

# Supplementary Materials showing the computations of absolute enthalpies and entropies for atmospheric components (N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and H<sub>2</sub>O) and for sea-salts anions and cations.

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## 1 Introduction

This document contains Supplementary Material to the papers where I have studied the absolute third-law values for the moist-air atmospheric and seawater oceanic entropy and/or enthalpy.

The aim of the next sections is to show the detailed computations of entropies and enthalpies, with:

- in the Section 2 is shown a synthesis of the results for the entropies and enthalpies of the atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and dry air;
- in the Section 3 are shown the detailed computations of the calorimetric absolute (third-law) entropies for the atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>;
- in the Section 4 are shown the detailed computations of the statistical-quantum absolute (third-law) entropies for the atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>;
- in the Section 5 are shown the detailed computations of the calorimetric (third-law) absolute enthalpies for the atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>;
- in the Section 6 are shown the detailed computations of the statistical-quantum (third-law) differences from 0 K enthalpies for the atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>;
- in the Section 7 are shown the Figures of the specific heats at constant pressure  $c_p(T)$  plotted against the absolute temperature  $T$  for the atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>;
- in the Section 8 are shown the Tables of numerical values of  $c_p(T)$  for the same atmospheric elements H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>;
- in the Section 9 are shown the detailed computations of the dry-air entropy and enthalpy;
- in the Section 10 are shown the absolute entropies of sea-salts cations and anions (historical background; values published in Latimer's papers and in the book by Lewis and Randall, 1961);
- in the Section 11 are listed the basic constants used throughout the paper (fundamental constants, composition of the dry air);
- in the Section 12 are shown several existing validations and physical meaning of the absolute entropies, together with answers to several FAQ.

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## 2 A synthesis of atmospheric gases absolute entropies and enthalpies

• The calorimetric absolute entropies is computed in the Section 3 at the standard temperatures  $T_0 = 273.15$  K (0°C), 273.16 K (triple point) or 298.15 K (25°C) and the standard pressures  $p_0 = 1000$  hPa or 1013.25 hPa, via the relationship

$$S(T_0, p_0) = \overbrace{S_0(T=0)}^{\text{Residual?}} + \int_0^{T_0} \frac{c_p(T)}{T} dT + \sum_{k=1}^n \frac{L_k(T_k)}{T_k} - R \ln \left[ \frac{p_0}{p_{\text{sat}}(T_n)} \right], \quad (1)$$

where  $T$  is the absolute temperature,  $c_p(T)$  are the specific heats at constant pressure,  $L_k(T_k)$  are the different latent heats of change of phases (from solids to liquid to vapour states) at the temperatures  $T_k$ , and  $p_{\text{sat}}(T_n)$  is the saturation pressure of the vapour state at the chosen vaporization or sublimation temperature  $T_n$ .

The first term  $S_0(T=0)$  in (1) is the possible residual entropy existing at 0 K for some molecules, like H<sub>2</sub>O for which hydrogen bonds generate the Pauling-Nagle entropy of about  $R \ln(3/2)$ . For the other atoms and molecules N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>, there is no residual entropy.

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• The quantum-statistical absolute entropies are computed in the Section section 4 by using the Boltzmann-Planck formula

$$S(T_0, p_0) = \overbrace{(\dots 0 \dots)}^{(\text{no residual})} + R \ln(W), \quad (2)$$

where  $W$  is the number of configuration in the quantum phase space, due to the

- translational (for all atoms and 2D or 3D molecules);
- rotational (for 2D and 3D molecules);
- vibrational (for 2D and 3D molecules); and
- electronic (for O<sub>2</sub> only)

degrees of freedom of the atoms (Ar), 2D molecules (N<sub>2</sub>, O<sub>2</sub> and linear CO<sub>2</sub>) or 3D molecules (H<sub>2</sub>O), and without any (residual) additional constant. In particular, the translational quantum-statistical absolute entropies is computed via the partition function noted  $Q_t$  and with the relationships:

$$Q_t = \frac{V}{(L_t)^3} = \frac{V (2\pi m k_B)^{3/2}}{h^3} T^{3/2}, \quad (3)$$

$$\text{where } L_t = \frac{h}{\sqrt{2\pi m k_B T}} \text{ is the "quantum thermal wavelength"}, \quad (4)$$

$$\text{with } S_{\text{trans}} = k \left[ \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) + T \frac{d}{dT} \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) \right] \text{ for } N_A \text{ molecules}, \quad (5)$$

$$\text{and thus with } S_{\text{trans}} = R_* \left[ \ln(Q_t) + T \frac{d \ln(Q_t)}{dT} \right] - k \ln(N_A!). \quad (6)$$

The additional impact of other degrees of freedom (rotational, vibrational and electronic) are computed via the relationship

$$\Delta S_{r/v/e} = R_* \left[ \ln(Q_{r/v/e}) + T \frac{d \ln(Q_{r/v/e})}{dT} \right], \quad (7)$$

where  $Q_{r/v/e}$  are the corresponding partition functions.



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- The third-law calorimetric absolute enthalpies for atoms and molecules are computed in the Section 5 at  $T_0 = 273.15$  K with the formula:

$$h(T_0) = \overbrace{h(T=0)}^{(=0)} + \int_0^{T_0} c_p(T) dT + \sum_k L_k(T_k). \quad (8)$$

The integral in (8) must be computed for all values of the specific heat at constant pressure  $c_p(T)$  between 0 K and  $T_0 = 273.15$  K (see the Tables BI and BII, p.81, in Marquet, 2015a) and with a third-law hypothesis  $h(T=0) = 0$  similar to the one made for the absolute entropies of the more stable state of solids. The last summation in (8) must be extended over all the possible changes of phases occurring at the temperatures  $T_k \leq T_0$  between solid(s), liquid and vapour states.

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- The third-law quantum-statistical difference in enthalpies  $H - H_0$  are computed for atoms and molecules in the Section 6 at  $T_0 = 273.15$  K, in particular with the translational part  $Q_t$  given by (3) leading to:

$$H_{\text{trans}}(T) - H_0 = R_* T^2 \left[ \frac{\partial \ln(Q_t)}{\partial T} \right]_V + R_* T V \left[ \frac{\partial \ln(Q_t)}{\partial V} \right]_T, \quad (9)$$

$$H_{\text{trans}}(T) = H_0 + \frac{5}{2} R_* T = H_0 + \Delta H_{\text{trans}}(T), \quad (10)$$

where  $H_0$  is a constant to be determined and which (a priori) depends on the gas under consideration. The additional impact of other degrees of freedom (rotational, vibrational and electronic) are computed via the relationship

$$\Delta H_{\text{r/v/e}}(T) = R_* T^2 \left[ \frac{\partial \ln(Q_{\text{r/v/e}})}{\partial T} \right]_V + R_* T V \left[ \frac{\partial \ln(Q_{\text{r/v/e}})}{\partial V} \right]_T, \quad (11)$$

where  $Q_{\text{r/v/e}}$  are the corresponding partition functions.

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- The way the dry-air entropy and enthalpy values are computed is described in the Section 9.

The values of absolute reference entropy and enthalpy for water vapor and dry air used in Hauf and Höller (1987), Marquet (2011a), Marquet (2015a) and Stevens and Siebesma (2020) were based on a dry-air reference values computed as a weighted sum of the reference values for  $\text{N}_2$  and  $\text{O}_2$  (see the Table 1).

The last two columns in the Table 1 correspond to the absolute entropy computations I have made between 2022 and 2025 for both the statistical physics and calorimetric formulations (see the Sections 3 and 4), with a more realistic composition including the four gases  $\text{N}_2$ ,  $\text{O}_2$ , Ar and  $\text{CO}_2$ .

I show in the Table 2 comparisons between my personal computations and the NIST JANAF-4 (Chase, 1998) absolute entropy values.

The impacts on the dry-air absolute entropy and enthalpy of changes in time of the concentration of  $\text{CO}_2$  (from 380 to 440 ppmv, and more and more) are shown in the Section 9.

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- It is worthwhile to note that, as recalled in the Table 3, all reference absolute entropies for the atmospheric gases  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  were already available in old Thermodynamics Tables, such as: Kelley (1932), Rossini et al. (1952), Lewis and Randall (1961), Wagman et al. (1965), Robie et al. (1978) and Gokcen and Reddy (1996). They are now accurately determined and available in NIST-JANAF Tables (Chase, 1998), with the same values retained for instance in Atkins and de Paula (2014).

**Specific absolute entropies at  $T_{\text{std}} = 273.15 \text{ K}$  (or  $0^\circ\text{C}$ ) and  $p_{\text{std}} = 1000 \text{ hPa}$ .**

	HH87	LEM00	M11	SS20	M25-Stat	M25-Calor ( $\delta$ )
Water vapor ( $s_{v0}$ )	10320	(-)	10320	10321	$10317.92 \pm 0.63$	$10319.9 \pm 13$ (+2.0 or 0.02 %)
Dry air ( $s_{d0}$ ) <sub>400ppmv</sub>	6775	$6776.6^{(1)}$	6775	6783	$6776.34 \pm 0.49$	$6783.0 \pm 23$ (+6.6 or 0.10 %)
$s_0(T_0, p_0)$ for $\text{N}_2$	(-)	$6748.7^{(2)}$	(-)	(-)	$6748.87 \pm 0.34$	$6754.5 \pm 19$ (+5.6 or 0.08 %)
$s_0(T_0, p_0)$ for $\text{O}_2$	(-)	$6330.8^{(2)}$	(-)	(-)	$6330.86 \pm 0.33$	$6341.3 \pm 37$ (+10.4 or 0.16 %)
$s_0(T_0, p_0)$ for Ar	(-)	$3830.5^{(2)}$	(-)	(-)	$3830.59 \pm 0.30$	$3832.7 \pm 2.5$ (+2.1 or 0.06 %)
$s_0(T_0, p_0)$ for $\text{CO}_2$	(-)	(-)	(-)	(-)	$4786.17 \pm 0.24$	$4780.6 \pm 12$ (-5.6 or -0.12 %)

Table 1: *Standard entropies  $s_0(T_0, p_0)$  (in  $\text{J/K/kg}$ ) for dry air and water vapour at  $T_0 = 273.15 \text{ K}$ ,  $p_0 = 1000 \text{ hPa}$  and 400 ppmv of  $\text{CO}_2$ . Data from: Hauf and Höller (1987, HH87), Lemmon et al. (2000, LEM00), Marquet (2011a, M11), Stevens and Siebesma (2020, SS20), personal Statistical Physics 2022 computations (M25-Stat) from Chase (1998, NIST-JANAF-4) and personal calorimetric 2022 computations (M25-Calor). In the last column ( $\delta$ ) is the (absolute and relative) difference between the calorimetric method compared to the (more accurate) statistical-physics formulation, namely:  $\delta = (\text{M25-Calor}) - (\text{M25-Stat})$ .*

- <sup>(1)</sup> The entropy of Lemmon et al. (2000) interpolated at the temperature 273.15 K from Table A2 p.367 is about 196.114 J/K/mol at the standard pressure 1013.25 hPa, leading to 6772.22 J/K/kg. The value at 1000 hPa is obtained by adding “ $-287.05 \ln(1000/1013.25)$ ”  $\approx 3.78 \text{ J/K/kg}$ .
- <sup>(2)</sup> The entropy of Lemmon et al. (2000) given (p.334-335) in J/K/mol at 298.15 K and 1013.25 hPa are converted in J/K/kg and transformed to values at 273.15 K and 1000 hPa by adding “ $C_p \ln(273.15/298.15) - R \ln(1000/1013.25)$ ,” with mean values of  $C_p$  and  $R$  between 298.15 K and 273.15 K, depending on the gas.

**Specific absolute entropies at  $T_{\text{std}} = 298.15 \text{ K}$  (or  $25^\circ\text{C}$ ) and  $p_{\text{std}} = 1000 \text{ hPa}$ .**

Standard entropies:	Stat. (Chase, 1998)	Calor. (Gokcen and Reddy, 1996)	Calor. (section 3.5)
$\text{N}_2$ (vap)	$6839.9 \pm 0.7$	$6861 \pm 30$	$6846 \pm 20$
$\text{O}_2$ (vap)	$6411.1 \pm 1$	$6423 \pm 13$	$6422 \pm 37$
Argon (vap)	$3876.2 \pm 0.1$	$3878 \pm 21$	$3878.4 \pm 2.5$
$\text{CO}_2$ (vap)	$4857.9 \pm 2.7$	$4861 \pm 10$	$4854 \pm 12$
dry-air (vap)	$6864.4 \pm 0.8$	$6883 \pm 26$	$6871 \pm 24$
$\text{H}_2\text{O}$ (vap)	$10482 \pm 2.3$	$10477 \pm 35$	$10482 \pm 13$

Table 2: *Absolute values of the vapour thermal entropies for gaseous  $\text{N}_2$ ,  $\text{O}_2$ , Argon,  $\text{CO}_2$ , dry-air and  $\text{H}_2\text{O}$  at  $T_{\text{std}} = 298.15 \text{ K}$  (or  $25^\circ\text{C}$ ) and  $p_{\text{std}} = 1000 \text{ hPa}$  (in units of  $\text{J K}^{-1} \text{ kg}^{-1}$ ). The first column shows the values from Chase (1998, NIST-JANAF4) computed by using the method of statistical physics based on the third law of thermodynamics included in the relationship  $S = k \ln(W)$  and the partition functions for translational, rotational, vibrational and electronic degrees of freedom. The second column shows the values from (Gokcen and Reddy, 1996, Table 7.1, p.114) computed from (1), and thus with the Calorimetric method and the third law value  $S(T = 0)$  valid for all gases except for  $\text{H}_2\text{O}$ , for which the residual entropy at 0 K of  $0.80574 \text{ cal K}^{-1} \text{ mol}^{-1}$  or  $189 \text{ J K}^{-1} \text{ kg}^{-1}$  must be added. The third column shows personal calculations made since 2022 by using the Calorimetric formula (1) and based on the new values of  $c_p(T)$  shown in the section 8. The dry-air values are computed with 440 ppmv of  $\text{CO}_2$ .*

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**Molar absolute entropies at  $T_{\text{std}} = 298.15 \text{ K}$  (or  $25^\circ\text{C}$ ) and  $p_{\text{std}} = 1013.25 \text{ hPa}$ .**

	ST12/S	LG17/C	LR23/C	K32/C	GB32-34/S	GS36/C	R52	LR61
N <sub>2</sub>		45.59	45.6	45.8 ± 0.3			45.767	45.77
O <sub>2</sub>		48.23	48	49.1			49.003	49.01
Ar	37.0	36.43	36.70	36.8 ± 0.2			36.983	36.99
CO <sub>2</sub>				50.0 ± 2	51.14		51.061	51.08
H <sub>2</sub> O				45.08 ± 0.1 <sup>(1)</sup>	45.101	45.09 ± 0.05 <sup>(2)</sup>	45.106	45.10 <sup>(3)</sup>

	W65	R78	GR96/C	GR96/S	$\delta(\text{GR96})$	C98/S	AP14
N <sub>2</sub>	45.77	45.796 ± 0.005	45.94 ± 0.2	45.78	+0.144 (0.31%)	45.796 ± 0.005	45.796
O <sub>2</sub>	48.996	49.032 ± 0.009	49.12 ± 0.1	49.02	+0.089 (0.18%)	49.031 ± 0.008	49.029
Ar	36.9822	37.008 ± 0.005	36.96 ± 0.2	37.00	−0.040 (0.11%)	37.000 ± 0.001	37.008
CO <sub>2</sub>	51.06	51.097 ± 0.009	51.13 ± 0.1	51.09	0.032 (0.06%)	51.098 ± 0.029	51.085
H <sub>2</sub> O	45.104	45.105 ± 0.009	45.11 <sup>(4)</sup>	45.12	−0.022 (0.05%)	45.132 ± 0.010	45.131

Table 3: *Standard molar entropies in cal/K/mol (with 4.184 J/cal) at 1013.25 hPa and 298.15 K for the gases: Nitrogen (N<sub>2</sub>), Oxygen (O<sub>2</sub>), Argon (Ar), Carbon dioxide (CO<sub>2</sub>) and Water vapour (H<sub>2</sub>O). The suffix “/C” is for the calorimetric methods, whereas the suffix “/S” is for the statistical-physics methods. The column “ $\delta(\text{GR96})$ ” is the difference between the calorimetric method GR96/C compared to the (more accurate) statistical-physics formulation C98/S: namely  $\delta(\text{GR96}) = \text{GR96/C} - \text{C98/S}$ .*

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*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  $\delta(\text{GR96})$ ), C98 (Chase, 1998, Statistical values), AP14 (Atkins and de Paula, 2014).*

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- <sup>(1)</sup> *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<sub>2</sub>O) 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 (2019c)), leading to 44.27 cal/K/mol. The residual entropy for H<sub>2</sub>O  $R \ln(3/2) \approx 0.80574 \text{ cal/K/mol}$  (with  $R = 1.98721 \text{ cal/K/mol}$ ) computed by Pauling (1935) and Nagle (1966) is added to this K32 value to give 45.08 cal/K/mol.*
  - <sup>(2)</sup> *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.*
  - <sup>(3)</sup> *The liquid-water entropy in LR61 is 16.73 cal/K/mol and includes the residual entropy  $16.73 - 15.9 = 0.83 \approx 0.80574 \text{ cal/K/mol}$ , leading to the water-vapour entropy 45.10 cal/K/mol.*
  - <sup>(4)</sup> *The same residual entropy of 0.80574 cal/K/mol is added to the CR96/C value 44.31 cal/K/mol for H<sub>2</sub>O, to give 45.11 cal/K/mol.*
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Specific absolute entropies at  $p_{\text{std}} = 1000 \text{ hPa}$  for temperatures  $T$  from 0 K to 340 K.

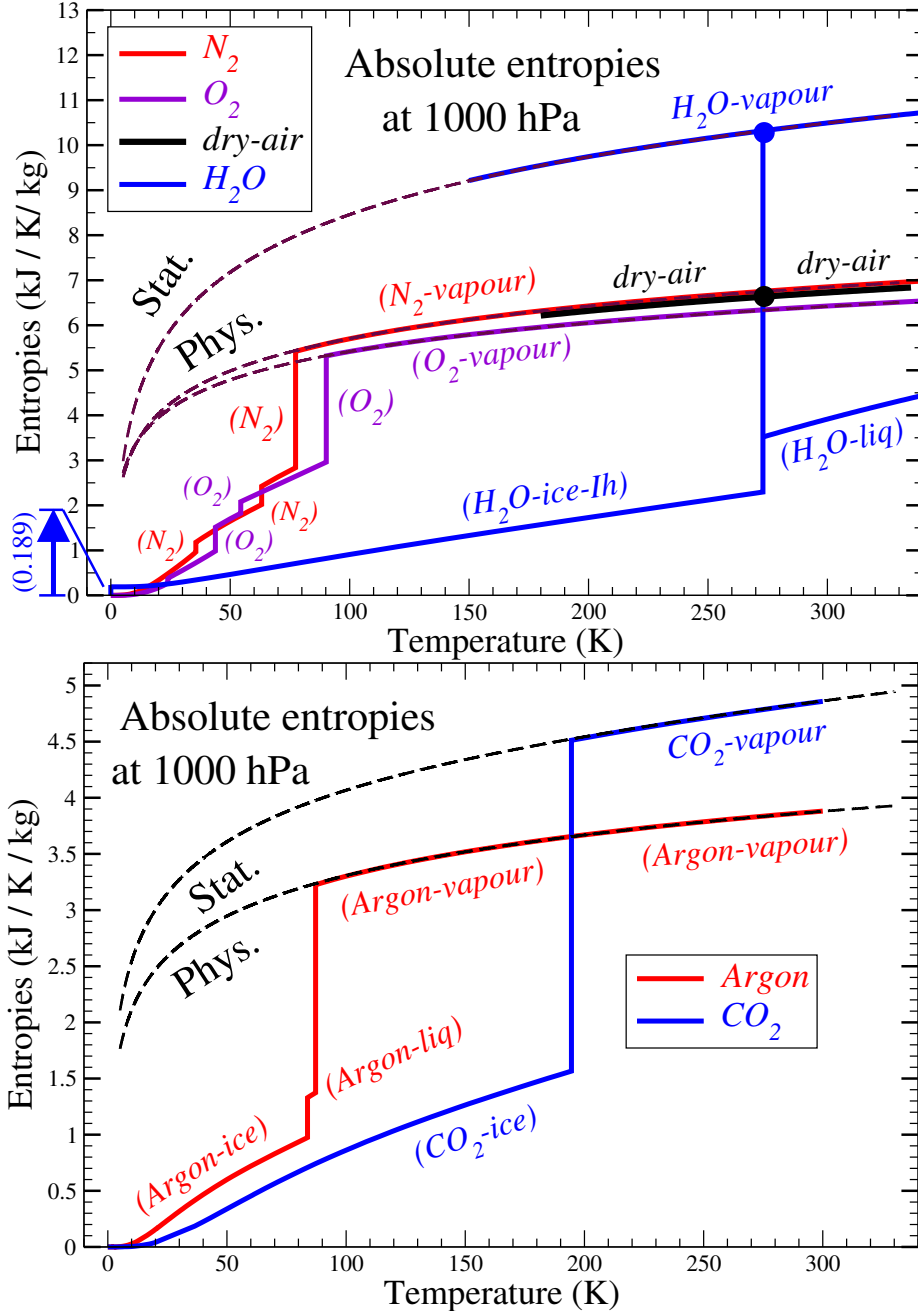
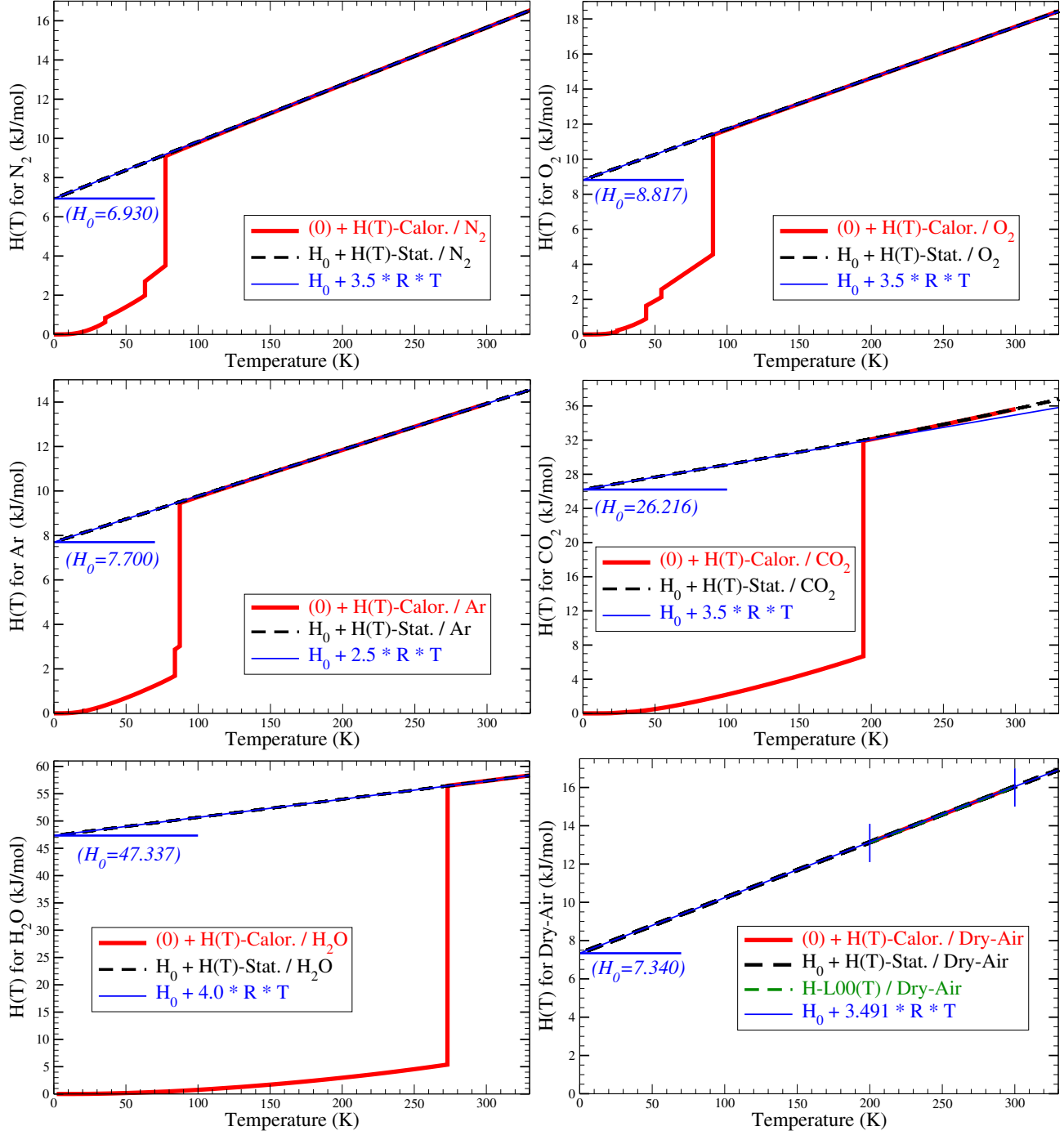


