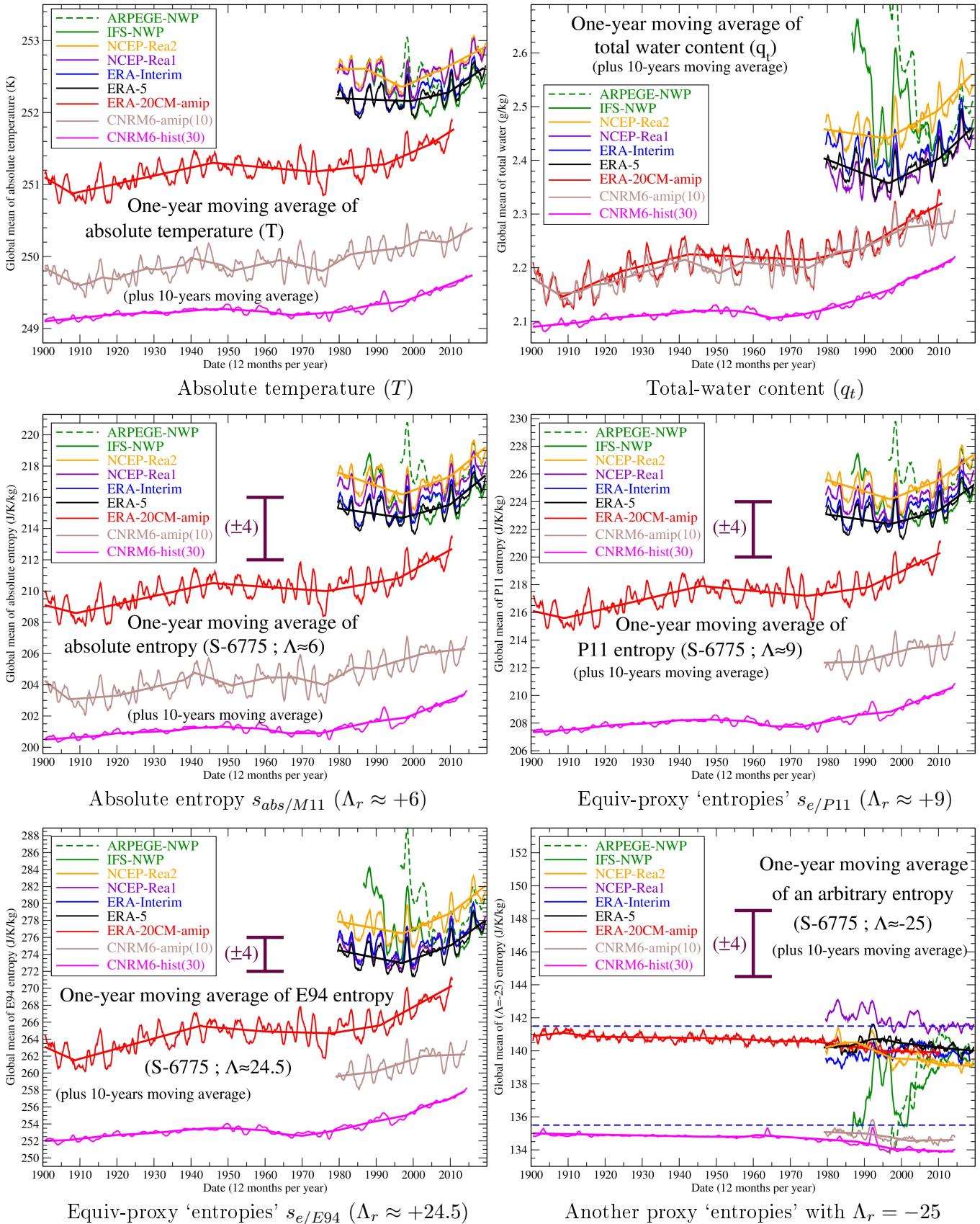


Figure 6: Evolution since 1900 of the basic properties T and q_t , the absolute entropy (from Marquet, 2011, with $\Lambda_r \approx +6$) and other equivalent-proxy 'entropies' from (from Pauluis, 2011; Emanuel, 1994, with $\Lambda_r \approx +9$ and $+24.5$), together with another arbitrary definition of the moist-air 'proxy-entropy' based on $\Lambda_r = -25$. Datasets from: two NWP models (IFS and ARPEGE); two NCEP reanalyses (1 and 2); three IFS-ERA reanalyses (Interim, 5 and 20CM-amip); two CNRM-CM6 GIEC simulations (ARPEGE, amip and historical).