Figure 1: Entropies for dry-air ( $N_2$ ,  $O_2$ , Ar,  $CO_2$  and water  $H_2O$ ) species plotted against the absolute temperature and computed at 1000 hPa. The calorimetric method (1) corresponds to the coloured solid lines. The third-law hypothesis is applied at 0 K with zero entropies for all the 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-physics values (black dashed lines) are computed from  $S = k \ln(W)$  for the vapour phases according to the method described in Chase (1998) for translational, rotational, vibrational and electronic partition functions.

Figure 2: The “calorimetric” (solid red) and “shifted-statistical” (dashed black) enthalpies for  $N_2$ ,  $O_2$ , Ar,  $CO_2$ ,  $H_2O$  and dry air (units in  $\text{kJ mol}^{-1}$ ). The vertical shifts at 0 K (blue line and numbers) are the starting points for the linear theoretical laws (thin blue solid lines proportional to  $R \times T$  with  $R \approx 8.31446 \text{ J K}^{-1} \text{ kg}^{-1}$ ). For the dry air, the molar enthalpies are computed with the concentrations rescaled from values of Picard et al. (2008) and with the resulting molar concentrations 0.780 847, 0.209 381, 0.009 332 and 0.000 440  $\text{mol mol}^{-1}$  for  $N_2$ ,  $O_2$ , Ar and  $CO_2$ , respectively. The green dashed line corresponds to values from 200 K to 300 K (see the vertical limits) listed in the Table A2 in Lemmon et al. (2000, “L00”, p.366-367), where the impact of  $CO_2$  was not taken into account and with the molar concentrations 0.7812, 0.2096 and 0.0092 for  $N_2$ ,  $O_2$  and Ar, respectively.

Specific absolute calorimetric enthalpies for temperatures  $T$  from 0 K to 340 K.



**Specific absolute calorimetric enthalpies at  $T_{\text{std}} = 273.15 \text{ K}$  (or  $0^\circ\text{C}$ ).**

(Standard Enthalpies)	$\text{N}_2(\text{vap})$	$\text{O}_2(\text{vap})$	$\text{Ar}(\text{vap})$	$\text{CO}_2(\text{vap})$	Dry-air(vap)	$\text{H}_2\text{O}(\text{vap})$
Marquet (2015a) ( $0^\circ\text{C}$ ):	532.4	525.6			530	3133
Marquet-2025 ( $0^\circ\text{C}$ ):	$530.9 \pm 1.3$	$524.0 \pm 1.5$	$335.3 \pm 1.7$	$787.4 \pm 1.5$	$527.0 \pm 1.3$	$3133.1 \pm 0.6$
Marquet-2025 ( $25^\circ\text{C}$ ):	$556.9 \pm 1.4$	$546.9 \pm 1.5$	$348.4 \pm 1.8$	$808.4 \pm 1.6$	$552.1 \pm 1.4$	$3179.3 \pm 0.6$

Table 4: *The calorimetric values of the vapour thermal enthalpies (in units of  $\text{kJ kg}^{-1}$ ) computed with the formula (8) for  $\text{N}_2$ ,  $\text{O}_2$ , Argon,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . The first line were computed by Marquet (2015a) at  $0^\circ\text{C}$ , with the dry air made of about 0.79 % of  $\text{N}_2$  and 0.21 %  $\text{O}_2$  gases. The second and third lines are for new, more accurate computations at both  $0^\circ\text{C}$  and  $25^\circ\text{C}$  including Argon and  $\text{CO}_2$  gases, with the dry-air value computed with the molar concentrations 0.780 847, 0.209 381, 0.009 332 and 0.000 440  $\text{mol mol}^{-1}$  for  $\text{N}_2$ ,  $\text{O}_2$ , Ar and  $\text{CO}_2$ , respectively, with moreover the accuracy information included for all gases.*

**Specific absolute calorimetric enthalpies for temperatures  $T$  from 0 K to 350 K.**

**Fig. 7 (a), p.6 of Hunt et al. (2023)**

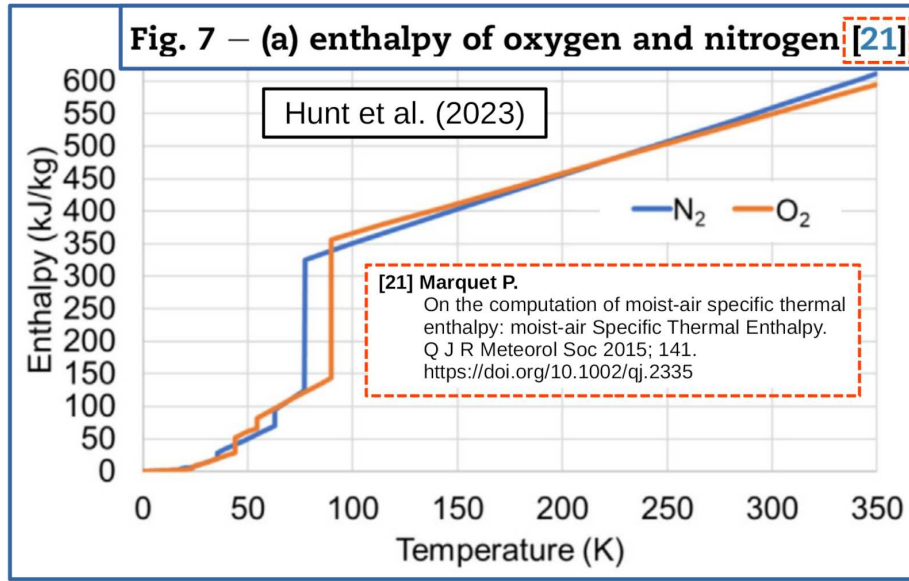


Figure 3: *The Fig. 7(a) published in Hunt et al. (2023, p.6) with the legend: “(a) enthalpy of oxygen and nitrogen [21]” where [21] was for “Marquet P. On the computation of moist-air specific thermal enthalpy: moist-air Specific Thermal Enthalpy. Q J R Meteorol Soc 2015; 141. (<https://doi.org/10.1002/qj.2335>)” with the same curves as those in the Figures 2 for  $\text{N}_2$  and  $\text{O}_2$ .*

- The agreement between the various way to compute the absolute entropies can be fairly appreciated in the Figs. 1, where the “calorimetric” and “statistical-physics” methods lead to very similar results in the range of atmospheric temperatures (up to better than 0.02 % for water vapour and 0.1 % for dry air).

The accuracy of the NIST-JANAF tables are indicated as being better than one tenth of the differences between calorimetric and the statistical methods. The accuracy of the calorimetric method (M25-Calor compared to M25-Stat = C98/S) shown in the Table 1 is of the same order (even smaller maybe) than the one evaluated in the column  $\delta$  of the Table 3.

It follows, as shown in the Fig. 1, that to know the reference-entropy values for gases one can either use the formula from “statistical physics,” or following the “calorimetric method,” namely by integrating the differential  $ds = c_p(T) d\ln(T)$  from 0 K to the ambient temperature  $T$  (first for the solid(s), then

for the liquid and gaseous phases) and also adding all the impacts due to latent heats and the phase changes between solid(s), liquid and gas, together with taking into account the possible residual entropy at 0 K (for H<sub>2</sub>O only).

- 
- The absolute calorimetric enthalpies for the the water vapour H<sub>2</sub>O, for the dry-air species N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>, and for the corresponding dry air, are shown in the Figs. 2 and the Table. 4.

Only the CO<sub>2</sub> curve shows significant and increasing departures from the linear law above about 150 K, where one of the vibrational mode starts to be activated.

The quantum-statistical physics values of the enthalpies contain unknown parameters  $H_0$  that are shown in the Figs. 2. However, up to now these values cannot be determined from the quantum theory and are still to be explained.

- Note that the Fig. 3 reproduces the Fig. 7(a) published by Hunt et al. (2023, p.6)<sup>1</sup> and is made of the same red curves I show in the two top panels of Figs. 2 for N<sub>2</sub> and O<sub>2</sub>. They are based on my previous dataset and figures published in Marquet (2015a), with the same hypothesis that the (thermal) enthalpy is to be computed with the calorimetric method from 0 K up to 300 K by integrating  $c_p(T)$  and by adding all latent heats  $L_k(T_k)$  due to changes of states.

- 
- The Tables for the specific heats at constant pressure  $c_p(T)$  are shown in the section 8, together with the figures of  $c_p(T)$  plotted in the section 7 against the absolute temperature, where the latent heats  $L_k(T_k)$  are also indicated for all changes of phases occurring from 0 K to 273.15 K or 300 K between all solid(s), liquid and vapour states.
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<sup>1</sup> Where the authors study the possibility to use “*solid nitrogen or oxygen as a medium for recycling cold energy across the hydrogen liquefaction supply chain*” for the development of the “*green hydrogen economy*” and to challenge the “*long-distance transportation*” problem.

### 3 Detailed computations of the third-law calorimetric entropies

The calorimetric standard entropy of the major atmospheric species ( $x = \text{N}_2, \text{O}_2, \text{H}_2\text{O}, \text{CO}_2, \text{Ar}$ ) can be computed at the standard temperature  $T_0$  and pressure  $p_0$  by using the relationship

$$S_{\text{x/calor.}}(T_0, p_0) = S_{\text{x/res.}}(0 \text{ K}) + \int_0^{T_0} \frac{c_{px}(T)}{T} dT + \sum_j \frac{L_x(T_j)}{T_j} - R_x \ln\left(\frac{p_0}{p_{\text{x/sat}}}\right). \quad (12)$$

This relationship (12) was explicitly described and used in Kelley (1932, Eq-4, p.4) and Gokcen and Reddy (1996, Eq-7.11, p.117), for instance.

The first term in (12) is the residual entropy at 0 K for  $\text{H}_2\text{O}$  (ice Ih) only (Pauling, 1935; Nagle, 1966), for which  $S_{\text{x/res.}}(0 \text{ K}) = (R_*/M_{\text{H}_2\text{O}}) \ln(3/2) \approx 187.130 \text{ J K}^{-1} \text{ kg}^{-1}$  for  $R_* \approx 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $M_{\text{H}_2\text{O}} \approx 0.01801528 \text{ kg mol}^{-1}$ . This residual entropy was logically missing in the previous Bulletin of Kelley (1932, published before 1935) and in the corresponding computations (p.25/26) of the standard entropy for  $\text{H}_2\text{O}$ .

The sum in (12) over all latent heat terms  $L_x(T_j)$  at the corresponding temperatures  $T_k$  corresponds to all possible changes of phases (first between the possible solid(s) states, and then due to melting, vaporisation or sublimation).

The last term in (12) corresponds to the impact on  $S_{\text{x/calor.}}$  to the change of pressure from the saturation value ( $p_{\text{x/sat}}$ ) to the standard value ( $p_0$ ), with  $R_x = R_*/M_x$ . The absolute status is due to the hypothesis  $S_{\text{x/calor.}} = S_{\text{x/res.}}(0 \text{ K})$  in (12) at  $T_0 = 0 \text{ K}$ , and thus to  $S_{\text{x/calor.}} - S_{\text{x/res.}}(0 \text{ K}) = 0$  for the more stable solid state at 0 K (i.e. the third law of thermodynamics)

Because  $c_{px}(T) \approx a_x T^3$  according to Debye (1912) and  $c_{px}/T \approx a_x T^2 = 0$  at 0 K, the integral in (12) is finite and can be performed between 0 K and the lowest available temperature  $T_1$ . This integral

$$\Delta S_{\text{x/calor.}}(T_1) = \int_0^{T_1} \frac{c_{px}(T)}{T} dT = \int_0^{T_1} \frac{a_x T^3}{T} dT = \int_0^{T_1} a_x T^2 dT = \frac{a_x T_1^3}{3} = \frac{c_{px}(T_1)}{3} \quad (13)$$

is one-third of the specific heat at  $T_1$ .

The integral of  $S_{\text{x/calor.}}(T_0, p_0)$  in (12) is computed between each intervals  $T_i$  and  $T_{i+1}$  with linear variations of the specific heats, leading to

$$c_{px}(T) = c_{px}(T_i) + (T - T_i) \left[ \frac{\Delta c_{px}}{\Delta T} \right] = \Delta c_{px} \left[ \frac{T}{\Delta T} \right] + \left[ c_{px}(T_i) - \frac{T_i \Delta c_{px}}{\Delta T} \right], \quad (14)$$

$$\Delta S_{\text{x/calor.}}(T_i, T_{i+1}) = S_{\text{x/calor.}}(T_{i+1}) - S_{\text{x/calor.}}(T_i) = \int_{T_i}^{T_i + \Delta T} \frac{c_{px}(T)}{T} dT, \quad (15)$$

$$\Delta S_{\text{x/calor.}}(T_i) = \Delta c_{px} + \left[ c_{px}(T_i) - \frac{T_i \Delta c_{px}}{\Delta T} \right] \ln\left(\frac{T_i + \Delta T}{T_i}\right), \quad (16)$$

where  $\Delta c_{px} = c_{px}(T_{i+1}) - c_{px}(T_i)$  and  $\Delta T = T_{i+1} - T_i$ .

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The accuracy of each of the terms of (12) are evaluated in the following ways:

- the uncertainty of the residual value  $(R_*/M_{\text{H}_2\text{O}}) \ln(3/2)$  at 0 K (for  $\text{H}_2\text{O}$  only)  
 $\Delta [R_*/M_{\text{H}_2\text{O}}] [\ln(3/2)]$ ;
- the uncertainty of the Debye's contribution " $c_p(T_1)/3$ "  
 $\Delta [c_p(T_1)] / 3$ ;
- the uncertainty of each integral of  $c_p(T)/T$  between the two limit temperatures  $T_p$  and  $T_{p+1}$  of a given phase " $p$ " (solid(s), liquid, vapour)  
 $\Delta(c_p) [\ln(T_{p+1}/T_p)] + \Delta T_{p+1} [c_p(T_{p+1})/T_{p+1}] - \Delta T_p [c_p(T_p)/T_p]$ ;



- the uncertainty of each term due to changes of phases  $L(T_j)/T_j$   
 $\Delta[L(T_j)]/T + \Delta(T_j)[L(T_j)/(T_j)^2]$ ;
- the uncertainty of the term  $R_x \ln(p_{sat}/p_0)$  due to change of pressures  
 $\Delta(p_{sat})[R_x/p_{sat}] + \Delta(R_*/M_x)[\ln(p_{sat}/p_0)]$ .

### 3.1 The calorimetric absolute entropies for Argon

The specific heat at constant pressure  $c_p(T)$  for Argon are given in the Table 8 for the range of temperatures from 0 to 273.15 K, and are plotted in Figure 13 in terms of the absolute temperature.

The changes in calorimetric absolute entropy for Argon are:

ARGON – Calor.	
The Debye region (below 3 K):	0.023 7 ± 0.000 ... J K <sup>-1</sup> mol <sup>-1</sup>
The Solid-Ice region (between 3 K and 83.81 K):	+ 38.835 7 ± 0.079 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (fusion at 83.81 K):	+ 14.150 3 ± 0.002 4 J K <sup>-1</sup> mol <sup>-1</sup>
The Liquid region (between 83.81 K and 87.18 K):	+ 1.754 6 ± 0.000 3 J K <sup>-1</sup> mol <sup>-1</sup>
Change of pressure (1013.25 hPa to 1000 hPa at 87.18 K):	+ 0.109 5 ± 0.010 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (vaporization at 87.18 K):	+ 73.754 6 ± 0.009 J K <sup>-1</sup> mol <sup>-1</sup>
The Vapour region (between 87.18 K and 273.15 K):	+ 24.211 8 ± 0.002 3 J K <sup>-1</sup> mol <sup>-1</sup>
-----	
Standard entropy of Argon at 1000 hPa and 273.15 K (0 ° C):	152.84 ± 0.10 J K <sup>-1</sup> mol <sup>-1</sup>
Standard entropy of Argon at 1000 hPa and 273.15 K (0 ° C):	3832.7 ± 2.5 J K <sup>-1</sup> kg <sup>-1</sup>
-----	
The Vapour region (between 273.15 K and 298.15 K):	+ 1.821 9 ± 0.000 2 J K <sup>-1</sup> mol <sup>-1</sup>
-----	
Standard entropy of Argon at 1000 hPa and 298.15 K (25 ° C):	154.66 ± 0.10 J K <sup>-1</sup> mol <sup>-1</sup>
Standard entropy of Argon at 1000 hPa and 298.15 K (25 ° C):	3878.4 ± 2.5 J K <sup>-1</sup> kg <sup>-1</sup>
-----	
Standard entropy of Argon at 1013.25 hPa and 298.15 K (25 ° C):	154.55 ± 2.5 J K <sup>-1</sup> mol <sup>-1</sup>
-----	

The latent heat of fusion  $29.739 \pm 0.005$  kJ kg<sup>-1</sup> occurs at 83.81 K, whereas the latent heat of evaporation  $161.24 \pm 0.02$  kJ kg<sup>-1</sup> occurs at the triple point temperature 87.18 K and at the saturating pressure  $1013.25 \pm 0.05$  hPa.

According to the Figure 13 (top) the lower available temperature 3 K is relevant because it is below the maximum of  $a$  observed at about 8 K. It is thus possible to use extrapolated values in the Debye region for  $T < 3$  K, where  $c_p(T) = a T^3$  with  $a \approx 0.06586 \pm 0.0001$  J K<sup>-4</sup> kg<sup>-1</sup>.

The uncertainty for the solid (ice) region from 3 K to 83.81 K is evaluated by parts:

- first from 3 K to 30 K with an uncertainty for  $a$  of about  $\pm 0.1$  mJ K<sup>-4</sup> kg<sup>-1</sup>;
- then from 30 K to 83.61 K with an uncertainty for  $c_p$  of about  $\pm 0.01$  cal K<sup>-1</sup> mol<sup>-1</sup>.

The uncertainty for the liquid region (from 83.81 K to 87.18 K) is evaluated with a mean uncertainty of  $c_p$  of about  $\pm 0.2$  J K<sup>-1</sup> kg<sup>-1</sup>.

The uncertainty for the vapour region (from 87.18 K to 298.15 K) is evaluated with a mean uncertainty of  $c_p$  of about  $\pm 0.05$  J K<sup>-1</sup> kg<sup>-1</sup>.

The standard value of  $154.55 \pm 0.10 \text{ J K}^{-1} \text{ kg}^{-1}$  or  $154.66 \pm 0.10 \text{ J K}^{-1} \text{ kg}^{-1}$  (computed at 298.15 K and 1013.25 hPa or 1000 hPa) are in agreement with the calorimetric values previous computed by Kelley (1932, p.14/15) and Gokcen and Reddy (1996, Table-7.1, p.114, with  $R \approx 1.987216 \text{ cal K}^{-1} \text{ mol}^{-1}$ ), which are both recalled in the Table 3:  $153.89 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $154.64 \pm 0.84 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

The larger impact on the standard entropy of Argon is due to the change of phase (sublimation) process (about  $+73.8 \text{ J K}^{-1} \text{ mol}^{-1}$ ), but is only 48 % of the total value  $153 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K. This means that all other impacts must be taken into account. The larger uncertainty is due to the solid (ice) region (79 % of the total value  $0.10 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K), with therefore other uncertainties due to other processes (vaporization and change from saturation to standard pressures).

### 3.2 The calorimetric absolute entropies for $\text{N}_2$

The specific heat at constant pressure  $c_p(T)$  for  $\text{N}_2$  are given in the Table 9 for the range of temperatures from 0 to 273.15 K, and are plotted in Figure 14 in terms of the absolute temperature.

The latent heat retained in this study and plotted in Figure 14 (with some arbitrary uncertainties) are:

- $7.67 \pm 0.05 \text{ kJ kg}^{-1}$  for the solid  $\alpha$ - $\beta$  transition at 35.62 K (Lipiński et al., 2007);
- $25.7 \pm 0.2 \text{ kJ kg}^{-1}$  at the melting point temperature 63.15 K (solid  $\alpha$  to liquid states) at the triple point with a saturating pressure of  $1023.75 \pm 0.05 \text{ hPa}$ ;
- $199.4 \pm 0.5 \text{ kJ kg}^{-1}$  for the vaporization at 77.35 K.

According to the Figure 14 (top) the lower temperature of 2 K is relevant to represent the extrapolated Debye region for  $T < 2 \text{ K}$ , with  $c_p = a T^3$  and  $a \approx 0.135 \pm 0.005 \text{ J K}^{-4} \text{ kg}^{-1}$ .

The uncertainty for the solid- $\alpha$  region from 2 K to 35.62 K is evaluated by parts:

- first from 2 K to 20 K (with a mean value  $a \approx 130 \pm 0.1 \text{ mJ K}^{-4} \text{ kg}^{-1}$ );
- then from 20 K to 35.62 K (with a mean value  $a \approx 50 \pm 0.2 \text{ mJ K}^{-4} \text{ kg}^{-1}$ ).

The other uncertainties of  $c_p$  are set to:  $\pm 0.1 \text{ J K}^{-1} \text{ mol}^{-1}$  for the solid- $\beta$  region;  $\pm 3 \text{ J K}^{-1} \text{ kg}^{-1}$  for the liquid region; and  $\pm 2 \text{ J K}^{-1} \text{ kg}^{-1}$  for the vapour region.

The standard entropies  $191.66 \pm 0.56 \text{ J K}^{-1} \text{ kg}^{-1}$  or  $191.77 \pm 0.56 \text{ J K}^{-1} \text{ kg}^{-1}$  computed at 298.15 K for  $\text{N}_2$  (for 1013.25 hPa or 1000 hPa, respectively) are in agreement with the calorimetric values previous computed by Kelley (1932, p.35) and Gokcen and Reddy (1996, Table-7.1, p.114, with  $R \approx 1.987216 \text{ cal K}^{-1} \text{ mol}^{-1}$ ), which are both recalled in the Table 3:  $191.63 \pm 1.26 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $192.21 \pm 0.84 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

Like for water ( $\text{H}_2\text{O}$ ), a comparisons can be made with the old dataset published by Kelley (1932, Bureau of Mines, Bulletin 350), which showed (p.35, for  $\text{N}_2$ ) that:

- the entropy of  $\text{N}_2$  due to the sole heating from 0 K to 273.15 K was about  $(0.47+11.59+2.77+9.57 \approx 24.4) \times 4.184 \approx 102.1 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is close to  $0.01 + 26.98 + 23.47 + 11.52 + 37.39 \approx 99.37 \text{ J K}^{-1} \text{ mol}^{-1}$  with the present dataset;
- the entropy due to the changes of phase was  $(51.4/35.4 + 170.95/63.08 + 1336/77.3) \times 4.184 \approx 6.08 + 11.34 + 72.31 \approx 89.73$ , which is close to  $6.032 + 11.401 + 72.216 \approx 89.65 \text{ J K}^{-1} \text{ mol}^{-1}$  with the present dataset.

Like for  $\text{H}_2\text{O}$ , the larger impact for  $\text{N}_2$  (about  $+72.2 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is due to the vaporisation process, but is only 38 % of the total value  $189.2 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K. This means that all other impacts must be taken into account. The larger uncertainty is also due to the vaporisation process (33 % of the total value  $0.55 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K), with therefore important uncertainties due to other processes.

The changes in calorimetric absolute entropy for N<sub>2</sub> are:

N <sub>2</sub> – Calor.	
The Debye region (below 2 K):	0.0100 ± 0.0004 J K <sup>-1</sup> mol <sup>-1</sup>
The Solid-α region (between 2 K and 35.62 K):	+ 26.9789 ± 0.076 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (from Solid-α to Solid-β at 35.62 K):	+ 6.0321 ± 0.039 J K <sup>-1</sup> mol <sup>-1</sup>
The Solid-β region (between 35.62 K and 63.15 K):	+ 23.4719 ± 0.060 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (fusion / Solid-β to Liquid) at 63.15 K):	+ 11.4007 ± 0.089 J K <sup>-1</sup> mol <sup>-1</sup>
The Liquid region (between 63.15 K and 77.35 K):	+ 11.5199 ± 0.017 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (vaporization at 77.35 K):	+ 72.2163 ± 0.181 J K <sup>-1</sup> mol <sup>-1</sup>
Change of pressure (1023.75 hPa to 1000 hPa at 77.35 K):	+ 0.1952 ± 0.017 J K <sup>-1</sup> mol <sup>-1</sup>
The Vapour region (between 77.35 K and 273.15 K):	+ 37.3947 ± 0.071 J K <sup>-1</sup> mol <sup>-1</sup>
-----	
Standard entropy of N <sub>2</sub> at 1000 hPa and 273.15 K (0° C):	189.22 ± 0.55 J K <sup>-1</sup> mol <sup>-1</sup>
Standard entropy of N <sub>2</sub> at 1000 hPa and 273.15 K (0° C):	6754.5 ± 19 J K <sup>-1</sup> kg <sup>-1</sup>
-----	
The vapour region (between 273.15 K and 298.15 K):	+ 2.5539 ± 0.005 J K <sup>-1</sup> mol <sup>-1</sup>
-----	
Standard entropy of N <sub>2</sub> at 1000 hPa and 298.15 K (25° C):	191.77 ± 0.56 J K <sup>-1</sup> mol <sup>-1</sup>
Standard entropy of N <sub>2</sub> at 1000 hPa and 298.15 K (25° C):	6845.7 ± 20 J K <sup>-1</sup> kg <sup>-1</sup>
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Standard entropy of N <sub>2</sub> at 1013.25 hPa and 298.15 K (25° C):	191.66 ± 0.56 J K <sup>-1</sup> mol <sup>-1</sup>
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### 3.3 The calorimetric absolute entropies for O<sub>2</sub>

The specific heat at constant pressure  $c_p(T)$  for O<sub>2</sub> are given in the Table 10 for the range of temperatures from 0 to 273.15 K, and are plotted in Figure 15 in terms of the absolute temperature.

According to Fagerstroem and Hallet (1969), the solid α-β transition occurs at about 23.85 K, with no latent heat associated with it. The impact on the standard entropy occurs via the very large values of  $c_p(T)$  close to  $R \approx 23.85$  K, with a kind of Dirac function with a finite integral.

The other solid β-γ transition occurs at about 43.8 K with a latent heat of  $23.2 \pm 0.2$  kJ kg<sup>-1</sup>. The latent heat of melting occurring at the triple point (54.4 K) is equal to  $13.9 \pm 0.2$  kJ kg<sup>-1</sup>. The latent heat of vaporization occurring at 90.2 K is equal to  $213 \pm 0.4$  kJ kg<sup>-1</sup>, at a saturating pressure of  $991.78 \pm 0.05$  hPa.

According to the Figure 15 (top) the lower temperature of 2 K is relevant (because well below the maximum of  $a$  observed at about 11 K) to represent the extrapolated Debye region for  $T < 2$  K, with  $c_p = a T^3$  and  $a \approx 0.059 \pm 0.002$  J K<sup>-4</sup> kg<sup>-1</sup>.

The uncertainty for the solid-α region from 2 K to 23.85 K is evaluated by parts:

- first from 2 K to 11 K (with a mean value  $a \approx 66 \pm 1$  mJ K<sup>-4</sup> kg<sup>-1</sup>);
- then from 20 K to 35.62 K (with a mean value  $a \approx 61 \pm 0.2$  mJ K<sup>-4</sup> kg<sup>-1</sup>).

The uncertainty for the solid-β, solid-γ and liquid regions are evaluated with a mean uncertainty of  $c_p$  of about  $\pm 0.2$  J K<sup>-1</sup> mol<sup>-1</sup>, whereas the uncertainty for the vapour region is evaluated with a mean uncertainty of  $c_p$  of about  $\pm 0.2$  J K<sup>-1</sup> kg<sup>-1</sup>.

The changes in calorimetric absolute entropy for O<sub>2</sub> are:

O <sub>2</sub> – Calor.	
The Debye region (below 2 K):	0.005 0 ± 0.000 ... J K <sup>-1</sup> mol <sup>-1</sup>
The Solid-α region (between 2 K and 23.84 K):	+ 10.613 4 ± 0.040 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (from Solid-α to Solid-β at 23.845 K):	0.0 ± 0.0 J K <sup>-1</sup> mol <sup>-1</sup>
The Solid-β region (between 23.85 K and 43.8 K):	+ 20.853 3 ± 0.367 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (fusion / Solid-β to Solid-γ at 43.8 K):	+ 16.949 1 ± 0.146 J K <sup>-1</sup> mol <sup>-1</sup>
The Solid-γ region (between 43.8 K and 54.4 K):	+ 9.943 0 ± 0.043 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (fusion / Solid-γ to Liquid at 54.4 K):	+ 8.176 1 ± 0.118 J K <sup>-1</sup> mol <sup>-1</sup>
The Liquid region (between 54.4 K and 90.2 K):	+ 28.161 4 ± 0.101 J K <sup>-1</sup> mol <sup>-1</sup>
Change of phase (vaporization at 90.2 K):	+ 75.562 5 ± 0.142 J K <sup>-1</sup> mol <sup>-1</sup>
Change of pressure (991.78 hPa to 1000 hPa at 90.2 K):	- 0.068 6 ± 0.013 J K <sup>-1</sup> mol <sup>-1</sup>
The Vapour region (between 90.2 K and 273.15 K):	+ 32.718 3 ± 0.222 J K <sup>-1</sup> mol <sup>-1</sup>
-----	
Standard entropy of O <sub>2</sub> at 1000 hPa and 273.15 K (0 °C):	202.91 ± 1.2 J K <sup>-1</sup> mol <sup>-1</sup>
Standard entropy of O <sub>2</sub> at 1000 hPa and 273.15 K (0 °C):	6341.3 ± 37 J K <sup>-1</sup> kg <sup>-1</sup>
-----	
The vapour region (between 273.15 K and 298.15 K):	+ 2.573 ± 0.000 6 J K <sup>-1</sup> mol <sup>-1</sup>
-----	
Standard entropy of O <sub>2</sub> at 1000 hPa and 298.15 K (25 °C):	205.49 ± 1.2 J K <sup>-1</sup> mol <sup>-1</sup>
Standard entropy of O <sub>2</sub> at 1000 hPa and 298.15 K (25 °C):	6421.7 ± 37 J K <sup>-1</sup> kg <sup>-1</sup>
-----	
Standard entropy of O <sub>2</sub> at 1013.25 hPa and 298.15 K (25 °C):	205.38 ± 1.2 J K <sup>-1</sup> mol <sup>-1</sup>
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The standard entropies  $205.38 \pm 1.2 \text{ J K}^{-1} \text{ kg}^{-1}$  or  $205.49 \pm 1.2 \text{ J K}^{-1} \text{ kg}^{-1}$  computed at 298.15 K for O<sub>2</sub> (for 1013.25 hPa or 1000 hPa, respectively) are in agreement with the calorimetric values previous computed by Kelley (1932, p.37/38) and Gokcen and Reddy (1996, Table-7.1, p.114, with  $R \approx 1.987 216 \text{ cal K}^{-1} \text{ mol}^{-1}$ ), which are both recalled in the Table 3:  $205.43 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $205.52 \pm 0.42 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

The larger impact on the standard entropy of O<sub>2</sub> (about  $+75.6 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is due to the vaporisation process, but is only 37 % of the total value  $203 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K. This means that all other impacts must be taken into account. The larger uncertainty is due to the solid-β region with the left side of the Dirac-like function (31 % of the total value  $1.2 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K), with therefore large uncertainties due to other processes.

Note that the (calorimetric) saturation entropy of gaseous O<sub>2</sub> is similarly computed at 90.13 K by Lewis and Randall (1961, p.126) from the values of  $c_p(T)$  shown in the Fig. (12). The corresponding value of  $40.59 \text{ cal K}^{-1} \text{ mol}^{-1}$  or  $40.59 \times 4.184 \approx 169.8 \text{ J K}^{-1} \text{ mol}^{-1}$  compares well with the value  $202.91 - 32.72 + 0.07 = 170.26 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$  I have computed at 90.2 K with more modern datasets.

### 3.4 The calorimetric absolute entropies for CO<sub>2</sub>

The specific heat at constant pressure  $c_p(T)$  for CO<sub>2</sub> are given in the Table 11 for the range of temperatures from 0 to 273.15 K, and are plotted in Figure 16 in terms of the absolute temperature.

The latent heat of sublimation occurring at the triple point (194.525 K) is equal to  $573 \pm 0.4 \text{ kJ kg}^{-1}$ , at a saturating pressure of 1000 hPa.

According to the Figure 16 (top) the lower temperature 2.112 K is relevant for  $\text{CO}_2$  because it is well below the maximum of  $a$  observed at about 16 K. It is thus possible to use extrapolated values in the Debye region for  $T < 2.112 \text{ K}$ , where  $c_p(T) = a T^3$  with  $a \approx 0.013 \pm 0.0002 \text{ J K}^{-4} \text{ kg}^{-1}$ .

The uncertainty for the solid (ice) region for  $\text{CO}_2$  from 2.112 K to 194.525 K is evaluated by parts:  
- first from 2 K to 36 K with an uncertainty for  $a$  of about  $\pm 0.2 \text{ mJ K}^{-4} \text{ kg}^{-1}$ ;  
- then from 36 K to 80 K with an uncertainty for  $c_p$  of about  $\pm 0.03 \text{ cal K}^{-1} \text{ mol}^{-1}$ ;  
- then from 80 K to 150 K with an uncertainty for  $c_p$  of about  $\pm 0.04 \text{ cal K}^{-1} \text{ mol}^{-1}$ ;  
- then from 150 K to 194.525 K with an uncertainty for  $c_p$  of about  $\pm 0.05 \text{ cal K}^{-1} \text{ mol}^{-1}$ .

The uncertainty for the vapour region (from 194.525 K to 298.15 K) is evaluated with a mean uncertainty of  $c_p$  of about  $\pm 0.05 \text{ cal K}^{-1} \text{ kg}^{-1}$ .

The changes in calorimetric absolute entropy for  $\text{CO}_2$  are:

----- $\text{CO}_2$ - Calor. -----		
The Debye region (below 2.112 K):	0.0018	$\pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}$
The Solid-Ice region (between 2.112 K and 194.525 K):	+ 68.9261	$\pm 0.356 \text{ J K}^{-1} \text{ mol}^{-1}$
Change of phase (sublimation at 194.525 K):	+ 129.6357	$\pm 0.090 \text{ J K}^{-1} \text{ mol}^{-1}$
Change of pressure (1000 hPa to 1000 hPa at 194.525 K):	0.0	$\pm 0.0 \text{ J K}^{-1} \text{ mol}^{-1}$
The Vapour region (between 194.525 K and 273.15 K):	+ 11.8254	$\pm 0.071 \text{ J K}^{-1} \text{ mol}^{-1}$
-----		
Standard entropy of $\text{CO}_2$ at 1000 hPa and 273.15 K (0 ° C):	210.39	$\pm 0.52 \text{ J K}^{-1} \text{ mol}^{-1}$
Standard entropy of $\text{CO}_2$ at 1000 hPa and 273.15 K (0 ° C):	4780.6	$\pm 12 \text{ J K}^{-1} \text{ kg}^{-1}$
-----		
The Vapour region (between 273.15 K and 298.15 K):	+ 3.2317	$\pm 0.018 \text{ J K}^{-1} \text{ mol}^{-1}$
-----		
Standard entropy of $\text{CO}_2$ at 1000 hPa and 298.15 K (25 ° C):	213.62	$\pm 0.54 \text{ J K}^{-1} \text{ mol}^{-1}$
Standard entropy of $\text{CO}_2$ at 1000 hPa and 298.15 K (25 ° C):	4854.0	$\pm 12 \text{ J K}^{-1} \text{ kg}^{-1}$
-----		
Standard entropy of $\text{CO}_2$ at 1013.25 hPa and 298.15 K (25 ° C):	213.51	$\pm 0.55 \text{ J K}^{-1} \text{ mol}^{-1}$
-----		

The standard entropies  $213.51 \pm 0.55 \text{ J K}^{-1} \text{ kg}^{-1}$  or  $213.62 \pm 0.54 \text{ J K}^{-1} \text{ kg}^{-1}$  computed at 298.15 K for  $\text{CO}_2$  (for 1013.25 hPa or 1000 hPa, respectively) are in agreement with the calorimetric values previous computed by Kelley (1932, p.20) and Gokcen and Reddy (1996, Table-7.1, p.114, with  $R \approx 1.987216 \text{ cal K}^{-1} \text{ mol}^{-1}$ ), which are both recalled in the Table 3:  $209.2 \pm 8 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $213.93 \pm 0.42 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

The larger impact on the standard entropy of  $\text{CO}_2$  (about  $+129.6 \text{ J K}^{-1} \text{ mol}^{-1}$ ) is due to the change of phase (sublimation) process, but is only 62 % of the total value  $210.4 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K. This means that all other impacts must be taken into account. The larger uncertainty is due to the solid (ice) region (68 % of the total value  $0.52 \text{ J K}^{-1} \text{ mol}^{-1}$  at 273.15 K), with therefore other uncertainties due to other processes (sublimation and vapour region).

### 3.5 The calorimetric absolute entropies for H<sub>2</sub>O

The specific heat at constant pressure  $c_p(T)$  for H<sub>2</sub>O (ice-Ih) are given in the Table 12 for the range of temperatures from 0 to 273.15 K, and are plotted in Figure 17 in terms of the absolute temperature.

According to the top panel of Figure 17, the sparse values of  $c_p(T)$  for  $T = 10, 20$  and  $30$  K provided in Feistel and Wagner (2006) correspond to some selected values of Flubacher et al. (1960). But the temperature of 10 K is not low enough to validate the constancy of Debye's law  $c_p(T) \approx aT^3$ , because “ $a$ ” clearly decreases from about 15 to about 10 mJ K<sup>-4</sup> kg<sup>-1</sup> in the top panel of Figure 17 for temperature below 2 K. Therefore, the 3 values of  $c_p(T)$  for  $T = 10, 20$  and  $30$  K in Feistel and Wagner (2006) are completed for even values from 2 to 28 K, as shown in the top panel of Figure 17 from interpolated values of the whole points of Flubacher et al. (1960), and as listed in the Table 12. With these temperature additions we ensure that the first value (2 K) is well below the maximum of  $a$  observed at about 14 K.

The uncertainty of the residual entropy at 0 K is computed with  $\Delta M_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}} \approx 0.22 \cdot 10^{-5}$  and  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ .

The uncertainty of the integral of  $c_p(T)/T$  between 2 K and 273.15 K is evaluated by separating this integral into those between 2 K and 30 K (with a “mean Debye law” constant of  $10 \pm 2$  mJ K<sup>-4</sup> kg<sup>-1</sup>), between 30 K and 100 K (with  $\Delta c_p \approx 0.2$  J K<sup>-1</sup> kg<sup>-1</sup>), and between 100 K and 273.15 K (with  $\Delta c_p \approx 0.4$  J K<sup>-1</sup> kg<sup>-1</sup>).

The latent heat of fusion, vaporization and sublimation at temperature 273.15 K are assumed to be  $333.7 \pm 0.25$  kJ kg<sup>-1</sup>,  $2500.8 \pm 0.25$  kJ kg<sup>-1</sup> and  $2834.5 \pm 0.5$  kJ kg<sup>-1</sup>, respectively.

The uncertainty on the saturation pressure is set to  $6.1115 \pm 0.0010$  hPa.

The standard entropies  $188.72 \pm 0.24$  J K<sup>-1</sup> kg<sup>-1</sup> or  $188.83 \pm 0.24$  J K<sup>-1</sup> kg<sup>-1</sup> computed at 298.15 K for H<sub>2</sub>O (for 1013.25 hPa or 1000 hPa, respectively) are in agreement with the calorimetric values previous computed by Kelley (1932, p.25/26) and Gokcen and Reddy (1996, Table-7.1, p.114, with  $R \approx 1.987216$  cal K<sup>-1</sup> mol<sup>-1</sup>), which are both recalled in the Table 3:  $188.61 \pm 0.42$  J K<sup>-1</sup> mol<sup>-1</sup> and  $188.74$  J K<sup>-1</sup> mol<sup>-1</sup>, respectively.