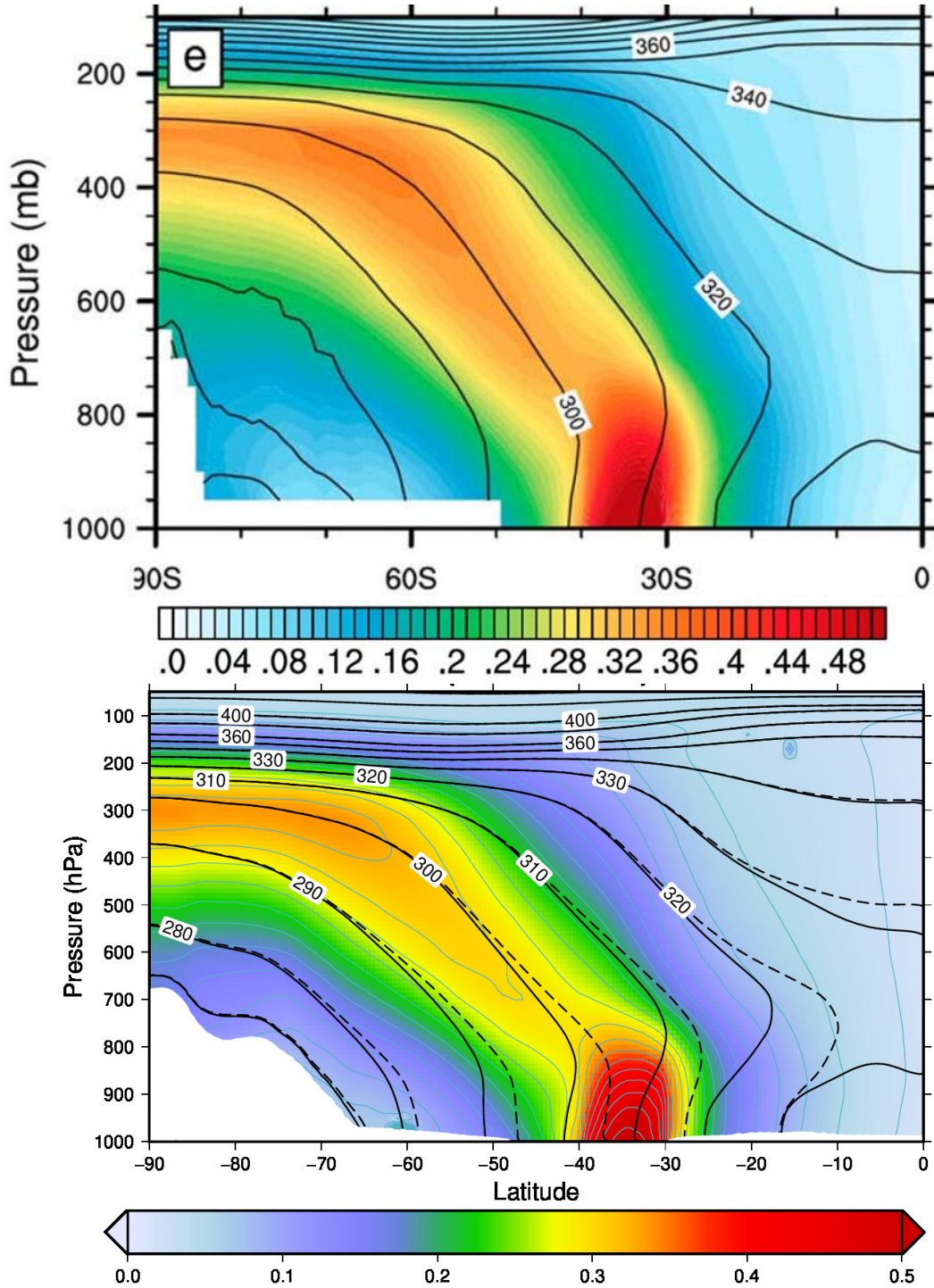


Figure 7: **Top:** The Fig.1 (e) of Bailey et al. (2019, *Geoph. Res. Let.*, 46 (13) p.7819-7827) showing the moisture plume evaporating from the latitude band 30°S to 40°S with the isentropes computed using θ_e (K). All variables come from a coupled CAM5-CLM4 simulation with prescribed sea surface temperatures, sea ice, greenhouse gases, and aerosols for the years 2000 – 2014. **Bottom:** the same $\text{proxi-}\theta_e$ (solid) lines plus the new absolute moist-air entropy potential temperature θ_s (dashed) lines published in Marquet and Bailey (2021).

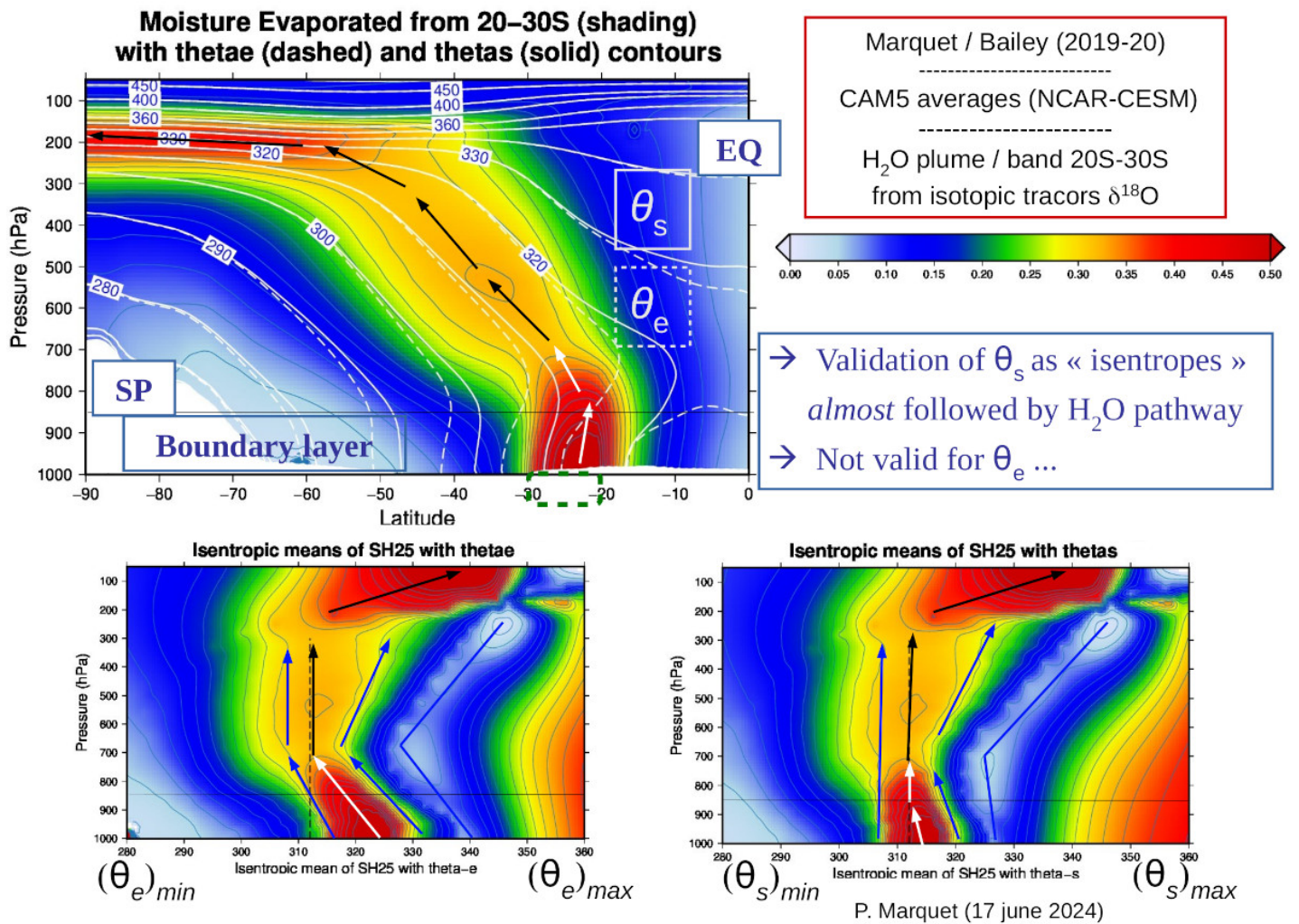


Figure 8: **Top:** The same as Fig. 7, but for the plume for the band 20°S to 30°S. **Bottom:** the “isentropic-means” version of this plume, for both the “equivalent entropy-proxy” potential temperature θ_e (on the left, the same as TEOS10) and the “absolute entropy” potential temperature θ_s (on the right). These figures show that the plume preferentially follows the absolute moist-air isentropes (θ_s) in the boundary layer, and not the (dashed) isolines for the (TEOS10) “equivalent entropy-proxy” potential temperature (θ_e).