A comparisons can be made with the old dataset published by Kelley (1932, Bureau of Mines, Bulletin 350), which showed (p.25, for water) that:

- the entropy of H<sub>2</sub>O due to the sole heating from 0 K to 273.15 K was about  $(0.02 + 9.02) \times 4.184 \approx 37.82$  J K<sup>-1</sup> mol<sup>-1</sup>, which is close to  $0.0005 + 37.9492 \approx 37.948$  J K<sup>-1</sup> mol<sup>-1</sup> with the present dataset;
- the entropy of fusion was  $(1435 \pm 1) \times 4.184 / 273.15 \approx 21.98 \pm 0.02$ , which is close to  $22.0089$  J K<sup>-1</sup> mol<sup>-1</sup> with the present dataset.

Except the small impact due to the Debye region ( $0.0005$  J K<sup>-1</sup> mol<sup>-1</sup>), all other impacts must be taken into account. However, the larger impact (about  $+164.94$  J K<sup>-1</sup> mol<sup>-1</sup>, which is 89 % of  $185.92$  J K<sup>-1</sup> mol<sup>-1</sup>) is due to the vaporisation process, whereas the larger uncertainty is due to the change of pressure (about  $0.17$  J K<sup>-1</sup> mol<sup>-1</sup>, which is 71 % of  $0.24$  J K<sup>-1</sup> mol<sup>-1</sup>).

The changes in calorimetric absolute standard entropy for H<sub>2</sub>O are:

H <sub>2</sub> O – Calor.		
Residual at 0 K:	3.404 9	$\pm 0.007 \text{ J K}^{-1} \text{ mol}^{-1}$
The Debye region (below 2 K):	+ 0.000 5	$\pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}$
The Ice (Ih) region (between 2 K and 273.15 K):	+ 37.949 2	$\pm 0.028 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (Ice-Ih) at 1000 hPa and 273.15 K (0 ° C):	41.354 6	$\pm 0.035 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (Ice-Ih) at 1000 hPa and 273.15 K (0 ° C):	2295.52	$\pm 1.9 \text{ J K}^{-1} \text{ kg}^{-1}$
Fusion (at 1000 hPa and 273.15 K):	+ 22.008 9	$\pm 0.016 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (liq.) at 1000 hPa and 273.15 K (0 ° C):	63.363 5	$\pm 0.051 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (liq.) at 1000 hPa and 273.15 K (0 ° C):	3517.20	$\pm 2.9 \text{ J K}^{-1} \text{ kg}^{-1} \quad (17)$
Vaporization (at 273.15 K and 6.111 5 hPa):	+ 164.937 9	$\pm 0.016 \text{ J K}^{-1} \text{ mol}^{-1}$
Change of pressure (6.111 5 hPa to 1000 hPa at 273.15 K):	– 42.384 0	$\pm 0.17 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (vap.) at 1000 hPa and 273.15 K (0 ° C):	185.92	$\pm 0.24 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (vap.) at 1000 hPa and 273.15 K (0 ° C):	10319.9	$\pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$
The vapour region (between 273.15 K and 298.15 K):	+ 2.912 6	$\pm 0.001 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (vap.) at 1000 hPa and 298.15 K (25 ° C):	188.83	$\pm 0.24 \text{ J K}^{-1} \text{ mol}^{-1}$
Std. entropy of H <sub>2</sub> O (vap.) at 1000 hPa and 298.15 K (25 ° C):	10481.6	$\pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$
Standard entropy of H <sub>2</sub> O (vap.) at 1013.25 hPa and 25 ° C:	188.72	$\pm 0.24 \text{ J K}^{-1} \text{ mol}^{-1}$

## 4 Detailed computations of the third-law statistical entropies

### 4.1 The statistical absolute reference entropies of translation

For a monoatomic gas like Argon, only translational degrees of freedom are to be considered. The corresponding entropy can be computed starting with the Planck-Boltzmann equation

$$S = k \ln(W) ,$$

namely with  $S = k \ln(W) + \text{const.}$  written with the additive constant cancelled, and thus for the absolute definition of the entropy (Grimus, 2013a,b).

The number of states  $W$  in phase space has been computed first by Sackur (1911), Tetrode (1912a,b) and Sackur (1913a,b, 1917) before the quantum-mechanics, with a size of the elementary cell of phase space set to  $(z h)^n$  according to the original ideas of quanta of radiation of Planck (1901), but applied to matter and with  $z = 1$  corresponding to the sole Planck's "elementary quantum of action"  $h$ . Independently, Planck (1915a,b,c, 1916) has computed values similar to those of Sackur and Tetrode.

According to Kennedy et al. (2019, Eq.9, p.3), the Sackur-Tetrode equation for the molar (i.e. per unit mole of substance) entropy of translation can be written as

$$S_{\text{trans}}(T, V, m) = R_* \left[ \frac{5}{2} + \frac{3}{2} \ln(T) + \ln(V) + \ln\left(\frac{(2 \pi m k_B)^{3/2}}{h^3 N_A}\right) \right] , \quad (18)$$

where  $T$  is the temperature,  $V$  the volume,  $m$  the mass of one atom (or one molecule) and  $h$  the Planck's constant. For one mole of matter  $R_* = k_B N_A$  is the product of the Boltzmann and Avogadro constants  $k_B$  and  $N_A$ . Note that the relationship (18) can be rewritten in the more compact forms

$$S_{\text{trans}}(T, V, m) = k_B N_A \ln \left[ \frac{e^{5/2} v}{h^3} (2 \pi m k_B T)^{3/2} \right] , \quad (19)$$

$$S_{\text{trans}}(T, V, m) = R_* \ln \left[ e^{5/2} T^{3/2} V M^{3/2} \frac{(2 \pi k_B)^{3/2}}{h^3 N_A^{5/2}} \right] , \quad (20)$$

where  $e = \exp(1)$ ,  $R_* = k_B N_A$  is the gas constant,  $v = V/N_A$  the "volume per molecule" and  $M = N_A m$  the molar mass. The last formula (20) corresponds to the following alternative relationship of (18):

$$S_{\text{trans}}(T, V, M) = R_* \left[ \frac{5}{2} + \frac{3}{2} \ln(T) + \ln(V) + \frac{3}{2} \ln(M) + \ln\left(\frac{(2 \pi k_B)^{3/2}}{h^3 N_A^{5/2}}\right) \right] , \quad (21)$$

where the last term of (21) into the squared brackets is a true constant only depending on 3 of the fundamental constants of physics ( $k_B$ ,  $h$  and  $N_A$ ).

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Equation (18) corresponds to Eqs. (1) and (6) in Grimus (2013a) with  $E = (3/2) R T$  and  $z = 1$ . This equation can be derived according to Mayer and Mayer (1940, Eq.6.17, p.128), Atkins and de Paula (2014, p.615) or Kennedy et al. (2019, Eqs.1 to 9) from the general link between the translation molar entropy  $S_{\text{trans}}$  and the corresponding partition function  $Q_t$  for a molecule of mass  $m$  of a gas at the temperature  $T$  located into a volume  $V$ :

$$Q_t = \frac{V}{(L_t)^3} = \frac{V (2 \pi m k_B)^{3/2}}{h^3} T^{3/2} , \quad (22)$$

$$\text{where } L_t = \frac{h}{\sqrt{2 \pi m k_B T}} \text{ is the "quantum thermal wavelength" ,} \quad (23)$$



$$\text{with } S_{\text{trans}} = k \left[ \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) + T \frac{d}{dT} \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) \right] \text{ for } N_A \text{ molecules,} \quad (24)$$

$$\text{and thus with } S_{\text{trans}} = R_* \left[ \ln(Q_t) + T \frac{d \ln(Q_t)}{dT} \right] - k \ln(N_A!) . \quad (25)$$

The exponent  $N_A$  of the two terms  $(Q_t)^{N_A}$  in (24) are due to the product of  $N_A$  similar partition functions  $Q_t$ , each valid for one molecule.

The two terms  $N_A!$  in (24) and  $-k \ln(N_A!)$  in (25) are due to for the inability to distinguish between the  $N_A$  identical molecules in a mole of constituent (see Kennedy et al., 2019, p.3).

The molar translational entropy given by (18) is obtained from (25) with  $R_* = k N_A$  and due to the Stirling approximation for the factorial:

$$N_A! \approx \sqrt{2 \pi N_A} \left( \frac{N_A}{e} \right)^{N_A} \quad \text{or} \quad \ln(N_A!) \approx N_A \ln \left( \frac{N_A}{e} \right) = N_A \ln(N_A) - N_A, \quad (26)$$

where  $e = \exp(1)$  and where the term  $0.5 \ln(2 \pi N_A) \approx 28.3$  has been dully dropped because it is much smaller than  $N_A \ln(N_A) \approx 328.5 \cdot 10^{23}$ ,  $N_A \approx 6 \cdot 10^{23}$  and  $N_A \ln(N_A) - N_A \approx 322.5 \cdot 10^{23}$ .

The entropy formulation (24) for  $S = (U - F)/T = \Psi + U/T$  can be computed from either the free energy  $F = U - T S$  or the Massieu-Planck  $\Psi = -F/T = S - U/T$  functions, on the one hand, and the internal energy  $U$  function, on the other hand, all defined in general statistical physics in terms of the partition function  $Q_t$  according to:

$$U_{\text{trans}} - U_0 = k T^2 \frac{d}{dT} \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) = N_A k T^2 \frac{d \ln(Q_t)}{dT} = R_* T^2 \frac{d \ln(Q_t)}{dT}, \quad (27)$$

$$F_{\text{trans}} - F_0 = -k T \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) = -R_* T \ln(Q_t) + k T \ln(N_A!) \approx -R_* T \ln \left( \frac{e Q_t}{N_A} \right), \quad (28)$$

$$\Psi_{\text{trans}} - \Psi_0 = k \ln \left( \frac{(Q_t)^{N_A}}{N_A!} \right) = R_* \ln(Q_t) - k \ln(N_A!) \approx R_* \ln \left( \frac{e Q_t}{N_A} \right), \quad (29)$$

$$S_{\text{trans}} = (\Psi_{\text{trans}} - \Psi_0) + \frac{(U_{\text{trans}} - U_0)}{T} \approx R_* \left[ \ln \left( \frac{e Q_t}{N_A} \right) + T \frac{d \ln(Q_t)}{dT} \right]. \quad (30)$$

The reference values  $U_0$ ,  $F_0 = U_0$  and  $\Psi_0 = -U_0/T$  are introduced to better show that only  $S_{\text{trans}}$  is defined in a clear absolute way, with  $S_0 = 0$ . This does not mean that it is impossible to compute the translational internal energy  $U$  and in an absolute way, with  $U_0$  to be determined. This only means that it has not been done yet in a theoretical way similar to what has been done for the entropy by Sackur, Tetrode and Planck in the years 1911 to 1916.

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The formulation  $L_t = h/\sqrt{2 \pi m k T}$  in (23) for the “*quantum thermal wavelength*” is close to, but different from, the de Broglie’s wave length  $\lambda = h/P$  associated with the classical formulations for the impulsion  $P$ , the kinetic energy  $E_c$  and the internal energy  $E_i$  of a particle of mass  $m$ , because the relationship  $E_c = E_i$  with  $E_c = P^2/(2 m)$  and  $E_i = (1/2) k T$  leads to  $L_t = h/\sqrt{m k T}$ , without the factor  $2 \pi$ . The true quantum formulation (23) corresponds to the quantum internal energy  $E_i = \pi k T$  instead, because the temperature dependent expression for the kinetic energy is not a property of a single particle, but for an ensemble of waves. The  $(1/2)$  factor comes from a statistical consideration of degrees of freedom of a mechanical particle scheme, whereas the factor “ $\pi$ ” comes from a wave picture.

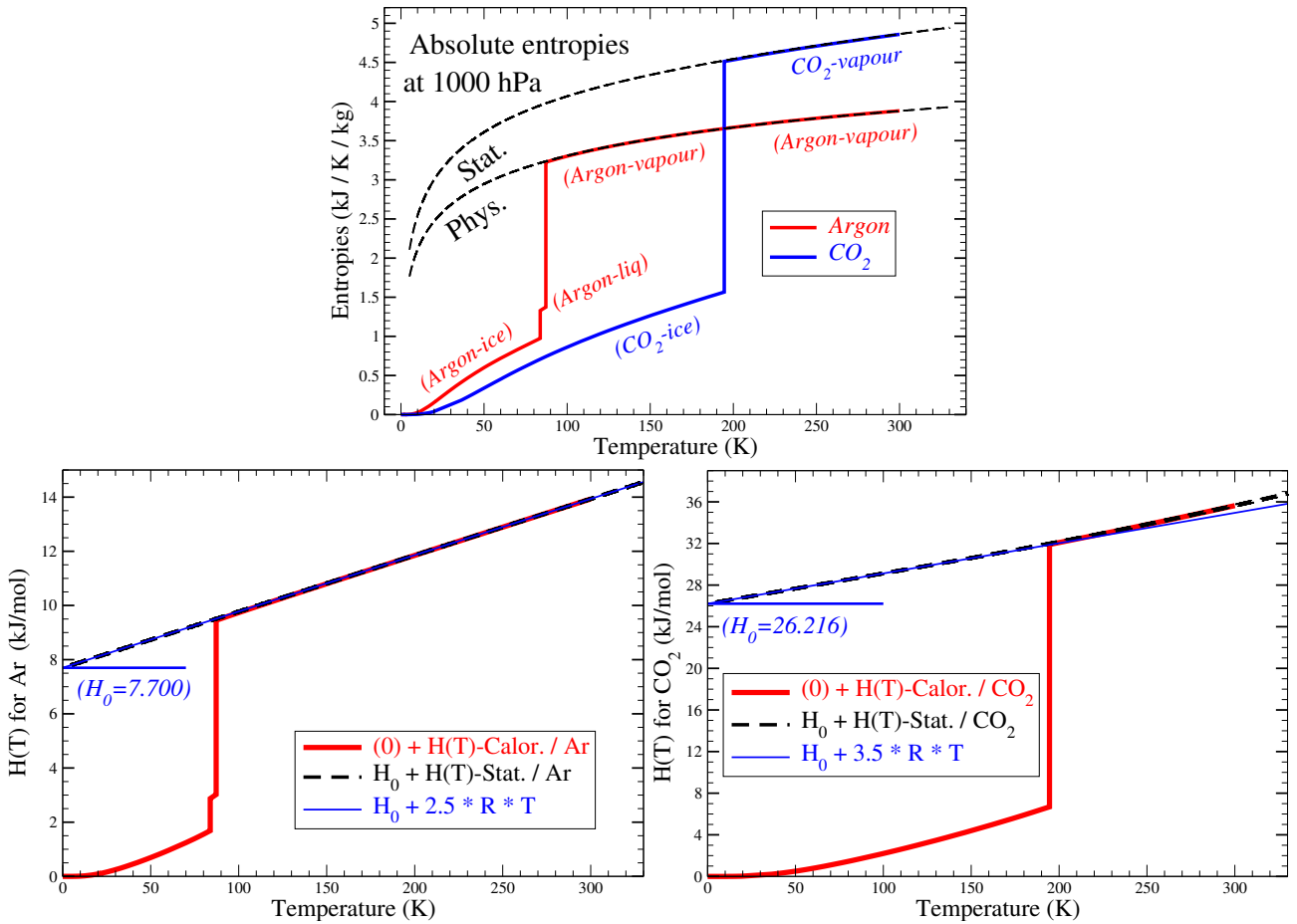


Figure 4: **Top:** the same as Figs. 1 for the absolute entropies for Ar and  $\text{CO}_2$ , with both the calorimetric values (red and blue curves) and the Sackur-Tetrode-absolute statistical-physic entropies (dashed black curves). **Bottom:** the same Figs. 9 for the calorimetric enthalpies  $H_0$  (in red) for Ar and  $\text{CO}_2$ , with the calorimetric value (red curves) and the expected statistical-physic values (dashed black curves) with the offset in enthalpies (in blue): namely the reference enthalpies  $H_0$  with the presently unexplained values of about 7700 and 26 216  $\text{J mol}^{-1}$  for Ar and  $\text{CO}_2$ , respectively.

The explanation for using the quantum relationship  $E_i = \pi k T$  can be found in Atkins and de Paula (2014, p.318 and 615), where the 3D translational partition function (22) is the product  $Q_t = (Q_{t/1D})^3$  of the value  $Q_{t/1D}$  for a particle (proton) of mass  $m \approx 10^{-27}$  kg, in a 1D box of width  $L \approx 1$  m, and for a thermal system at a temperature  $T \approx 300$  K. For this particle the quantized energy for a stationary wave function  $\psi(0) = \psi(L) = 0$  is  $E_n = n^2 h^2 / (8 m L^2) = n^2 E_1$ , where the fundamental energy is  $E_1 = h^2 / (8 m L^2) \approx 10^{-40}$  J and thus with  $k T \approx 4 \cdot 10^{-21}$  J and  $E_1 / (k T) \approx 10^{-20}$ .

The 1D partition function

$$Q_{t/1D} = \sum_{n=1}^{\infty} \exp[-n^2 E_1 / (k T)]$$

is defined with an infinite sum depending on the discrete energy levels  $E_n$  and can be approximated by the Riemann integral  $\int_1^{+\infty} \exp[-y^2 E_1 / (k T)] dy$ , which in turn can be approximated by the integral  $\int_0^{+\infty} \exp[-z^2 E_1 / (k T)] dz$ , because the translational energy levels  $E_n = n^2 E_1$  are very close together since  $E_1 / (k T) \approx 10^{-20}$  is very small, with  $\exp[-n^2 E_1 / (k T)]$  remaining very close to 1 except for very large values of  $n$  or  $z$  of the order of  $10^{10}$  (leading to an integral from 1 to  $+\infty$  of the order of  $10^{-20}$ , whereas the integral from 0 to  $+1$  is of the order of unity and can be discarded

or added if needed). Then the substitution  $x^2 = z^2 E_1 / (k T)$  with  $dz = dx / \sqrt{E_1 / (k T)}$  leads to  $Q_{t/1D} \approx \sqrt{E_1 / (k T)} \int_0^\infty \exp(-x^2) dx$ , where the known integral  $\int_0^\infty \exp(-x^2) dx = \sqrt{\pi}/2$  (here is the explanation for the appearance of the factor  $\sqrt{\pi}$ ) leads to  $Q_t = (Q_{t/1D})^3$  given by (22) with  $L_t$  is given by (23).

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It may be valuable to explain with some details how the relationships (22) to (25) indeed lead to any of the absolute entropy formulas (18) to (21), with an attempt to trace the origin of the different terms.

If (22) is rewritten as:

$$Q_t = T^{3/2} V M^{3/2} \frac{(2\pi k_B)^{3/2}}{h^3 N_A^{3/2}}, \quad (31)$$

and with the translational entropy (25) rewritten with three different terms labelled with three different colors (red, blue and green):

$$S_{\text{trans}} = R_* \ln(Q_t) + R_* T \frac{d \ln(Q_t)}{dT} - k \ln(N_A!), \quad (32)$$

it is possible to rely on the Stirling's approximation (26) –very accurate for  $N_A \sim 10^{23}$ – with  $R_* = k N_A$  to give:

$$S_{\text{trans}} = R_* \left[ \frac{3}{2} \ln(T) + \ln(V) + \frac{3}{2} \ln(M) + \ln \left( \frac{(2\pi k_B)^{3/2}}{h^3 N_A^{3/2}} \right) \right] + \frac{3 R_*}{2} - R_* \ln(N_A) + R_*, \quad (33)$$

$$S_{\text{trans}} = R_* \left[ \left( \frac{3}{2} + \frac{2}{2} \right) R_* + \frac{3}{2} \ln(T) + \ln(V) + \frac{3}{2} \ln(M) + \ln \left( \frac{(2\pi k_B)^{3/2}}{h^3 N_A^{3/2} N_A^{2/2}} \right) \right], \quad (34)$$

which is indeed the same as (21).

According to (34):

- Most of the terms (in red) come from the red (Massieu-Planck) variable part  $R_* \ln(Q_t)$ ;
  - The two green terms  $(2/2) R_* = R_*$  and  $N_A^{2/2} = N_A$  coming from the green part  $-k \ln(N_A!)$  represent the impacts of the perfect-gas hypothesis of “*inability to distinguish between the  $N_A$  identical molecules into a mole of constituent*”;
  - The first of these green terms  $(2/2)$  combines with the blue fraction  $(3/2)$  to form the first constant purely numerical term  $(5/2) R_*$  in (21);
  - The second of these green terms  $N_A^{2/2}$  combines with a similar red term  $N_A^{3/2}$  to form the term  $N_A^{5/2}$  at the denominator of the constant fraction in the last logarithm term in (21).
- 

The Sackur-Tetrode translational entropy (18) to (21) can also be expressed in a way similar to Tetrode (1915, Eq.16) and ready to use in atmospheric science, namely in terms of the absolute temperature  $T$ , the molar pressure  $p = R_* T / V$  or  $V = N_A k_B T / p$  and the molar mass  $M = m N_A$ , leading to

$$S_{\text{trans}}(T, p, M) = R_* \left[ \frac{5}{2} + \frac{5}{2} \ln(T) - \ln(p) + \frac{3}{2} \ln(M) + K_{\text{ST}} \right], \quad (35)$$

$$\text{where } K_{\text{ST}} = \ln \left( \frac{(2\pi)^{3/2} k^{5/2}}{h^3 N_A^{3/2}} \right) \approx 18.22285 \text{ is the Sackur-Tetrode constant.} \quad (36)$$

The special value for  $K_{\text{ST}}$  would be different if a non-zero additive constant  $S_0$  had been added to the Planck-Boltzmann equation  $S = k \ln(W) + S_0$ , with  $S_0$  left undefined and allowed to depend on this or that gas. For this reason, Tetrode (1912a) explained that “*according to Nernst’s heat theorem in its broadest version*<sup>2</sup>, *however, this is not the case. Therefore, one has to omit the addition ( $S_0$ ), so that in general:  $S = k \ln(W)$  applies*” and leads to an absolute definition of the translational entropy.

The same translational entropy (35), with  $K$  given by (36), is valid for mono-atomic (Ar), diatomic ( $\text{N}_2$  and  $\text{O}_2$ ), linear triatomic ( $\text{CO}_2$ ) and other triatomic ( $\text{H}_2\text{O}$ ) atoms and molecules, with the only degree of freedom given by the molar mass  $M$ , which depends on the given gas. Additional rotational, vibrational and electronic degrees of freedom must be taken into account and are different for each diatomic or triatomic gases. However, the translational molar entropy is always fully given by (35), with the same  $K_{\text{ST}}$  given by (36) for all atoms and molecules and bringing the absolute definition for the entropy of all atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , etc).

## 4.2 The statistical absolute reference entropies: Argon

The standard absolute entropy for Argon  $S_{\text{trans./Ar}}$  can be computed from (35) for  $T = 298.15$  K,  $p_0 = 1000$  hPa and with the constants  $R_* \approx 8.3144$  J K<sup>-1</sup> mol<sup>-1</sup>,  $M = M_{\text{Ar}} \approx 0.039948$  kg mol<sup>-1</sup> and  $K_{\text{ST}} \approx 18.22285$  recalled in Tables 24 and 25 for CODATA-1973 and NIST-JANAF-4, leading to

$$S_{\text{trans./Ar}} \approx 154.845 \pm 0.006 \text{ J K}^{-1} \text{ mol}^{-1} \quad (37)$$

$$\text{and } s_{\text{trans.}} = \frac{S_{\text{trans./Ar}}}{M_{\text{Ar}}} \approx 3876.2 \pm 0.3 \text{ J K}^{-1} \text{ kg}^{-1}. \quad (38)$$

The agreement with the NIST-JANAF-4 (Chase, 1998, p.175) and Atkins and de Paula (2014, Table 2C.5, p.973) values of  $154.845 \pm 0.003$  J K<sup>-1</sup> mol<sup>-1</sup> and 154.845, respectively, is very good. The uncertainty of  $\pm 0.006$  J K<sup>-1</sup> mol<sup>-1</sup> in (37) is mainly due to the impact of the relative error  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$  in the formula

$$\frac{\Delta S_{\text{trans./Ar}}}{S_{\text{trans./Ar}}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{trans./Ar}}} \left( \frac{3}{2} \frac{\Delta M_{\text{Ar}}}{M_{\text{Ar}}} + \frac{\Delta K_{\text{ST}}}{K_{\text{ST}}} \right) \approx 3.9 \cdot 10^{-5}, \quad (39)$$

whereas the impacts of  $\Delta M_{\text{Ar}}/M_{\text{Ar}} \approx 2.5 \cdot 10^{-5}$  and  $\Delta K_{\text{ST}}/K_{\text{ST}} \approx 0.55 \cdot 10^{-5}$  are reduced due to the factor  $R_*/(S_{\text{trans./Ar}}) \approx 1/19$ . The larger uncertainty of the specific value  $s_{\text{trans./Ar}} = (S_{\text{trans./Ar}})/M_{\text{Ar}}$  is computed via

$$\frac{\Delta s_{\text{trans./Ar}}}{s_{\text{trans./Ar}}} \approx \frac{\Delta S_{\text{trans./Ar}}}{S_{\text{trans./Ar}}} + \frac{\Delta M_{\text{Ar}}}{M_{\text{Ar}}}. \quad (40)$$

A more recent value for the standard absolute entropy for Argon can be computed at  $T = 298.15$  K and  $p_0 = 1000$  hPa with the use of the CODATA-2017 and IUPAC-2017 values of  $R_*$ ,  $M_{\text{Ar}}$  and  $K_{\text{ST}}$  (see the Tables 24 and 25), leading to  $154.824 \pm 0.020$  J K<sup>-1</sup> mol<sup>-1</sup> and  $3882.4 \pm 7$  J K<sup>-1</sup> kg<sup>-1</sup>. The larger uncertainties of about  $0.02$  J K<sup>-1</sup> mol<sup>-1</sup> and  $7$  J K<sup>-1</sup> kg<sup>-1</sup> are mainly due to the (much) larger relative error on  $\Delta M_{\text{Ar}}/M_{\text{Ar}} \approx 1.6 \cdot 10^{-3}$ .

Due to the smaller IUPAC-2017 value for  $M_{\text{Ar}}$  ( $39.948 \rightarrow 39.878$  g kg<sup>-1</sup>), the absolute molar entropy for Argon is logically smaller than for the NIST-JANAF-4 and IUPAC-1993 value expressed in units of J K<sup>-1</sup> mol<sup>-1</sup> in (37), but with a larger specific value in units of J K<sup>-1</sup> kg<sup>-1</sup> in (38). This can be explained from Eq. (35) where  $S_{\text{trans./Ar}}$  depends on the molar mass via the term  $(3/2) R_* \ln(M_{\text{Ar}})$ ,

<sup>2</sup>Namely the generalization of Planck (1917), nowadays called the third law of thermodynamics: the entropy of the most stable phase of all solid is 0 at the absolute temperature 0 K.

and thus is smaller because of the large decrease of  $M_{\text{Ar}}$ . Differently, the impact on the absolute specific entropy  $s_{\text{trans./Ar}}$  expressed in units of  $\text{J K}^{-1} \text{kg}^{-1}$  is dominated in (38) by the division by a smaller value of  $M_{\text{Ar}}$ , this explaining the increase of this specific formulation of entropy. However, due to the increase in uncertainties, the agreements of the NIST-JANAF-4 and CODATA-2013 values of  $s_{\text{trans./Ar}} = S_{\text{trans./Ar}}/M_{\text{Ar}}$  with the IUPAC-2017 and CODATA-2017 values are still valid. It will be important to recalculate these values of the absolute entropy of Argon according to the evolution of the next IUPAC recommendations of  $M_{\text{Ar}}$ .

Since the standard molar entropy  $154.845 \pm 0.006 \text{ J K}^{-1} \text{mol}^{-1}$  computed in (37) for Argon at 1000 hPa and 298.15 K is the same as the value  $154.845 \text{ J K}^{-1} \text{mol}^{-1}$  in the NIST-JANAF-4 Table (Chase, 1998, p.175), and is in agreement with the rounded value value of about  $154.84 \text{ J K}^{-1} \text{mol}^{-1}$  published in the Table 2C.5 of Atkins and de Paula (2014, p.973), it is possible to use the formulation (35) with  $K$  given by (36) to compute the standard molar entropy of Argon at 1000 hPa and 273.15 K, with about the same accuracy as in (37) and (38), leading to

$$\boxed{S_{\text{Ar}}(1000 \text{ hPa and } 273.15 \text{ K}) = 153.024 \pm 0.006 \text{ J K}^{-1} \text{mol}^{-1}}, \quad (41)$$

$$\boxed{s_{\text{Ar}}(1000 \text{ hPa and } 273.15 \text{ K}) = 3830.59 \pm 0.3 \text{ J K}^{-1} \text{kg}^{-1}}. \quad (42)$$

An alternative solution was to rely on thermodynamic tables (such as Chase, 1998, for Argon, p.175) and extrapolate the values given at  $T_1 = 298.15 \text{ K}$  and  $T_2 = 300 \text{ K}$ , i.e.  $S_1 \approx 154.845$  and  $S_2 \approx 154.973 \text{ J K}^{-1} \text{mol}^{-1}$ . But, unfortunately, most of the atmospheric science community does not seem to trust these thermodynamic tables, hence the concern to show in this note how to redo the calculations yourself, in a scientifically transparent way. The logarithmic-extrapolated value of  $S_{\text{Ar}}$  at  $T = 275.15 \text{ K}$  is  $[S_1 \ln(T/T_2) - S_2 \ln(T/T_1)] / \ln(T_1/T_2) \approx 153.033 \text{ J K}^{-1} \text{mol}^{-1}$ , which is close to the computed value given by (41) and almost within the (one  $\sigma$ ) uncertainty range between 153.018 and 153.030  $\text{J K}^{-1} \text{mol}^{-1}$ .

The good agreement between these calculated and extrapolated values of the absolute entropy of Argon indicates that this whole section 4.2 could have been reduced to (41) and (42) only, but with the extrapolated values from Chase (1998, p.175). One can only regret this guilty lack of confidence in the thermodynamic tables for so many atmospheric scientists.

### 4.3 The statistical absolute reference entropies: $\text{N}_2$

Still in a scientifically transparent way, let us (re)compute the absolute molar entropy for  $\text{N}_2$ , and compare it with the extrapolated value from Chase (1998, p.1621) and Table 2C.5 of Atkins and de Paula (2014, p.973).

The translational molar entropy of  $\text{N}_2$  can be computed at  $T = 298.15 \text{ K}$  and 1000 hPa from the same Eqs. (35) and (36) with the constants  $R_* \approx 8.3144 \text{ J K}^{-1} \text{mol}^{-1}$ ,  $M = M_{\text{N}_2} \approx 0.0280134 \text{ kg mol}^{-1}$  and  $K_{\text{ST}} \approx 18.22285$  for CODATA-1973 and NIST-JANAF-4 (see Tables 24 and 25), but with the accuracy of  $M_{\text{N}_2}$  from TEOS10 (McDougall et al., 2010), leading to

$$S_{\text{trans./N}_2} \approx 150.419 \pm 0.006 \text{ J K}^{-1} \text{mol}^{-1}. \quad (43)$$

According to Atkins and de Paula (2014, Eq. 15E.12b, p.641) or Kennedy et al. (2019, Eq. 17, p.5), the molar rotational entropy for a diatomic molecule like  $\text{N}_2$  is given by

$$S_{\text{rot.0}}(T, \Theta_{\text{rot.0}}) = R_* \left[ 1 - \ln \left( \sigma_r \frac{\Theta_{\text{rot.0}}}{T} \right) \right] \quad \text{or} \quad S_{\text{rot.0}}(T, I) = R_* \left[ 1 + \ln \left( \frac{T \times I}{\sigma_r C_R} \right) \right], \quad (44)$$

where the rotational temperature  $\Theta_{\text{rot.0}}$  is computed from the principal moment of rotational inertia  $I$  according to  $\Theta_{\text{rot.0}} = C_R/I$  with  $C_R = h^2/(8 \pi^2 k)$ , or  $\Theta_{\text{rot.0}} = c_2 \tilde{B}$  where  $c_2 = h c/k$  and with

$\tilde{B} = h/(8\pi^2 c I)$  the rotational constant of the molecule. For the molecule  $N_2$  the rotational resonance symmetry number is  $\sigma_r = 2$ , the principal moment of rotational inertia is  $I_{N_2} \approx 14.235 \cdot 10^{-47} \text{ kg m}^2$  and the rotational temperature is  $\Theta_{\text{rot},0/N_2} = C_R/I_{N_2} \approx 40.276 \cdot 10^{-47}/I_{N_2} \approx 2.83 \text{ K}$  due to  $\tilde{B} = \Theta_{\text{rot},0}/c_2 \approx 1.9669 \text{ cm}^{-1}$ .

However, corrections due to rota-vibration must be taken into account, like in Mayer and Mayer (1940, Eq.7.17, p.155), JANAF-2 (Stull and Prophet, 1971, p.9) and NIST-JANAF-4 (Chase, 1998, p.18, with the exponent 2 forgotten in the quadratic correction term), where (44) is modified so that

$$S_{\text{rot.}/N_2} \left( \frac{\Theta_{\text{rot.}/N_2}}{T} \right) \approx R_* \left[ 1 - \ln \left( \sigma_r \frac{\Theta_{\text{rot.}/N_2}}{T} \right) - \frac{1}{90} \left( \frac{\Theta_{\text{rot.}/N_2}}{T} \right)^2 \right] \quad (45)$$

includes a quadratic correction term due to the effect of centrifugal distortion on the roto-vibrational partition function of linear molecules, namely the first term of the expression  $(1 + b^2/90 + 8b^3/2835 + \dots)$  in Martin et al. (1991, Eq. 2, p.8375) with  $b = c_2 B/T$  for the semirigid-rotor partition function, whereas  $\Theta_{\text{rot},0/N_2} \approx c_2 \tilde{B}$  is modified so that

$$\Theta_{\text{rot.}/N_2} = c_2 \left( \tilde{B}_e - \frac{\tilde{\alpha}_e}{2} \right). \quad (46)$$

The formulation (45) corresponds to the rotational energy levels  $F(J) = \tilde{B}_e J(J+1)$  recalled in Martin et al. (1991, Eq. 1, p.8375), with a degeneracy  $2J+1$  and where  $J$  are the rotational quantum non-negative integer numbers. These rotational energy levels of Eq. 1 in Martin et al. (1991) are valid for homonuclear diatomic ( $N_2$ ,  $O_2$ ) and symmetrical linear ( $CO_2$ ) molecules, for which  $\sigma_r = 2$  due to rotation through  $180^\circ$  leading to indistinguishable states. The rotational partition function can then be written as

$$Q_{\text{rot}} \approx \frac{T}{\sigma_r \Theta_{\text{rot.}}} \left[ 1 + \frac{1}{90} \left( \frac{\Theta_{\text{rot.}}}{T} \right)^2 \right], \quad (47)$$

$$\text{where } S_{\text{rot}} = R_* \left[ \ln(Q_{\text{rot}}) + T \frac{d \ln(Q_{\text{rot}})}{dT} \right] = R_* \left[ \ln(Q_{\text{rot}}) - u \frac{d \ln(Q_{\text{rot}})}{du} \right] \quad (48)$$

leads to (45) for small values of  $u = \Theta_{\text{rot.}}/T \approx 1/100$  at  $T = 298.15 \text{ K}$  for  $\Theta_{\text{rot.}} \approx 2.8 \text{ K}$ , and thus with  $\ln(1 + u^2/90) \approx u^2/90$ . The term  $\exp(u/3)$  in McDowell (1988, Eq.5, p.357) and Martin et al. (1991, Eq.2, p.8375) is omitted in (47) because it gives no contribution to  $S_{\text{rot}}$  in (48) since  $\ln[\exp(u/3)] = u/3$  is linear in  $u$  and its contribution to  $S_{\text{rot}}$  via (48) is  $R_* [1 - (u/u)]/3 = 0$ .

The values  $\sigma_r = 2$  and  $c_2 \approx 1.438786 \text{ cm K}$  from NIST-JANAF-4 (see Chase, 1998, and Table 24), with the rotational spectroscopic constants  $\tilde{B}_e \approx 1.99824 \text{ cm}^{-1}$  and  $\tilde{\alpha}_e \approx 0.017318 \text{ cm}^{-1}$  from Laher and Gilmore (1991, Table 2, p.688, for the ground state configuration  $X^1\Sigma_g^+$ ), lead to  $\Theta_{\text{rot.}/N_2} \approx 2.86258 \text{ K}$ . The other spectroscopic constants  $\tilde{B}_e \approx 1.998197 \text{ cm}^{-1}$  and  $\tilde{\alpha}_e \approx 0.017279 \text{ cm}^{-1}$  from Chase (1998, p.1621, the first two terms of  $B$ ) lead to the other close value  $\Theta_{\text{rot.}/N_2} \approx 2.86255 \text{ K}$ , and to an accuracy likely of about  $\pm 0.00005 \text{ K}$  for  $\Theta_{\text{rot.}/N_2}$ .

These two values for  $\Theta_{\text{rot.}/N_2}$  lead to the same molar rotational entropy for  $N_2$ :

$$S_{\text{rot.}/N_2} \approx 41.179 \pm 0.002 \text{ J K}^{-1} \text{ mol}^{-1}, \quad (49)$$

where the quadratic correction term of (45) leads to a tiny impact ( $< 10^{-6}$ ) and might have been omitted for the standard temperature of  $298.15 \text{ K} \gg \Theta_{\text{rot.}/N_2} \approx 2.86 \text{ K}$ . However, the quadratic correction term has larger impacts to plot dashed lines for smaller temperatures ( $T < 50 \text{ K}$ ) in Figs. (1).

The accuracy of  $S_{\text{rot.}/N_2}$  is computed at  $T = 298.15 \text{ K}$  from (45) and

$$\frac{\Delta S_{\text{rot.}/N_2}}{S_{\text{rot.}/N_2}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{rot.}/N_2}} \left| 1 - \frac{1}{45} \left( \frac{\Theta_{\text{rot.}/N_2}}{T} \right)^2 \right| \frac{\Delta \Theta_{\text{rot.}/N_2}}{\Theta_{\text{rot.}/N_2}} \approx 4 \cdot 10^{-5} \quad (50)$$

with  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $(R_*/S_{\text{rot.}/N_2}) \approx 0.2$ ,  $T = 298.15$  K,  $\Theta_{\text{rot.}/N_2} \approx 2.86$  K,  $(\Theta_{\text{rot.}/N_2}/T) \approx 0.0096$  and  $(\Delta\Theta_{\text{rot.}/N_2}/\Theta_{\text{rot.}/N_2}) \approx 2 \cdot 10^{-5}$ .

The molar vibrational entropy for a diatomic molecule like  $N_2$  used in Chase (1998, p.18) corresponds to Atkins and de Paula (2014, Eq. 15E.13b, p.642) or Kennedy et al. (2019, Eq. 25, p.8):

$$S_{\text{vibr.}/N_2}(u) = R_* \left( \frac{u}{\exp(u) - 1} - \ln[1 - \exp(-u)] \right), \quad (51)$$

$$\text{where } u = c_2 \left( \frac{\omega_e - 2\omega_e x_e}{T} \right) = \frac{\Theta_{\text{vib.}/N_2}}{T}. \quad (52)$$

The vibrational spectroscopic constants for  $N_2$  are:  $\omega_e \approx 2358.57$   $\text{cm}^{-1}$  and  $\omega_e x_e \approx 14.324$   $\text{cm}^{-1}$  in Laher and Gilmore (1991, Table 1, p.687, for  $X^1\Sigma_g^+$ );  $\omega_e \approx 2358.583$   $\text{cm}^{-1}$  and  $\omega_e x_e \approx 14.33594$   $\text{cm}^{-1}$  in Chase (1998, p.1621, the first two terms of  $G$ ), leading to  $\Theta_{\text{vib.}/N_2} \approx 3352.26$  K and  $3352.24$  K, respectively. The values of these vibrational temperatures are large (with respect to the standard temperature  $298.15$  K) and the molar vibrational entropy for  $N_2$  is logically smaller than those for the translational and rotational molar entropies (i.e. the vibration degrees of freedom are almost non activated at  $298.15$  K):

$$S_{\text{vib.}/N_2} \approx 0.001 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}. \quad (53)$$

The accuracy is computed from derivative of (51) with respect to  $u = \Theta_{\text{vib.}/N_2}/T \approx 11.24 \gg 1$  given by (52), which can be approximated for very large  $\exp(u) \approx 7.6 \cdot 10^4$  and very small  $\exp(-u) \approx 1.3 \cdot 10^{-5}$ , and thus with  $\exp(u) - 1 \approx \exp(u)$  and  $\ln[1 - \exp(-u)] \approx -\exp(-u)$ , leading to

$$S_{\text{vibr.}/N_2}(u) \approx R_* (u + 1) \exp(-u), \quad (54)$$

$$\ln[S_{\text{vibr.}/N_2}(u)] \approx \ln(R_*) + \ln(u + 1) - u, \quad (55)$$

and the relative change

$$\frac{\Delta S_{\text{vib.}/N_2}}{S_{\text{vib.}/N_2}} \approx \frac{\Delta R_*}{R_*} + \left| \frac{1}{u + 1} - 1 \right| \Delta u \approx \frac{\Delta R_*}{R_*} + \left( \frac{u^2}{u + 1} \right) \frac{\Delta \Theta_{\text{vib.}/N_2}}{\Theta_{\text{vib.}/N_2}} \approx 7 \cdot 10^{-5}, \quad (56)$$

where  $\Theta_{\text{vib.}/N_2} \approx 3352.26 \pm 0.01$  K,  $T = 298.15$  K,  $u = (\Theta_{\text{vib.}/N_2})/T \approx 12$  and with the relative uncertainties  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$  and  $\Delta u/u = \Delta(\Theta_{\text{vib.}/N_2})/\Theta_{\text{vib.}/N_2} \approx 0.01/3352 \approx 0.3 \cdot 10^{-5}$  at constant  $T = 298.15$  K.

Corrections to the molar entropy of  $N_2$  due to anharmonic vibrations are computed in JANAF-2 (Stull and Prophet, 1971, p.10) and NIST-JANAF-4 (Chase, 1998, p.18) from the correction partition function of Mayer and Mayer (1940, Eq.7.42, p.164), leading to

$$S_{\text{v-an.}/N_2}(u) = R_* \left[ \frac{16 g_e}{u} + \frac{d_e}{\exp(u) - 1} + \frac{d_e u \exp(u)}{[\exp(u) - 1]^2} + \frac{4 x_e u^2 \exp(u)}{[\exp(u) - 1]^3} \right], \quad (57)$$

where  $g_e = \tilde{B}_e/\omega_e$ ,  $d_e = \tilde{\alpha}_e/\tilde{B}_e$ ,  $x_e = (\omega_e x_e)/\omega_e$  and  $u = c_2 [\omega_e - 2(\omega_e x_e)]/T = \Theta_{\text{vib.}/N_2}/T$  is the same as in (52).