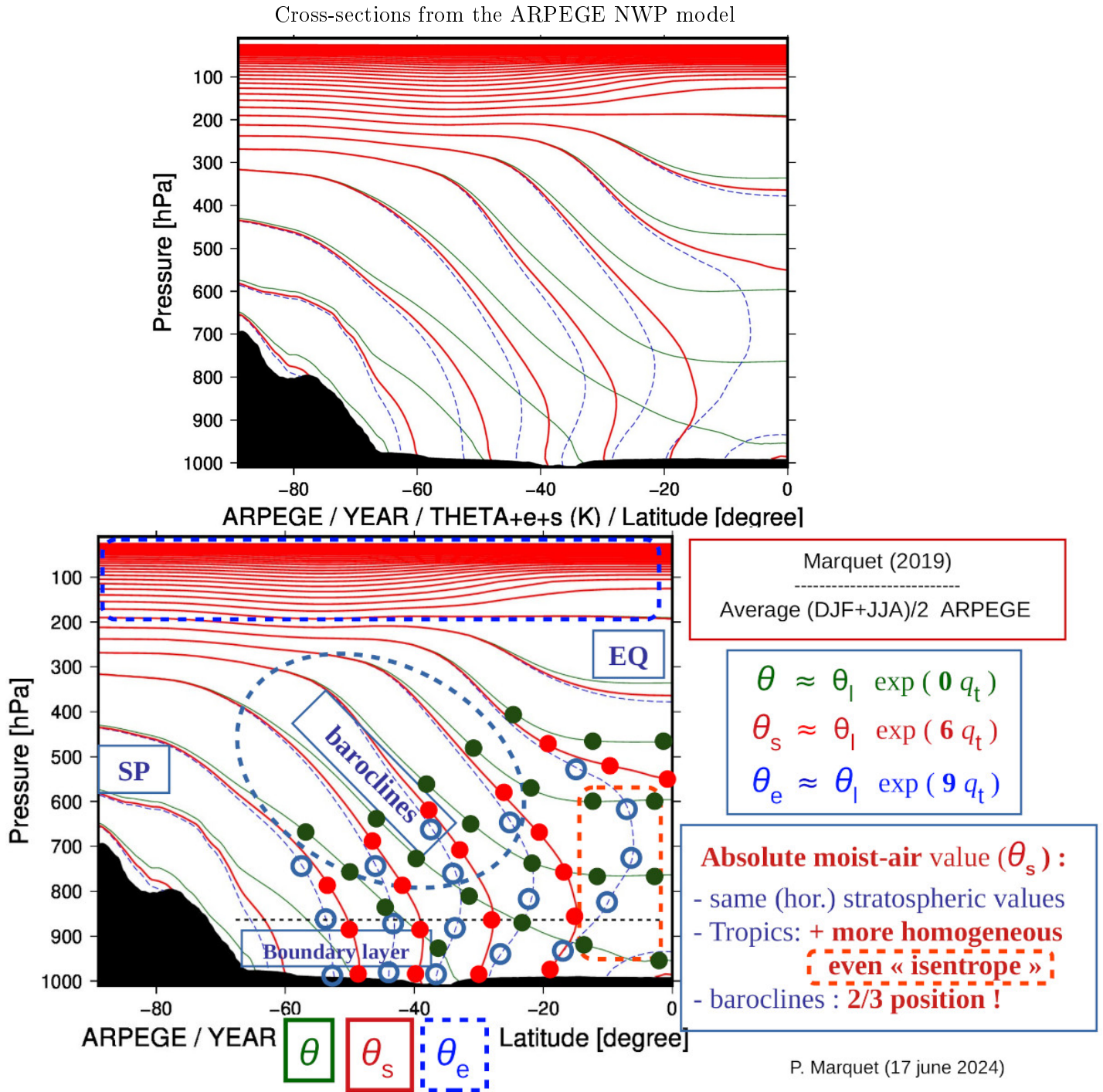


Figure 9: A (south-hemisphere) latitude-pressure cross-section I have plotted from mean winter+summer conditions and from outputs from the French operational ARPEGE NWP model. **Top:** a rough version of the figure. **Bottom:** an annotated version showing the large differences between the “equivalent entropy-proxy” potential temperature θ_e dashed-blue lines (the same as TEOS10); the “liquid-water entropy-proxy” potential temperature θ_l solid-green lines; the “absolute entropy” potential temperature θ_s solid-red lines.

Gibbs (1875-1878, p.211) explained that: “*when the scope of our investigations is not thus limited (namely for a variable composition of gases), we may have determined the states of the substance of the gas for which $e_i = 0$ and $s = 0$ with reference to some other form in which the substance appears, or, if the substance is compound, the state of its components for which $e_i = 0$ and $s = 0$ may be already determined ; so that the constants E and H cannot in general be treated as arbitrary*” (see the Fig. 10). The aim of Gibbs (p.215) was then to “*obtain corresponding fundamental equations for a mixture of gases, in which the proportion of the components shall be variable*” (see Fig. 10). Gibbs arrived at the definitions of the entropy, free energy and free enthalpy of a mixture of ($k = 1, \dots, n$) ideal gases in equations 278, 279 and 293, respectively (pages 217 and 224), with for the entropy an equivalent of:

$$\eta = s(T, p, q_k) = \sum_k q_k c_{pk} \ln(T/T_0) - \sum_k q_k R_k \ln(p_k/p_0) + \sum_k \boxed{q_k s_{0k}(T_0, p_0)}. \quad (25)$$

Gibbs then explained (p.217) that “*if we regard the proportion (q_k) of the various ($k = 1, \dots, n$) components as constant, (...) the value of (...) $\sum_k q_k s_{0k}$ will then be constant.*”

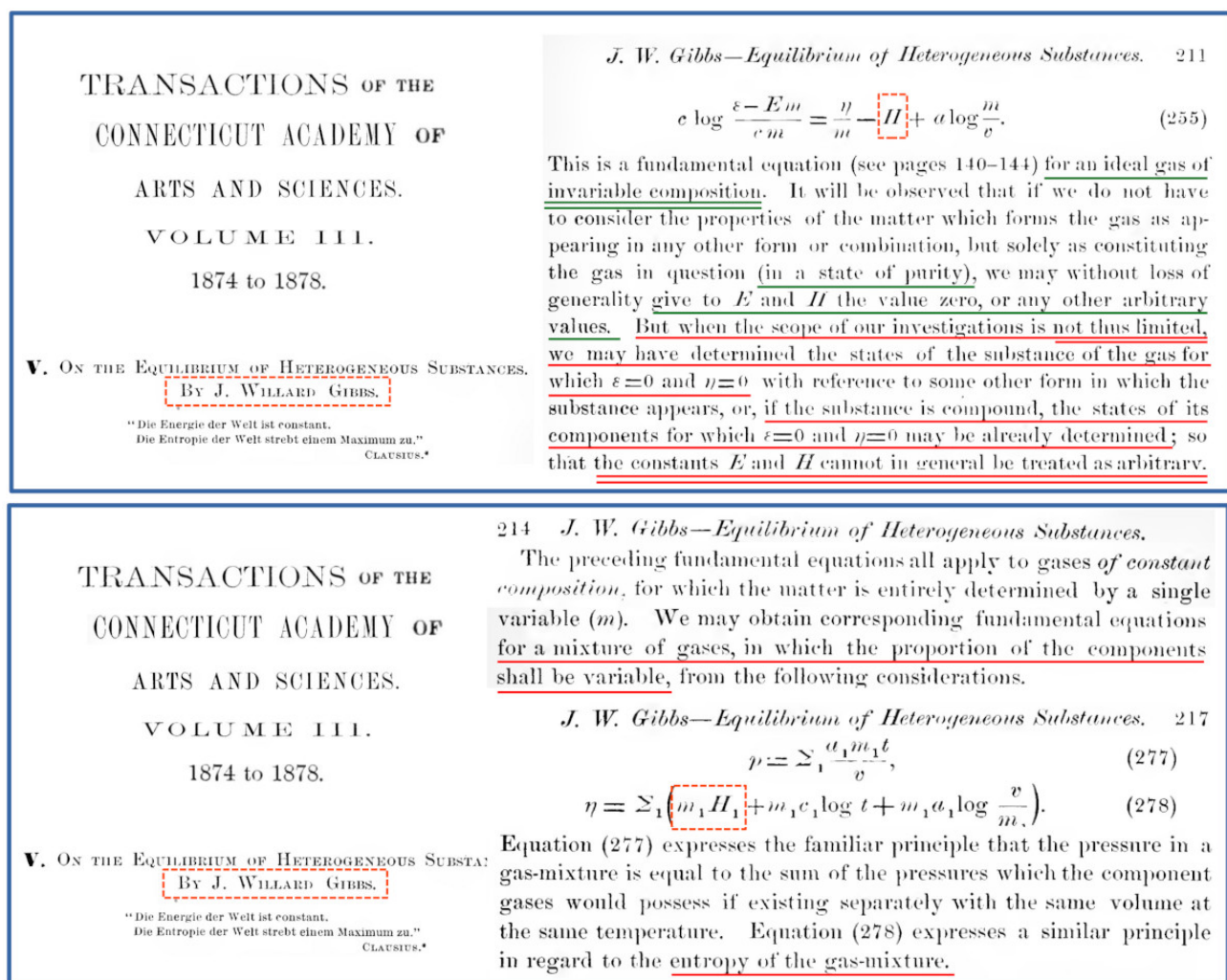


Figure 10: Excerpts from the fundamental papers of Gibbs (1875-1878), where the entropy (noted “ η ” by Gibbs) of a given gas (top) and for a mixture of gases (bottom) are defined, together with the need to determine the constant of integration (where “... H cannot in general be treated as arbitrary”), noted $\sum_1 m_1 H_1$ by Gibbs in (278) and corresponding to $\sum_k q_k s_{k0}$ with modern notations.