The first set of spectroscopic constants for  $N_2$  from Laher and Gilmore (1991, Tables 1 and 2, p.687 and 688 for the ground state configuration  $X^1\Sigma_g^+$ ) are

$$\tilde{B}_e \approx 1.99824 \text{ cm}^{-1}, \tilde{\alpha}_e \approx 0.017318 \text{ cm}^{-1}, \omega_e \approx 2358.57 \text{ cm}^{-1}, \omega_e x_e \approx 14.324 \text{ cm}^{-1},$$

leading to the rotational and vibrational temperatures

$$\Theta_{\text{rot.0}/N_2} = c_2 \tilde{B}_e \approx 2.87504 \text{ K},$$

$$\Theta_{\text{rot}/N_2} = c_2 [\tilde{B}_e - \tilde{\alpha}_e/2] \approx 2.86258 \text{ K},$$

$$\Theta_{\text{vib.0}/N_2} = c_2 \omega_e \approx 3393.49 \text{ K},$$

$$\Theta_{\text{vib.}/N_2} = c_2 [\omega_e - 2(\omega_e x_e)] \approx 3352.26 \text{ K}$$

and to the dimensionless values

$$g_e \approx 8.472\,3\,10^{-4}, d_e \approx 8.666\,6\,10^{-3}, x_e \approx 6.073\,2\,10^{-3}, u \approx 11.243\,54.$$

The other set of spectroscopic constants for N<sub>2</sub> from Chase (1998, p.1621, the first two terms of  $B$  and  $G$ ) are

$$\tilde{B}_e \approx 1.998\,197\,\text{cm}^{-1}, \tilde{\alpha}_e \approx 0.0172\,79\,\text{cm}^{-1}, \omega_e \approx 2358.583\,\text{cm}^{-1}, \omega_e x_e \approx 14.335\,94\,\text{cm}^{-1},$$

leading to the rotational and vibrational temperatures

$$\Theta_{\text{rot.0/N}_2} = c_2 \tilde{B}_e \approx 2.874\,98\,\text{K},$$

$$\Theta_{\text{rot/N}_2} = c_2 [\tilde{B}_e - \tilde{\alpha}_e/2] \approx 2.862\,55\,\text{K},$$

$$\Theta_{\text{vib.0/N}_2} = c_2 \omega_e \approx 3393.50\,\text{K},$$

$$\Theta_{\text{vib./N}_2} = c_2 [\omega_e - 2(\omega_e x_e)] \approx 3352.24\,\text{K}$$

and to the dimensionless values

$$g_e \approx 8.472\,0\,10^{-4}, d_e \approx 8.647\,3\,10^{-3}, x_e \approx 6.078\,2\,10^{-3} \text{ and } u \approx 11.243\,48.$$

The values 2.875 04 K and 2.874 98 K for  $\Theta_{\text{rot.0/N}_2}$ , and those 3393.49 K and 3393.50 K for  $\Theta_{\text{vib.0/N}_2}$ , are in agreement with the rounded rotation and vibration temperatures of about 2.88 K and 3393 K published in the Table 12.D1 of Atkins and de Paula (2014, p.987).

The molar entropy of N<sub>2</sub> at 298.15 K due to anharmonic vibrations is therefore

$$S_{\text{v-an./N}_2} \approx 0.010 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}. \quad (58)$$

The accuracy is computed by using the approximations  $u \approx 11$ ,  $\exp(u) \approx 7.6\,10^4 \gg 1$  and thus  $\exp(u) - 1 \approx \exp(u)$ , leading to

$$S_{\text{v-an./N}_2}(u) \approx R_* \left[ \frac{16\,g_e}{u} + \frac{d_e(u+1)}{\exp(u)} + \frac{4\,x_e\,u^2}{[\exp(u)]^2} \right] \approx R_* \frac{16\,g_e}{u}, \quad (59)$$

because the three bracketed terms are of the order of  $1.2\,10^{-3}$ ,  $1.4\,10^{-6}$  and  $5.3\,10^{-10}$ , respectively. Then, the relative change of (59) gives

$$\frac{\Delta S_{\text{v-an./N}_2}}{S_{\text{v-an./N}_2}} \approx \frac{\Delta R_*}{R_*} + \frac{\Delta u}{u} \approx 4.10^{-5} \quad (60)$$

for  $\Delta R_*/R_* \approx 3.6\,10^{-5}$  and  $\Delta u/u \approx 0.3\,10^{-5}$ .

The standard molar entropy of N<sub>2</sub> at 1000 hPa and 298.15 K is the sum of all components due to quantum and statistical degrees of freedom:

N <sub>2</sub> / Translation:	150.419	±0.006	J K <sup>-1</sup> mol <sup>-1</sup>	
N <sub>2</sub> / Rotation:	41.179	±0.002	J K <sup>-1</sup> mol <sup>-1</sup>	
N <sub>2</sub> / Vibration:	0.001	±0.000 ...	J K <sup>-1</sup> mol <sup>-1</sup>	
N <sub>2</sub> / Anharmonic:	0.010	±0.000 ...	J K <sup>-1</sup> mol <sup>-1</sup>	
N <sub>2</sub> / Total:	191.609	±0.008	J K <sup>-1</sup> mol <sup>-1</sup>	(61)

N <sub>2</sub> / NIST-JANAF-4:	191.609	±0.020	J K <sup>-1</sup> mol <sup>-1</sup>	(62)
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N <sub>2</sub> / Total:	6839.904	±0.34	J K <sup>-1</sup> kg <sup>-1</sup>	(63)
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The uncertainty of  $\pm 0.34 \text{ J K}^{-1} \text{ kg}^{-1}$  in (63) for the specific value  $s_{\text{N}_2} = S_{\text{N}_2}/M_{\text{N}_2}$  is computed like in (40) for Argon from NIST-JANAF-4 molar mass and IUPAC-2013 accuracy recalled in Table 25, but for N<sub>2</sub>, leading to

$$\frac{\Delta s_{\text{N}_2}}{s_{\text{N}_2}} \approx \frac{\Delta S_{\text{N}_2}}{S_{\text{N}_2}} + \frac{\Delta M_{\text{N}_2}}{M_{\text{N}_2}} \approx 4.2\,10^{-5} + 1.1\,10^{-5} \approx 5.3\,10^{-5}. \quad (64)$$

Since the total molar entropy  $191.609 \pm 0.008 \text{ J K}^{-1} \text{ mol}^{-1}$  computed in (61) for N<sub>2</sub> at 1000 hPa and 298.15 K is the same as the value in the NIST-JANAF-4 Table (Chase, 1998, p.1621) recalled in (62),



and is very close to the rounded value of about  $191.61 \text{ J K}^{-1} \text{ mol}^{-1}$  published in the Table 2C.5 of Atkins and de Paula (2014, p.976), it is possible to use the same JANAF-4 formulations recalled in this section to compute the standard molar entropy of  $\text{N}_2$  at 1000 hPa and 273.15 K, with about the same accuracy as at 298.15 K, leading to

$$S_{\text{N}_2} (1000 \text{ hPa and } 273.15 \text{ K}) = 189.059 \pm 0.008 \text{ J K}^{-1} \text{ mol}^{-1}, \quad (65)$$

$$s_{\text{N}_2} (1000 \text{ hPa and } 273.15 \text{ K}) = 6748.87 \pm 0.34 \text{ J K}^{-1} \text{ kg}^{-1}. \quad (66)$$

As for Argon, it would also have been possible to rely on the NIST-JANAF-4 table of Chase (1998, p.1621) and calculate the logarithmic-extrapolated value at 273.15 K from the standard molar entropy of  $\text{N}_2$  at 298.15 K and 300 K ( $191.609$  and  $191.789 \text{ J K}^{-1} \text{ mol}^{-1}$ ), leading to the extrapolated value  $189.061 \text{ J K}^{-1} \text{ mol}^{-1}$  in full agreement with the computed value  $189.059 \pm 0.008 \text{ J K}^{-1} \text{ mol}^{-1}$  in (65).

#### 4.4 The statistical absolute reference entropies: $\text{O}_2$

Still in a scientifically transparent way, let us (re)compute the absolute molar entropy for  $\text{O}_2$ , and compare it with the extrapolated value from Chase (1998, p.1745) and Table 2C.5 of Atkins and de Paula (2014, p.973).

The same formulations as for  $\text{N}_2$  can be used for the translational, rotational, vibrational and anharmonic components of the absolute entropy for  $\text{O}_2$ , but with an additional component due to the electronic component.

The translational absolute entropy can be computed with the formula (35) and with the molar mass  $M_{\text{O}_2} \approx 0.0319988 \pm 0.0000004 \text{ kg mol}^{-1}$ , leading to

$$S_{\text{trans./O}_2} \approx 152.077 \pm 0.006 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (67)$$

The accuracy of  $S_{\text{trans./O}_2}$  is computed with the formula (39)

$$\frac{\Delta S_{\text{trans./O}_2}}{S_{\text{trans./O}_2}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{trans./O}_2}} \left( \frac{3}{2} \frac{\Delta M_{\text{O}_2}}{M_{\text{O}_2}} + \frac{\Delta K_{\text{ST}}}{K_{\text{ST}}} \right) \approx 3.7 \cdot 10^{-5}, \quad (68)$$

where the relative accuracies are  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $\Delta(M_{\text{O}_2})/M_{\text{O}_2} \approx 1.25 \cdot 10^{-5}$ ,  $R_*/S_{\text{trans./O}_2} \approx 1/18$  and  $\Delta K_{\text{ST}}/K_{\text{ST}} \approx 0.55 \cdot 10^{-5}$ .

The rotational, vibrational and anharmonic components of the entropy for  $\text{O}_2$  can be computed with the same rotational resonance symmetry number  $\sigma_r = 2$  as for  $\text{N}_2$  and with the same formulas (45), (52) and (57).

The rotation and vibration constants of Laher and Gilmore (1991, Tables 3 and 4, p.688 and 689, for the ground state configuration  $X^3\Sigma_g^-$ ) are:

$$\tilde{B}_e \approx 1.4451 \text{ cm}^{-1}, \tilde{\alpha}_e \approx 0.01523 \text{ cm}^{-1}, \omega_e \approx 1580.39 \text{ cm}^{-1}, \omega_e x_e \approx 12.112 \text{ cm}^{-1},$$

leading to the characteristic temperatures and dimensionless values:

$$\Theta_{\text{rot.0/O}_2} = c_2 \tilde{B}_e \approx 2.0792 \text{ K},$$

$$\Theta_{\text{rot/O}_2} = c_2 [\tilde{B}_e - \tilde{\alpha}_e/2] \approx 2.0682 \text{ K},$$

$$\Theta_{\text{vib.0/O}_2} = c_2 \omega_e \approx 2273.84 \text{ K},$$

$$\Theta_{\text{vib./O}_2} = c_2 [\omega_e - 2(\omega_e x_e)] \approx 2238.99 \text{ K},$$

$$g_e = \tilde{B}_e/\omega_e \approx 9.1439 \cdot 10^{-4},$$

$$d_e = \tilde{\alpha}_e/\tilde{B}_e \approx 1.0539 \cdot 10^{-2},$$

$$x_e = (\omega_e x_e)/\omega_e \approx 7.6639 \cdot 10^{-3},$$

$$u = \Theta_{\text{vib.}/\text{O}_2}/T \approx 7.5096 \quad (\text{at } T = 298.15 \text{ K}).$$

The rotation and vibration constants of Chase (1998, for the ground state configuration  $X^3\Sigma_g^-$  in the top line of the Table p.1745) are:

$$\begin{aligned} \tilde{B}_e &\approx 1.445662 \text{ cm}^{-1}, \tilde{\alpha}_e \approx 0.01593268 \text{ cm}^{-1}, \omega_e \approx 1580.3932 \text{ cm}^{-1}, \omega_e x_e \approx 11.980804 \text{ cm}^{-1}, \\ &\text{leading to the characteristic temperatures and dimensionless values:} \\ \Theta_{\text{rot.0}/\text{O}_2} &= c_2 \tilde{B}_e \approx 2.07994 \text{ K}, \\ \Theta_{\text{rot}/\text{O}_2} &= c_2 [\tilde{B}_e - \tilde{\alpha}_e/2] \approx 2.06848 \text{ K}, \\ \Theta_{\text{vib.0}/\text{O}_2} &= c_2 \omega_e \approx 2273.56 \text{ K}, \\ \Theta_{\text{vib.}/\text{O}_2} &= c_2 [\omega_e - 2(\omega_e x_e)] \approx 2239.08 \text{ K}, \\ g_e &= \tilde{B}_e/\omega_e \approx 9.148388 \cdot 10^{-4}, \\ d_e &= \tilde{\alpha}_e/\tilde{B}_e \approx 1.102133 \cdot 10^{-2}, \\ x_e &= (\omega_e x_e)/\omega_e \approx 7.581860 \cdot 10^{-3}, \\ u &= \Theta_{\text{vib.}/\text{O}_2}/T \approx 7.509927 \quad (\text{at } T = 298.15 \text{ K}). \end{aligned}$$

The values 2.0792 K and 2.07994 K for  $\Theta_{\text{rot.0}/\text{O}_2}$ , and those 2273.84 K and 2273.56 K for  $\Theta_{\text{vib.0}/\text{O}_2}$ , are in agreement with the rounded rotation and vibration temperatures of about 2.08 K and 2274 K published in the Table 12.D1 of Atkins and de Paula (2014, p.987).

The rotational entropy of  $\text{O}_2$  computed with (45) leads to

$$S_{\text{rot.}/\text{O}_2} \approx 43.880 \pm 0.002 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (69)$$

The accuracy of  $S_{\text{rot.}/\text{O}_2}$  is computed at  $T = 298.15 \text{ K}$  like in (50) from

$$\frac{\Delta S_{\text{rot.}/\text{O}_2}}{S_{\text{rot.}/\text{O}_2}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{rot.}/\text{O}_2}} \left| 1 - \frac{1}{45} \left( \frac{\Theta_{\text{rot.}/\text{O}_2}}{T} \right)^2 \right| \frac{\Delta \Theta_{\text{rot.}/\text{O}_2}}{\Theta_{\text{rot.}/\text{O}_2}} \approx 5.3 \cdot 10^{-5}, \quad (70)$$

where  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $(R_*/S_{\text{rot.}/\text{O}_2}) \approx 0.19$ ,  $T = 298.15 \text{ K}$ ,  $\Theta_{\text{rot.}/\text{O}_2} \approx 2.07 \text{ K}$ ,  $(\Theta_{\text{rot.}/\text{O}_2}/T) \approx 0.0069$  and  $(\Delta \Theta_{\text{rot.}/\text{O}_2}/\Theta_{\text{rot.}/\text{O}_2}) \approx 0.0002/2.07 \approx 9.7 \cdot 10^{-5}$ .

The vibrational entropy of  $\text{O}_2$  computed with (52) leads to

$$S_{\text{vib.}/\text{O}_2} \approx 0.039 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}. \quad (71)$$

This value is larger than for  $\text{N}_2$  because  $\Theta_{\text{vib.}/\text{O}_2} \approx 2239 \text{ K}$  is smaller than  $\Theta_{\text{vib.}/\text{O}_2} \approx 3352 \text{ K}$  for  $\text{N}_2$ , and therefore with more vibrational degrees of freedom exited at  $T = 298.15 \text{ K}$  for  $\text{O}_2$  than for  $\text{N}_2$ . The accuracy of  $S_{\text{vib.}/\text{O}_2}$  is computed at  $T = 298.15 \text{ K}$  like in (50) from

$$\frac{\Delta S_{\text{vib.}/\text{O}_2}}{S_{\text{vib.}/\text{O}_2}} \approx \frac{\Delta R_*}{R_*} + \left( \frac{u^2}{u+1} \right) \frac{\Delta \Theta_{\text{vib.}/\text{O}_2}}{\Theta_{\text{vib.}/\text{O}_2}} \approx 18 \cdot 10^{-5}, \quad (72)$$

where  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $u = (\Theta_{\text{vib.}/\text{O}_2})/T \approx 7.5$ ,  $\Theta_{\text{vib.}/\text{O}_2} \approx 2239.08 \pm 0.05 \text{ K}$ ,  $\Delta(\Theta_{\text{vib.}/\text{O}_2})/\Theta_{\text{vib.}/\text{O}_2} \approx 2.2 \cdot 10^{-5}$  at constant  $T = 298.15 \text{ K}$  and  $\Delta S_{\text{vib.}/\text{O}_2} \approx 0.000007 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The anharmonic components of the entropy for  $\text{O}_2$  can be computed like for  $\text{N}_2$  from (57), leading to

$$S_{\text{v-an.}/\text{O}_2} \approx 0.016 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}. \quad (73)$$

The accuracy of  $S_{\text{v-an.}/\text{O}_2}$  is computed at  $T = 298.15 \text{ K}$  like in (60) from

$$\frac{\Delta S_{\text{v-an.}/\text{O}_2}}{S_{\text{v-an.}/\text{O}_2}} \approx \frac{\Delta R_*}{R_*} + \frac{\Delta u}{u} \approx 5.8 \cdot 10^{-5} \quad (74)$$

for  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$  and  $\Delta u/u = \Delta(\Theta_{\text{vib.}/\text{O}_2})/\Theta_{\text{vib.}/\text{O}_2} \approx 2.2 \cdot 10^{-5}$  at constant  $T = 298.15 \text{ K}$ , leading to.  $\Delta S_{\text{v-an.}/\text{O}_2} \approx 0.000001 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The statistical entropy for Oxygen vapour ( $O_2$ ) depends on an additional electronic contribution

$$S_{\text{elec.}/O_2} = R_* \ln(Q_e) \approx 9.134 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1} . , \quad (75)$$

where according to Kennedy et al. (2019, p.15): “*In the case of  $O_2$ , the ground state electronic partition function  $Q_e$  is 3 because this molecule has two unpaired electrons that can have their two spins oriented three ways with respect to the nuclear spin –both up, both down, and oppositely. Since they can be distinguished, the three different oxygen species have three times the volume per particle, affecting their action because of the greater radial separation than if only a single species existed. This gives an additional electronic entropy contribution of  $S_e = R_* \ln(Q_e)$  or  $R_* \ln(3)$ .*” Values of  $Q_e$  is 1, with thus  $S_{\text{elec.}} = 0$ , for  $N_2$  and  $CO_2$  (see Table 2a, p.15 in Kennedy et al., 2019).

The accuracy of  $S_{\text{elec.}/O_2}$  is computed from  $\Delta(S_{\text{v-an.}/O_2})/S_{\text{v-an.}/O_2} \approx \Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ , leading to  $\Delta S_{\text{v-an.}/O_2} \approx 0.0003 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The standard molar entropy of  $O_2$  at 1000 hPa and 298.15 K is the sum of all components due to quantum and statistical degrees of freedom:

$O_2$ / Translation:	152.077	$\pm 0.006$	$\text{J K}^{-1} \text{ mol}^{-1}$	
$O_2$ / Rotation:	43.880	$\pm 0.002$	$\text{J K}^{-1} \text{ mol}^{-1}$	
$O_2$ / Vibration:	0.039	$\pm 0.000 \dots$	$\text{J K}^{-1} \text{ mol}^{-1}$	
$O_2$ / Anharmonic:	0.016	$\pm 0.000 \dots$	$\text{J K}^{-1} \text{ mol}^{-1}$	
$O_2$ / Electronic:	9.134	$\pm 0.000 \dots$	$\text{J K}^{-1} \text{ mol}^{-1}$	
$O_2$ / Total:	205.148	$\pm 0.008$	$\text{J K}^{-1} \text{ mol}^{-1}$	(76)
$O_2$ / NIST-JANAF-4:	205.147	$\pm 0.035$	$\text{J K}^{-1} \text{ mol}^{-1}$	(77)
$O_2$ / Total:	6411.102	$\pm 0.33$	$\text{J K}^{-1} \text{ kg}^{-1}$	(78)

The uncertainty of  $\pm 0.33 \text{ J K}^{-1} \text{ kg}^{-1}$  in (78) for the specific value  $s_{O_2} = S_{O_2}/M_{O_2}$  is computed like in (40) for Argon from NIST-JANAF-4 molar mass and IUPAC-2013 accuracy recalled in Table 25, but for  $O_2$ , leading to

$$\frac{\Delta s_{O_2}}{s_{O_2}} \approx \frac{\Delta S_{O_2}}{S_{O_2}} + \frac{\Delta M_{O_2}}{M_{O_2}} \approx 3.9 \cdot 10^{-5} + 1.25 \cdot 10^{-5} \approx 5.2 \cdot 10^{-5} . \quad (79)$$

Since the total molar entropy  $205.148 \pm 0.008 \text{ J K}^{-1} \text{ mol}^{-1}$  computed in (76) for  $O_2$  at 1000 hPa and 298.15 K is almost the same as the value in the NIST-JANAF-4 Table (Chase, 1998, p.1745) recalled in (77), and is close to the value of about  $205.138 \text{ J K}^{-1} \text{ mol}^{-1}$  published in the Table 2C.5 of Atkins and de Paula (2014, p.977), it is possible to use the same JANAF-4 formulations recalled in this section to compute the standard molar entropy of  $O_2$  at 1000 hPa and 273.15 K, with about the same accuracy as at 298.15 K, leading to

$$\boxed{S_{O_2} (1000 \text{ hPa and } 273.15 \text{ K}) = 202.580 \pm 0.008 \text{ J K}^{-1} \text{ mol}^{-1}} , \quad (80)$$

$$\boxed{s_{O_2} (1000 \text{ hPa and } 273.15 \text{ K}) = 6330.86 \pm 0.33 \text{ J K}^{-1} \text{ kg}^{-1}} . \quad (81)$$

As for Argon and  $N_2$ , it would also have been possible to rely on the NIST-JANAF-4 table of Chase (1998, p.1745) and calculate the logarithmic-extrapolated value at 273.15 K from the standard molar entropy of  $O_2$  at 298.15 K and 300 K ( $205.147$  and  $205.329 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively) leading to the extrapolated value  $202.570 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is in agreement (almost within the one- $\sigma$  uncertainty range) with the computed value  $202.580 \pm 0.008 \text{ J K}^{-1} \text{ mol}^{-1}$  in (80).

## 4.5 The statistical absolute reference entropies: CO<sub>2</sub>

Still in a scientifically transparent way, let us (re)compute the absolute molar entropy for CO<sub>2</sub>, and compare it with the extrapolated value from Chase (1998, p.643) and Table 2C.5 of Atkins and de Paula (2014, p.974).

Like N<sub>2</sub> and O<sub>2</sub>, the CO<sub>2</sub> is a linear molecule (with Carbon atom in between the two Oxygen atoms, see the Fig. 5-left), with the same resonance symmetry number  $\sigma_r = 2$  because rotation through 180° leads to indistinguishable states.