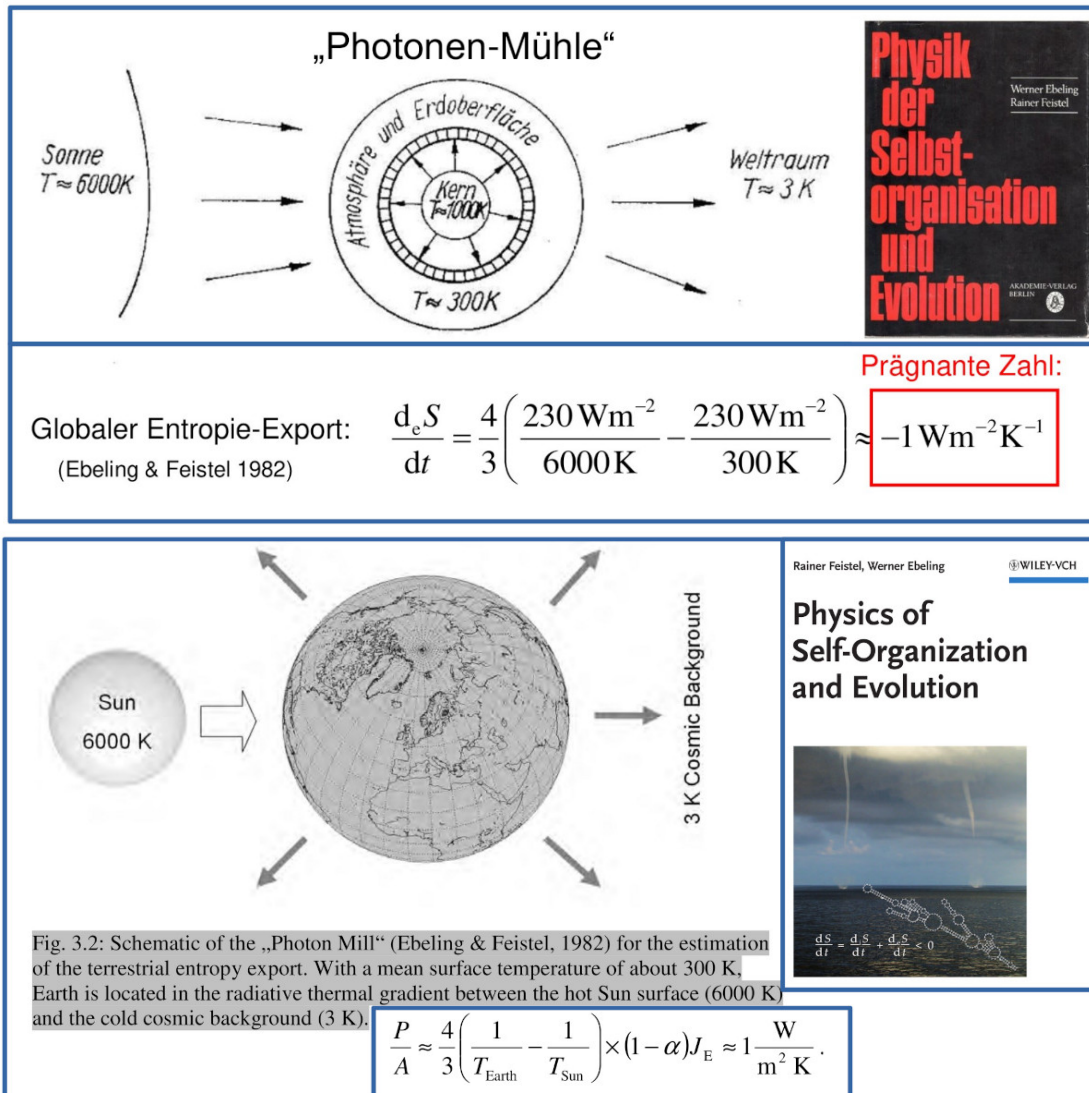


Figure 11: **Top:** The *Photonen-Mühle* (*Photon-Mill*) vision of Ebeling and Feistel (1982) as recalled in Feistel (2016); **Bottom:** The same *Photon Mill* vision (re-)published in Feistel and Ebeling (2011, p.97).