The same formulations as for N<sub>2</sub> and O<sub>2</sub> can be used for the translational components of the absolute entropy, but with modified rotational, vibrational and anharmonic components, and without the additional component taken into account for O<sub>2</sub> due to the electronic component ( $Q_e = 1$  for CO<sub>2</sub>).

The translational absolute entropy can be computed with the formula (35) and with the molar mass  $M_{\text{CO}_2} \approx 0.044\,009\,8 \pm 0.000\,000\,9 \text{ kg mol}^{-1}$  leading to

$$S_{\text{trans./CO}_2} \approx 156.052 \pm 0.006 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (82)$$

The accuracy of  $S_{\text{trans./CO}_2}$  is computed with the formula (39)

$$\frac{\Delta S_{\text{trans./CO}_2}}{S_{\text{trans./CO}_2}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{trans./CO}_2}} \left( \frac{3}{2} \frac{\Delta M_{\text{CO}_2}}{M_{\text{CO}_2}} + \frac{\Delta K_{\text{ST}}}{K_{\text{ST}}} \right) \approx 3.8 \cdot 10^{-5}, \quad (83)$$

where the relative accuracies are  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $\Delta(M_{\text{CO}_2})/M_{\text{CO}_2} \approx 2.0 \cdot 10^{-5}$ ,  $R_*/(S_{\text{trans./CO}_2}) \approx 1/19$  and  $\Delta K_{\text{ST}}/K_{\text{ST}} \approx 0.55 \cdot 10^{-5}$ .

Even if CO<sub>2</sub> (O=C=O) is made of linear molecule (180°) with Carbon atom in between the two Oxygen atoms, both rotation and vibration properties can be modified by configuration like in Fig. 5 (right) where the molecule is no longer linear, i.e. is out of equilibrium with  $\Delta\alpha \neq 0$  and an angle  $\neq 180^\circ$  between the two C–O elements. For this reason, in the presence of such “centrifugal distortion”,

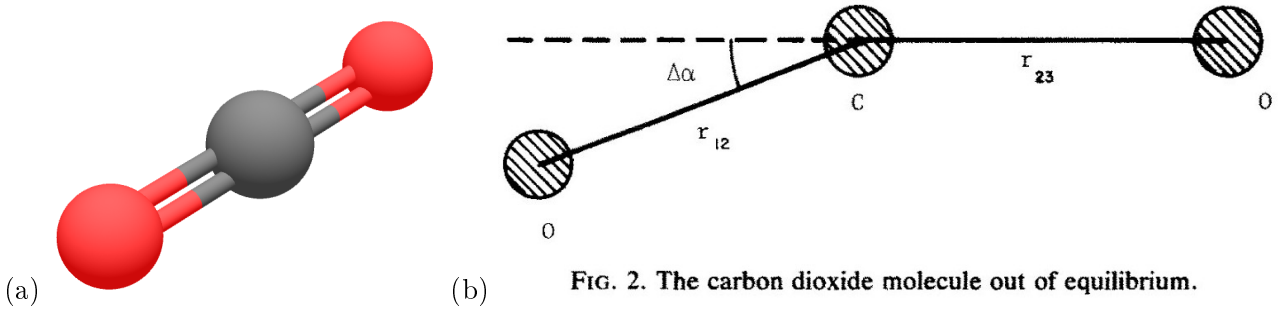


Figure 5: (a) the 3D-vision of the CO<sub>2</sub> (O=C=O) molecule; (b) the Fig.2 of Chedin (1979).

the expression for the “vibrationless rotational energy levels”  $F(J) = \tilde{B}_e J(J+1)$  of McDowell (1988, Eq. 1, p.357) and Martin et al. (1991, Eq. 1, p.8375) becomes, according to Chedin (1979, Eq. 20, p.437), McDowell (1988, Eq. 6, p.358) and Martin et al. (1991, Eq. 12, p.8375):

$$F(J) \approx \tilde{B}_e J(J+1) - \tilde{D}_e J^2(J+1)^2 + \tilde{H}_e J^3(J+1)^3, \quad (84)$$

where  $\tilde{B}_e$  is the “rotational” (or “inertia”) constant,  $\tilde{D}_e$  is the “quartic” (or “centrifugal”) distortion constant and  $\tilde{H}_e$  is the “sextic” (or “fourth order diagonal”) distortion constant.

McDowell (1988, p.358) explains that “*when the energy levels of a linear molecule can be adequately fitted by the first two terms of (84), the result is to multiply the calculated rigid-rotator partition function by the first-order correction factor  $f_c = 1 + 2(\tilde{D}_e/\tilde{B}_e)/u$ .*” This is easy to verify and is valid for CO<sub>2</sub>,

leading to a first-order rotation partition function ( $Q_{\text{rot}}$ ) and the corresponding molar entropy ( $S_{\text{rot}}$ ), which could be written as

$$Q_{\text{rot}} \approx \frac{1}{\sigma_r u} \left( 1 + \frac{u^2}{90} \right) \left( 1 + \frac{\tilde{\alpha}_e}{u} \right), \quad (85)$$

$$S_{\text{rot}} = R_* \left[ \ln(Q_{\text{rot}}) - u \frac{d \ln(Q_{\text{rot}})}{du} \right], \quad (86)$$

$$S_{\text{rot}} \approx R_* \left[ 1 - \ln(\sigma_r u) - \frac{u^2}{90} + \frac{2 \tilde{\alpha}_e}{u} \right], \quad (87)$$

where  $\Theta_{\text{rot.}} = c_2 \tilde{B}_e$ ,  $u = \Theta_{\text{rot.}}/T \ll 1$  (because  $\tilde{B}_e \approx 0.39 \text{ cm}^{-1}$ ,  $\Theta_{\text{rot.}} \approx 0.56 \text{ K}$  and  $u \approx 2.10^{-3}$  for  $T = 298.15 \text{ K}$ ),  $\tilde{\alpha}_e = 2 \tilde{D}_e / \tilde{B}_e$  and  $2 \tilde{\alpha}_e / u \ll 1$  (because  $\tilde{D}_e \approx 1.3 \cdot 10^{-7} \text{ cm}^{-1}$ ,  $\tilde{\alpha}_e \approx 7.10^{-7} \text{ cm}^{-1}$  and  $u \approx 2.10^{-3}$  for  $T = 298.15 \text{ K}$  leads to  $2 \tilde{\alpha}_e / u \approx 8.10^{-4}$ ).

Like for  $\text{N}_2$  and  $\text{O}_2$  the term  $\exp(u/3)$  in McDowell (1988, Eq.5, p.357) and Martin et al. (1991, Eq.2, p.8375) is omitted in (85) for  $\text{CO}_2$  because it gives no contribution to  $S_{\text{rot}}$  in (87). The difference between the rotation molar entropy (87) for  $\text{CO}_2$  and the formula (45) valid for  $\text{N}_2$  and  $\text{O}_2$  is the last term  $2 \tilde{\alpha}_e / u \approx 8.10^{-4}$ , which is small but cannot be neglected at  $T = 298.15 \text{ K}$  with respect to 1 and  $-\ln(\sigma_r u) \approx 5.6$ , and is much larger than  $-u^2/90 \approx 4 \cdot 10^{-8}$ .

The use of the  $\text{CO}_2$  experimental values  $\tilde{B}_e \approx 0.387141 \text{ cm}^{-1}$  and  $\tilde{D}_e \approx 1.30 \cdot 10^{-7} \text{ cm}^{-1}$  from Chedin (1979, Table XII, p.481) lead to  $\Theta_{\text{rot.}/\text{CO}_2} \approx 0.557013 \text{ K}$ ,  $u \approx 1.86823 \cdot 10^{-3}$  for  $T = 298.15 \text{ K}$ ,  $\tilde{\alpha}_e \approx 6.716 \cdot 10^{-7}$  and  $2 \tilde{\alpha}_e / u \approx 7.1896 \cdot 10^{-4}$ , with the rotation molar entropy of  $\text{CO}_2$  of about

$$S_{\text{rot.}/\text{CO}_2} \approx 54.795 \pm 0.002 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (88)$$

The contribution of the distortion term  $2 \tilde{\alpha}_e / u$  to  $S_{\text{rot.}/\text{CO}_2}$  is of about  $0.006 \text{ J K}^{-1} \text{ mol}^{-1}$ . The accuracy of  $S_{\text{rot.}/\text{CO}_2}$  is computed at  $T = 298.15 \text{ K}$  like in (50), but with the impact of  $2 \tilde{\alpha}_e / u$  included, leading to

$$\frac{\Delta S_{\text{rot.}/\text{CO}_2}}{S_{\text{rot.}/\text{CO}_2}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{rot.}/\text{CO}_2}} \left| 1 - \frac{u^2}{45} - \frac{2 \tilde{\alpha}_e}{u} \right| \frac{\Delta u}{u} \approx 4 \cdot 10^{-5}, \quad (89)$$

where  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $(R_*/S_{\text{rot.}/\text{CO}_2}) \approx 0.15$ ,  $T = 298.15 \text{ K}$ ,  $\Theta_{\text{rot.}/\text{CO}_2} \approx 0.557 \text{ K}$ ,  $u \approx 1.87 \cdot 10^{-3}$ ,  $2 \tilde{\alpha}_e / u \approx 7.2 \cdot 10^{-4}$  and  $\Delta u/u \approx 0.00005/1.87 \approx 3 \cdot 10^{-5}$ .

The vibration molar entropy of  $\text{CO}_2$  can be computed at  $T = 298.15 \text{ K}$  with the same formula (51) used for  $\text{N}_2$  and  $\text{O}_2$ , but for three vibration constants ( $\omega_A$ ,  $\omega_B$ ,  $\omega_C$ ) and three different vibration temperatures. According to (Atkins and de Paula, 2014, p.620): “*In a polyatomic molecule, each normal mode has its own partition function (provided the anharmonicities are so small that the modes are independent). The overall vibrational partition function  $Q_v$  is the product of the individual partition functions, and we can write  $Q_v = Q_v(1) Q_v(2) \dots$ , where  $Q_v(N)$  is the partition function for the  $N$ th normal mode (...).*” Due to the logarithmic definition of the entropy in terms of the partition functions  $\ln(Q_v) = \ln[Q_v(1) Q_v(2) \dots] = \ln[Q_v(1)] + \ln[Q_v(2)] + \dots$  and the total vibration entropy is the sum of the vibration entropies computed for all normal modes, leading to

$$S_{\text{vibr.}}(u) = R_* \left( \frac{u}{\exp(u) - 1} - \ln[1 - \exp(-u)] \right) \text{ for each vibration constant}, \quad (90)$$

$$\omega_A \approx 2349.150 \text{ cm}^{-1}, \quad \Theta_{\text{vib.A}/\text{CO}_2} = c_2 \omega_A \approx 3379.924 \text{ K}, \quad u_A = \frac{\Theta_{\text{vib.A}/\text{CO}_2}}{T} \approx 11.33632, \quad (91)$$

$$\omega_B \approx 1388.188 \text{ cm}^{-1}, \quad \Theta_{\text{vib.B}/\text{CO}_2} = c_2 \omega_B \approx 1997.305 \text{ K}, \quad u_B = \frac{\Theta_{\text{vib.B}/\text{CO}_2}}{T} \approx 6.69899, \quad (92)$$

$$\omega_C \approx 667.381 \text{ cm}^{-1}, \quad \Theta_{\text{vib.C}/\text{CO}_2} = c_2 \omega_C \approx 960.218 \text{ K}, \quad u_C = \frac{\Theta_{\text{vib.C}/\text{CO}_2}}{T} \approx 3.22059, \quad (93)$$

$$\text{with the sum } S_{\text{vibr.}/\text{CO}_2} = S_{\text{vibr.}}(u_A) + S_{\text{vibr.}}(u_B) + 2 \times S_{\text{vibr.}}(u_C), \quad (94)$$

where the three vibration constants are those for the “band center” in Chedin (1979, Table X, p.457):

$\omega_A$  / (001) strong and asymmetric stretch / degeneracy 1,

$\omega_B$  / (100) symmetric stretch / degeneracy 1,

$\omega_C$  / (010) greenhouse bending / degeneracy 2  $\Rightarrow$  the factor 2 in the last term of (94).

Numerical values of the three vibration constants ( $\omega_A$ ,  $\omega_B$ ,  $\omega_C$ ) in (91)-(93) are close to those of Atkins and de Paula (2014, p.515) and correspond to the normal modes described in the Fig. 6.

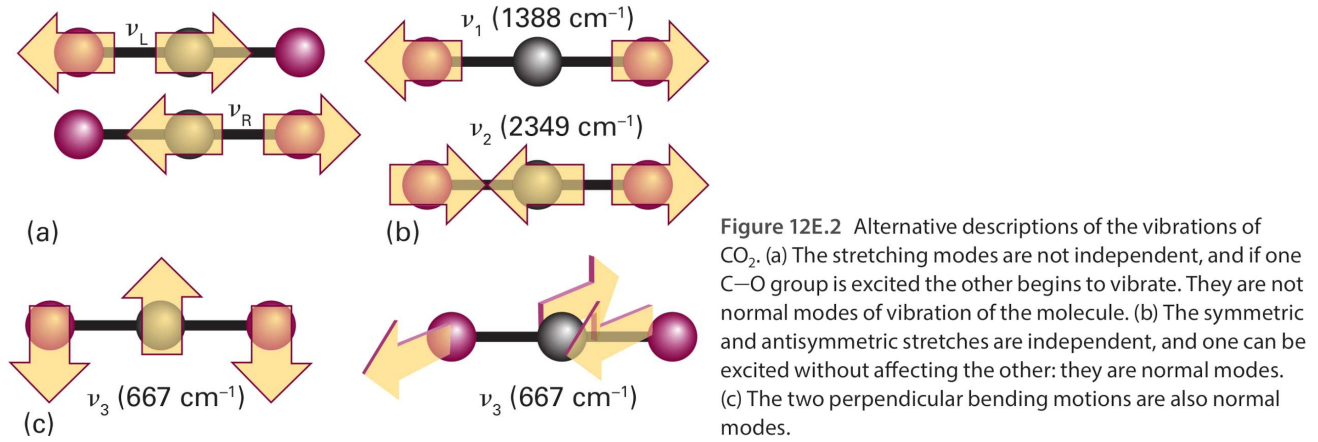


Figure 6: *Fig. 12E.2 of Atkins and de Paula (2014, p.515).*

The vibration molar entropy of CO<sub>2</sub> can be computed at  $T = 298.15$  K from (90)-(94), giving

$$S_{\text{vib./CO}_2} \approx 2.985 \pm 0.0005 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (95)$$

The accuracy in (95) is computed at constant  $T = 298.15$  K with (72) applied to the three vibration constants ( $\omega_A$ ,  $\omega_B$ ,  $\omega_C$ ) and the three corresponding values ( $u_A$ ,  $u_B$ ,  $u_C$ ):

$$\frac{\Delta S_{\text{vib./CO}_2}}{S_{\text{vib./CO}_2}} \approx \frac{\Delta R_*}{R_*} + \left( \frac{u_A^2}{u_A + 1} \right) \frac{\Delta u_A}{u_A} + \left( \frac{u_B^2}{u_B + 1} \right) \frac{\Delta u_B}{u_B} + 2 \left( \frac{u_C^2}{u_C + 1} \right) \frac{\Delta u_C}{u_C} \approx 21 \cdot 10^{-5}, \quad (96)$$

where  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $u_A \approx 11.3$ ,  $u_B \approx 6.7$  and  $u_C \approx 3.2$  up to about  $\pm 0.00006$  and with  $\Delta u_A/u_A \approx 0.44 \cdot 10^{-5}$ ,  $\Delta u_B/u_B \approx 0.75 \cdot 10^{-5}$  and  $\Delta u_C/u_C \approx 1.6 \cdot 10^{-5}$ .

The standard molar entropy of CO<sub>2</sub> at 1000 hPa and 298.15 K is the sum of all components due to quantum and statistical degrees of freedom:

CO <sub>2</sub> / Translation:	156.052	$\pm 0.006$	J K <sup>-1</sup> mol <sup>-1</sup>	
CO <sub>2</sub> / Rotation:	54.795	$\pm 0.002$	J K <sup>-1</sup> mol <sup>-1</sup>	
CO <sub>2</sub> / Vibration:	2.985	$\pm 0.0006$	J K <sup>-1</sup> mol <sup>-1</sup>	
CO <sub>2</sub> / Total:	213.832	$\pm 0.009$	J K <sup>-1</sup> mol <sup>-1</sup>	(97)
CO <sub>2</sub> / NIST-JANAF-4:	213.795	$\pm 0.120$	J K <sup>-1</sup> mol <sup>-1</sup>	(98)
CO <sub>2</sub> / Total:	4858.744	$\pm 0.24$	J K <sup>-1</sup> kg <sup>-1</sup>	(99)

The uncertainty of  $\pm 0.24 \text{ J K}^{-1} \text{ kg}^{-1}$  in (99) for the specific value  $s_{\text{CO}_2} = S_{\text{CO}_2}/M_{\text{CO}_2}$  is computed like in (40) for Argon, N<sub>2</sub> and O<sub>2</sub> from NIST-JANAF-4 molar mass and IUPAC-2013 accuracy recalled in Table 25, but for CO<sub>2</sub> and  $M_{\text{CO}_2} \approx 0.0440098 \pm 0.0000009 \text{ kg mol}^{-1}$ , leading to

$$\frac{\Delta s_{\text{CO}_2}}{s_{\text{CO}_2}} \approx \frac{\Delta S_{\text{CO}_2}}{S_{\text{CO}_2}} + \frac{\Delta M_{\text{CO}_2}}{M_{\text{CO}_2}} \approx 3.9 \cdot 10^{-5} + 2.0 \cdot 10^{-5} \approx 5 \cdot 10^{-5}. \quad (100)$$

Since the total molar entropy  $213.832 \pm 0.009 \text{ J K}^{-1} \text{ mol}^{-1}$  computed in (97) for  $\text{CO}_2$  at 1000 hPa and 298.15 K is almost the same as the value in the NIST-JANAF-4 Table (Chase, 1998, p.1745)  $213.795 \pm 0.120 \text{ J K}^{-1} \text{ mol}^{-1}$  recalled in (77), and is close to the value of about  $213.74 \text{ J K}^{-1} \text{ mol}^{-1}$  published in the Table 2C.5 of Atkins and de Paula (2014, p.974), it is possible to use the same JANAF-4 formulations recalled in this section to compute the standard molar entropy of  $\text{O}_2$  at 1000 hPa and 273.15 K, with about the same accuracy as at 298.15 K, leading to

$$S_{\text{CO}_2}(\text{1000 hPa and 273.15 K}) = 210.638 \pm 0.009 \text{ J K}^{-1} \text{ mol}^{-1}, \quad (101)$$

$$s_{\text{CO}_2}(\text{1000 hPa and 273.15 K}) = 4786.168 \pm 0.24 \text{ J K}^{-1} \text{ kg}^{-1}. \quad (102)$$

As for Argon,  $\text{N}_2$  and  $\text{O}_2$ , it would also have been possible to rely on the NIST-JANAF-4 table of Chase (1998, p.643) and calculate the logarithmic-extrapolated value at 273.15 K from the standard molar entropy of  $\text{CO}_2$  at 298.15 K and 300 K ( $213.795$  and  $214.025 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively) leading to the extrapolated value  $210.539 \pm 0.120 \text{ J K}^{-1} \text{ mol}^{-1}$ , which is in agreement (within the one- $\sigma$  uncertainty range of the NIST-JANAF-4 value) with the computed value  $210.638 \text{ J K}^{-1} \text{ mol}^{-1}$  in (101).

#### 4.6 The statistical absolute reference entropies: $\text{H}_2\text{O}$

$\text{H}_2\text{O}$  (H-O-H) is an “asymmetric tops (rotors)” 3D but flat molecule (see Fig. 7). For this reason, the resonance symmetry number  $\sigma_r = 2$  is the same for  $\text{H}_2\text{O}$  as for  $\text{N}_2$ ,  $\text{O}_2$  and the  $\text{CO}_2$  linear molecules (Atkins and de Paula, 2014, Table 12.D1, p.987), because like  $\text{CO}_2$  rotation through  $180^\circ$  of the 3D-molecule  $\text{H}_2\text{O}$  leads to indistinguishable states for either Fig. 7 (a) or (b) seen from “above” or “below”.