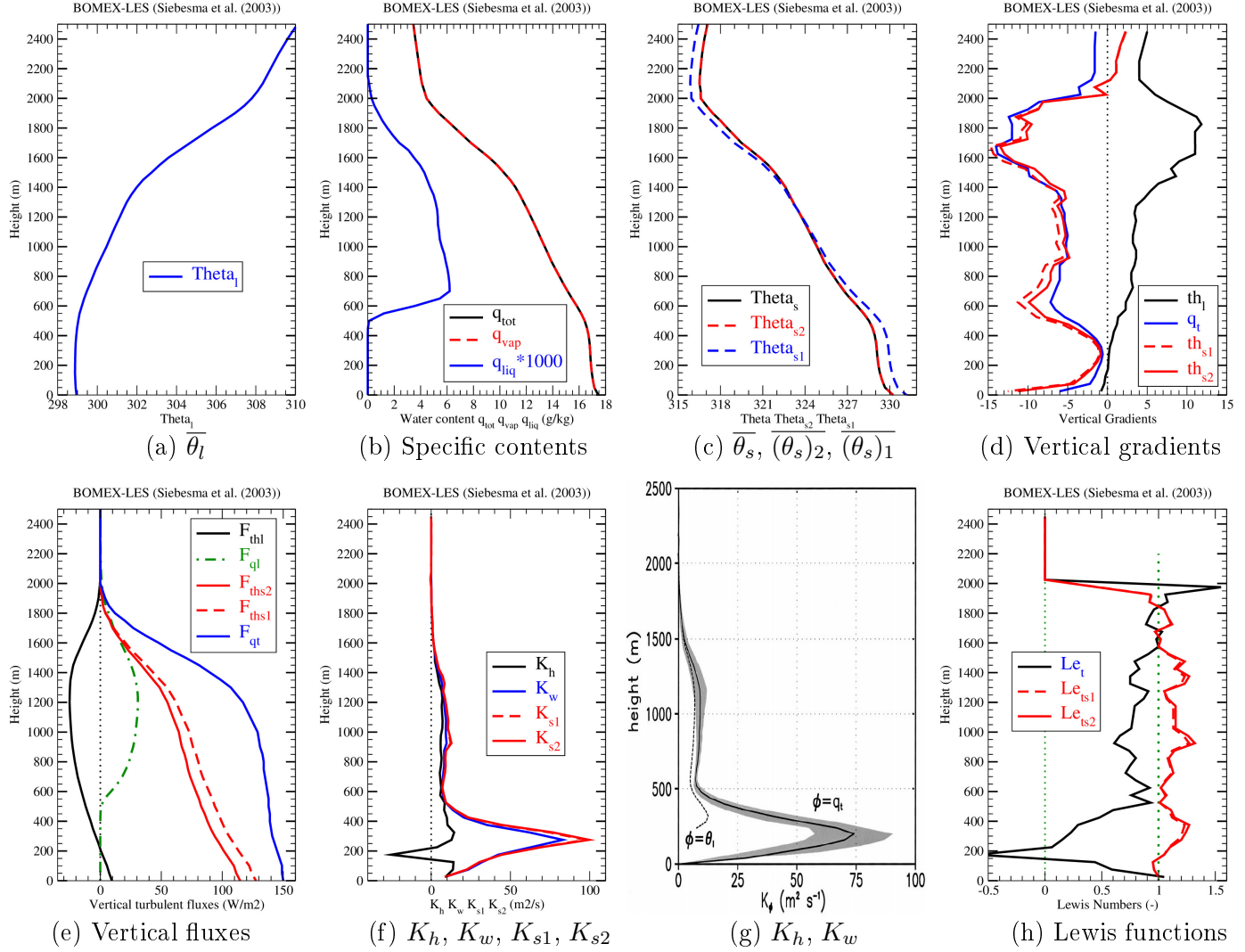


Figure 12: Vertical profiles (last 3 hours) of LES outputs from digitized datasets for the BOMEX case published in Siebesma et al. (2003), with the Fig. 3 of that 2003 paper reproduced in (g) for $K_h = K(\phi = \theta_l)$ and $K_w = K(\phi = q_t)$.

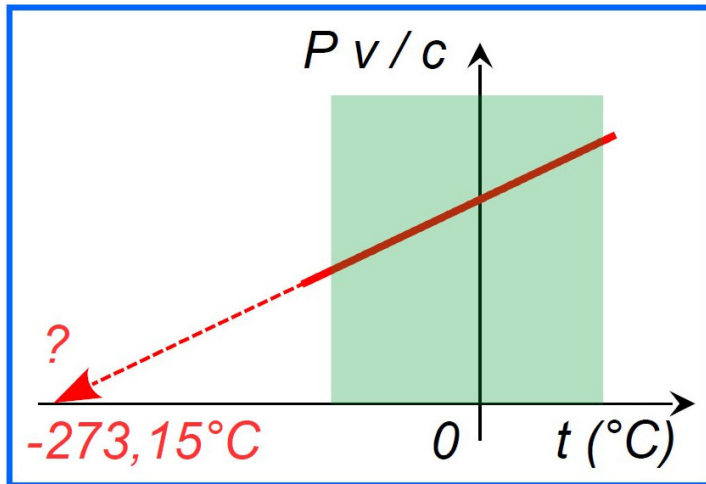


Figure 13: (The Fig. 1 in Marquet, 2019b): We draw here the quantity “ Pv/c ” as a function of the temperature “ t ” in Celsius. The usual range of atmospheric temperatures is drawn in green. The result is of the form “ $(t + a)$ ”. It is therefore a straight line that can be prolonged (in dashed lines) up to the ordinate “ $Pv/c = 0$ ”, where the temperature was “ $-a \approx -1/0.00375 \approx -266.7$ ” degrees after Gay-Lussac (1802) and in Carnot (1824), $-a \approx -1/0.00366 \approx -273.2$ degrees after Regnault (1847) and Thomson (1848), and set to -273.15 degrees in the modern Kelvin scale of temperature.

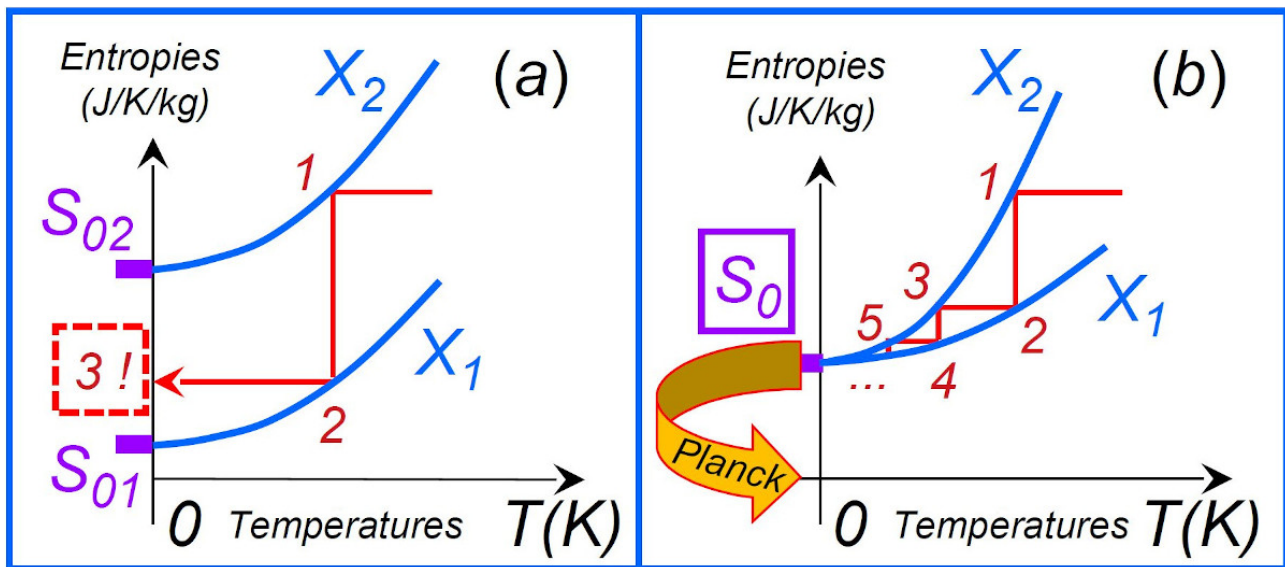


Figure 14: (The Fig. 3 in Marquet, 2019b): The unattainability of absolute zero temperature derived by Nernst (1912), with $S_{02} \neq S_{01}$ and $T = 0$ K reached in 3 steps in (a) becoming $S_{02} = S_{01} = S_0$ and $T = 0$ K unreachable in (b); with in (b) the additional “third-law” hypothesis of Planck (1917): S_0 becoming a “universal constant” set to $S_0 = 0$ at 0 K for the entropy of the most stable crystalline phase of all solids.

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