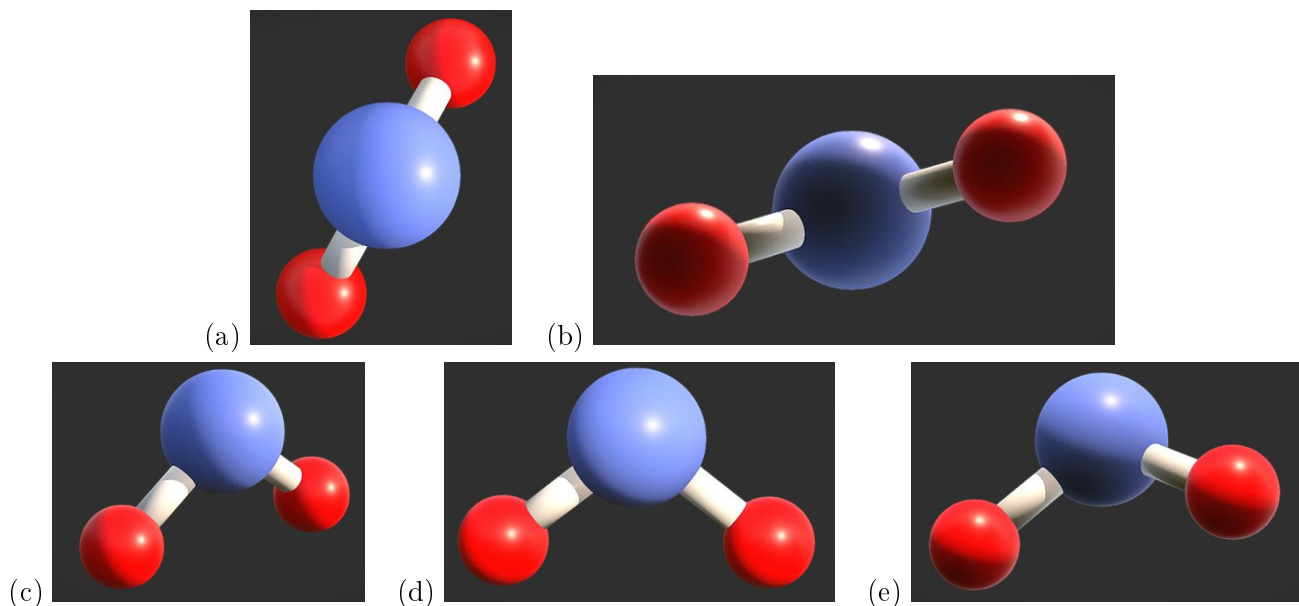


Figure 7: 3D visions of the  $\text{H}_2\text{O}$  (H-O-H) molecule made with the applet of Mehdi Mirzaie (<https://sketchfab.com/3d-models/h2o-molecule-e181944932084b5dbb4d5b625a5e9b10>)

The translational absolute entropy of  $\text{H}_2\text{O}$  can be computed at 1000 hPa and 298.15 K with the formula (35) and with the molar mass  $M_{\text{H}_2\text{O}} \approx 0.01801528 \pm 0.00000004 \text{ kg mol}^{-1}$ , leading to

$$S_{\text{trans./H}_2\text{O}} \approx 144.913 \pm 0.006 \text{ J K}^{-1} \text{ mol}^{-1}. \quad (103)$$

The accuracy of  $S_{\text{trans./H}_2\text{O}}$  is computed with the formula (39)

$$\frac{\Delta S_{\text{trans./H}_2\text{O}}}{S_{\text{trans./H}_2\text{O}}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{trans./H}_2\text{O}}} \left( \frac{3}{2} \frac{\Delta M_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} + \frac{\Delta K_{\text{ST}}}{K_{\text{ST}}} \right) \approx 3.7 \cdot 10^{-5}, \quad (104)$$

where the relative accuracies are  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $\Delta M_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}} \approx 0.22 \cdot 10^{-5}$ ,  $R_*/(S_{\text{trans./H}_2\text{O}}) \approx 1/17.4$  and  $\Delta K_{\text{ST}}/K_{\text{ST}} \approx 0.55 \cdot 10^{-5}$ , leading to  $\Delta S_{\text{trans./H}_2\text{O}} \approx 5.4 \cdot 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}$  upper-rounded to 0.006 in (103).

The rotational entropy of  $\text{H}_2\text{O}$  can be computed with the formula (105) valid for triatomic molecules:

$$s_{\text{rot.}}(T, \Theta_{\text{rot.}}) = R_* \left( \frac{3}{2} - \ln \left[ \frac{\sigma_r}{\sqrt{\pi}} \left( \frac{\Theta_{\text{rot.}}}{T} \right)^{3/2} \right] \right), \quad (105)$$

where  $\sigma_r = 2$  and where  $\Theta_{\text{rot}}$  is computed as a “bulk rotational value”  $\Theta_{\text{rot}} = \sqrt[3]{\Theta_A \Theta_B \Theta_C}$ , with the three rotational value  $\Theta_A$ ,  $\Theta_B$  and  $\Theta_C$  computed from either the three:

- (a) principal moments of rotational inertia / ex. Table 2b, p.11 in Kennedy et al. (2019);
- (b) rotational constants / ex. items 15F.2 p.646 and 15E.7(a) p.656 in Atkins and de Paula (2014), or p.1324 in Chase (1998).

The formulation (105) can easily be derived from the usual semi-classical (rigid rotator) rotation partition function published in Wolley (1956, Eq.2, p.105), Wolley (1987, Eq.3, p.36) and Martin et al. (1991, Eq.26, p.8376) for nonlinear molecules like  $\text{H}_2\text{O}$  and for three rotational constants  $(A, B, C)$  for the ground vibrational state, with the associated rotational temperature  $\Theta_{\text{rot}} = \sqrt[3]{(c_2 A) (c_2 B) (c_2 C)}$  and with:

$$Q_{\text{rot}} = \frac{\sqrt{\pi}}{\sigma_r} \left( \frac{T}{\Theta_{\text{rot}}} \right)^{3/2}, \text{ with } S_{\text{rot}} = R_* \left[ \ln(Q_{\text{rot}}) + T \frac{d \ln(Q_{\text{rot}})}{dT} \right] \text{ leading to (105)}. \quad (106)$$

As an example, the three principal moments of rotational inertia for water vapour from Kennedy et al. (2019, Table 2b, p.11) are  $I_A \approx 1.024 \cdot 10^{-47} \text{ kg m}^2$ ,  $I_B \approx 1.920 \cdot 10^{-47} \text{ kg m}^2$  and  $I_C \approx 2.947 \cdot 10^{-47} \text{ kg m}^2$ , leading to three rotational temperatures computed with  $\Theta_R = C_R / (I_A, I_B, I_C)$  ( $C_R \approx 40.276 \cdot 10^{-47} \text{ J s}^2 \text{ K}^2$ ):  $\Theta_A \approx 39.33 \text{ K}$ ,  $\Theta_B \approx 20.98 \text{ K}$  and  $\Theta_C \approx 13.67 \text{ K}$ , and to the bulk rotational value  $\Theta_{\text{rot}} = \sqrt[3]{\Theta_A \Theta_B \Theta_C} \approx 22.43 \text{ K}$ .

Similarly, the three rotational constants for water vapour in Chase (1998, p.1324) are  $A_0 = 27.8847 \text{ cm}^{-1}$ ,  $B_0 = 14.5118 \text{ cm}^{-1}$  and  $C_0 = 9.2806 \text{ cm}^{-1}$ , leading to three rotational temperatures computed with  $\Theta_R = c_2 \times (A, B, C)$  ( $c_2 \approx 1.438786 \text{ cm K}$ ):  $\Theta_A \approx 40.1201 \text{ K}$ ,  $\Theta_B \approx 20.8794 \text{ K}$  and  $\Theta_C \approx 13.353 \text{ K}$ , and to the bulk rotational value  $\Theta_{\text{rot}} = \sqrt[3]{\Theta_A \Theta_B \Theta_C} \approx 22.364 \text{ K}$ .

The NIST-JANAF-4 value  $\Theta_{\text{rot}} \approx 22.364 \text{ K}$  can be used to compute the rotational entropy of  $\text{H}_2\text{O}$  at 298.15 K from (105):

$$S_{\text{rot./H}_2\text{O}} \approx 43.771 \pm 0.005 \text{ J K}^{-1} \text{ mol}^{-1}, \quad (107)$$

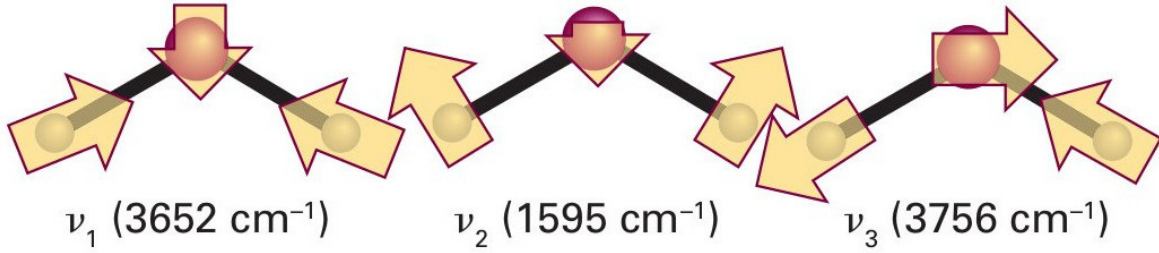
with the accuracy of  $S_{\text{rot./H}_2\text{O}}$  computed with the formula

$$\frac{\Delta S_{\text{rot./H}_2\text{O}}}{S_{\text{rot./H}_2\text{O}}} \approx \frac{\Delta R_*}{R_*} + \frac{R_*}{S_{\text{rot./H}_2\text{O}}} \frac{3}{2} \frac{\Delta \Theta_{\text{rot./H}_2\text{O}}}{\Theta_{\text{rot./H}_2\text{O}}} \approx 10 \cdot 10^{-5}, \quad (108)$$

where the accuracies  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$  and  $\Delta(\Theta_{\text{rot./H}_2\text{O}})/\Theta_{\text{rot./H}_2\text{O}} \approx 0.005/22.43 \approx 22 \cdot 10^{-5}$  lead to  $\Delta S_{\text{rot./H}_2\text{O}} \approx 4.4 \cdot 10^{-3} \text{ J K}^{-1} \text{ mol}^{-1}$ , which is upper-rounded to 0.005 in (107).

An additional part of rotational entropy of  $\text{H}_2\text{O}$  at 298.15 K must be computed from the first three terms in Eq. 14 of Martin et al. (1991, p.8376) and Eq. 16 of Martin et al. (1992, p.7636), namely with





**Figure 12E.3** The three normal modes of  $\text{H}_2\text{O}$ . The mode  $\nu_2$  is predominantly bending, and occurs at lower wavenumber than the other two.

Figure 8: *Fig. 12E.3 of Atkins and de Paula (2014, p.516).*

$Q_{\text{rot}}$  in (106) to be multiplied by a factor  $f_{\text{dist.}}(T)$ , and thus with the additional centrifugal distortion component of the vibrational entropy of  $\text{H}_2\text{O}$  written as

$$f_{\text{dist.}}(T) = 1 + \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3 + \dots \approx 1 + \rho_0 + \rho_1 T, \quad (109)$$

$$s_{\text{rot./dist}}(T) = R_* \left[ \ln(f_{\text{dist.}}) + T \frac{d \ln(f_{\text{dist.}})}{dT} \right] = R_* \left[ \ln(f_{\text{dist.}}) + \frac{T}{f_{\text{dist.}}} \frac{df_{\text{dist.}}}{dT} \right], \quad (110)$$

$$s_{\text{rot./dist}}(T) \approx R_* \left[ \ln(1 + \rho_0 + \rho_1 T) + \frac{\rho_1 T}{1 + \rho_0 + \rho_1 T} \right] \approx R_* (2 \rho_1 T). \quad (111)$$

The dimensionless numbers  $\rho_0 = -3.663 \cdot 10^{-5}$  and  $\rho_1 = 2.0364 \cdot 10^{-5}$  are given in table IV of Martin et al. (1991, p.8384) for  $\text{H}_2\text{O}$ . The second- and third-order terms  $\rho_2 T^2$  and  $\rho_3 T^3$  has negligible impacts on  $f_{\text{dist.}}(T)$  in (109) for the atmospheric range of temperatures  $T < 350$  K because  $|\rho_2| \propto 10^{-4} |\rho_0|$  and  $|\rho_3| \propto 10^{-8} |\rho_0|$ , this explaining the truncation to the first 3 terms 1,  $\rho_0$  and  $\rho_1 T$  in (109) and (111), with  $\rho_0 \ll 1$  and  $\rho_1 T \ll 1$  leading to the leading order approximation  $s_{\text{rot./dist}}(T) \approx R_* (2 \rho_1 T)$ , and then to the distortion component of the molar rotation entropy of  $\text{H}_2\text{O}$

$$S_{\text{rot.dist/H}_2\text{O}} \approx 0.100 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}. \quad (112)$$

The accuracy in (112) is computed at constant  $T = 298.15$  K from the differential of the first-order approximation of (111) in terms of  $R_*$  and  $\rho_1$ :

$$\frac{\Delta S_{\text{rot.dist/H}_2\text{O}}}{S_{\text{rot.dist/H}_2\text{O}}} \approx \frac{\Delta R_*}{R_*} + \frac{\Delta \rho_1}{\rho_1} \approx 29 \cdot 10^{-5}, \quad (113)$$

where the accuracies  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$  and  $\Delta \rho_1 / \rho_1 \approx 0.0005/2.0364 \approx 25 \cdot 10^{-5}$  jointly lead to  $\Delta S_{\text{rot.dist/H}_2\text{O}} \approx 3 \cdot 10^{-5} \text{ J K}^{-1} \text{ mol}^{-1}$ .

The vibrational entropy of  $\text{H}_2\text{O}$  can be computed at  $T = 298.15$  K with the same formulations (90)-(94) as for the  $\text{CO}_2$  molecule, but with the three normal modes described in Fig. 8 and with the vibration constants of Chase (1998, p.1324), leading to

$$S_{\text{vibr.}}(u) = R_* \left( \frac{u}{\exp(u) - 1} - \ln[1 - \exp(-u)] \right) \text{ for each vibration constant}, \quad (114)$$

$$\omega_A \approx 3755.9 \text{ cm}^{-1}, \quad \Theta_{\text{vib.A/H}_2\text{O}} = c_2 \omega_A \approx 5403.93 \text{ K}, \quad u_A = \frac{\Theta_{\text{vib.A/H}_2\text{O}}}{T} \approx 18.1249, \quad (115)$$

$$\omega_B \approx 3651.1 \text{ cm}^{-1}, \quad \Theta_{\text{vib.B/H}_2\text{O}} = c_2 \omega_B \approx 5253.15 \text{ K}, \quad u_B = \frac{\Theta_{\text{vib.B/H}_2\text{O}}}{T} \approx 17.6192, \quad (116)$$

$$\omega_C \approx 1594.7 \text{ cm}^{-1}, \quad \Theta_{\text{vib.C/H}_2\text{O}} = c_2 \omega_C \approx 2294.43 \text{ K}, \quad u_C = \frac{\Theta_{\text{vib.C/H}_2\text{O}}}{T} \approx 7.69556, \quad (117)$$

$$\text{with the sum } S_{\text{vibr./H}_2\text{O}} = S_{\text{vibr.}}(u_A) + S_{\text{vibr.}}(u_B) + S_{\text{vibr.}}(u_C) \quad (118)$$

leading to

$$S_{\text{vib.}/\text{H}_2\text{O}} \approx 0.033 \pm 0.000 \dots \text{ J K}^{-1} \text{ mol}^{-1}. \quad (119)$$

The accuracy in (119) is computed at constant  $T = 298.15 \text{ K}$  with (120) applied to the three vibration constants ( $\omega_A, \omega_B, \omega_C$ ) and the three corresponding values ( $u_A, u_B, u_C$ ):

$$\frac{\Delta S_{\text{vib.}/\text{H}_2\text{O}}}{S_{\text{vib.}/\text{H}_2\text{O}}} \approx \frac{\Delta R_*}{R_*} + \left( \frac{u_A^2}{u_A + 1} \right) \frac{\Delta u_A}{u_A} + \left( \frac{u_B^2}{u_B + 1} \right) \frac{\Delta u_B}{u_B} + \left( \frac{u_C^2}{u_C + 1} \right) \frac{\Delta u_C}{u_C} \approx 88.10^{-5}, \quad (120)$$

where  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $u_A \approx 18.1$ ,  $u_B \approx 17.6$  and  $u_C \approx 7.7$  up to about  $\pm 0.0003$  and with  $\Delta u_A/u_A \approx 1.7 \cdot 10^{-5}$ ,  $\Delta u_B/u_B \approx 1.7 \cdot 10^{-5}$  and  $\Delta u_C/u_C \approx 3.9 \cdot 10^{-5}$ .

The standard molar entropy of  $\text{H}_2\text{O}$  at 1000 hPa and 298.15 K is the sum of all components due to quantum and statistical degrees of freedom:

H <sub>2</sub> / Translation:	144.913	±0.006	J K <sup>−1</sup> mol <sup>−1</sup>	
H <sub>2</sub> O / Rotation:	43.771	±0.005	J K <sup>−1</sup> mol <sup>−1</sup>	
H <sub>2</sub> O / Rotation-distortion:	0.100	±0.000 ...	J K <sup>−1</sup> mol <sup>−1</sup>	
H <sub>2</sub> O / Vibration:	0.033	±0.000 ...	J K <sup>−1</sup> mol <sup>−1</sup>	
H <sub>2</sub> O / Total:	188.817	±0.011	J K <sup>−1</sup> mol <sup>−1</sup>	(121)

H <sub>2</sub> O / NIST-JANAF-4:	188.834	±0.042	J K <sup>−1</sup> mol <sup>−1</sup>	(122)
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H <sub>2</sub> O / Total:	10480.911	±0.63	J K <sup>−1</sup> kg <sup>−1</sup>	(123)
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The uncertainty of  $\pm 0.63 \text{ J K}^{-1} \text{ kg}^{-1}$  in (78) for the specific value  $s_{\text{H}_2\text{O}} = S_{\text{H}_2\text{O}}/M_{\text{H}_2\text{O}}$  is computed like in (40) for Argon from NIST-JANAF-4 molar mass and IUPAC-2013 accuracy recalled in Table 25, but for  $\text{H}_2\text{O}$ , leading to

$$\frac{\Delta s_{\text{H}_2\text{O}}}{s_{\text{H}_2\text{O}}} \approx \frac{\Delta S_{\text{H}_2\text{O}}}{S_{\text{H}_2\text{O}}} + \frac{\Delta M_{\text{H}_2\text{O}}}{M_{\text{H}_2\text{O}}} \approx 5.8 \cdot 10^{-5} + 0.22 \cdot 10^{-5} \approx 6.10^{-5}. \quad (124)$$

Since the total molar entropy  $188.817 \pm 0.011 \text{ J K}^{-1} \text{ mol}^{-1}$  computed in (121) for  $\text{H}_2\text{O}$  at 1000 hPa and 298.15 K is almost the same as the value in the NIST-JANAF-4 Table (Chase, 1998, p.1324) recalled in (122), and is close to the value of about  $188.83 \text{ J K}^{-1} \text{ mol}^{-1}$  published in the Table 2C.5 of Atkins and de Paula (2014, p.975), it is possible to use the same JANAF-4 formulations recalled in this section to compute the standard molar entropy of  $\text{H}_2\text{O}$  at 1000 hPa and 273.15 K, with about the same accuracy as at 298.15 K, leading to

$S_{\text{H}_2\text{O}} (1000 \text{ hPa and } 273.15 \text{ K}) = 185.880 \pm 0.011 \text{ J K}^{-1} \text{ mol}^{-1}$	(125)
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$s_{\text{H}_2\text{O}} (1000 \text{ hPa and } 273.15 \text{ K}) = 10317.92 \pm 0.63 \text{ J K}^{-1} \text{ kg}^{-1}$	(126)
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As for Argon, N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>, it would also have been possible to rely on the NIST-JANAF-4 table of Chase (1998, p.1324) and calculate the logarithmic-extrapolated value at 273.15 K from the standard molar entropy of  $\text{H}_2\text{O}$  at 298.15 K and 300 K (188.834 and 189.042 J K<sup>−1</sup> kg<sup>−1</sup>, respectively) leading to the extrapolated value  $185.889 \text{ J K}^{-1} \text{ kg}^{-1}$ , which is in agreement (within the one- $\sigma$  uncertainty range) with the computed value  $185.880 \pm 0.011 \text{ J K}^{-1} \text{ mol}^{-1}$  in (125).

## 5 Detailed computations of the third-law calorimetric enthalpies

According to (8), the third-law calorimetric enthalpies are computed at  $T_0 = 273.15$  K and  $p_0 = 1000$  hPa with the formula

$$h(T_0) = \overbrace{h(T=0)}^{(=0)} + \int_0^{T_0} c_p(T) dT + \sum_k L_k(T_k). \quad (127)$$

where  $T$  is the absolute temperature,  $c_p(T)$  are the specific heats at constant pressure and  $L_k(T_k)$  are the different latent heats of change of phases (from possible solids to solids, next from solid to liquid and next from liquid to vapour states) at the temperatures  $T_k$ .

### 5.1 The calorimetric absolute thermal enthalpy for Argon

The changes in calorimetric (absolute) standard thermal enthalpy for Argon is computed by using the relationship (127) with the third-law hypothesis  $h = 0$  at 0 K for the solid state, with the specific heat  $c_p(T)$  given in the Table 8 and with the latent heats mentioned in the Fig. 13.

The corresponding changes in calorimetric (absolute) standard thermal enthalpy for Argon are:

----- [ $H_{x/calor.}$ ] of Argon at 1000 hPa. -----		
-----		
Std. enthalpy of Argon (Solid- $\alpha$ ) at 0 K	0.0	$\text{kJ kg}^{-1}$
-----		
The Debye region enthalpy for Solid Argon (below 3 K):	+ 0.001 34	$\pm 0.000 10 \text{ kJ kg}^{-1}$
The Solid region for Argon (between 3 K and 83.81 K):	+ 42.3	$\pm 0.7 \text{ kJ kg}^{-1}$
Fusion (at 83.81 K):	+ 29.739	$\pm 0.005 \text{ kJ kg}^{-1}$
The Liquid region for Argon (between 83.81 K and 87.18 K):	+ 3.76	$\pm 0.02 \text{ kJ kg}^{-1}$
Vaporization (at 87.18 K):	+ 161.24	$\pm 0.05 \text{ kJ kg}^{-1}$
The vapour region of Argon (between 87.18 K and 273.15 K):	+ 98.3	$\pm 0.9 \text{ kJ kg}^{-1}$
-----		
Std. enthalpy of Argon (vapor) at 273.15 K (0 ° C):	335.3	$\pm 1.7 \text{ kJ kg}^{-1}$
Std. enthalpy of Argon (vapor) at 273.15 K (0 ° C):	13 373	$\pm 68 \text{ J mol}^{-1}$
-----		
The vapour region of Argon (between 273.15 K and 298.15 K):	+ 13.04	$\pm 0.13 \text{ kJ kg}^{-1}$
-----		
Std. enthalpy of Argon (vapor) at 298.15 K (25 ° C):	348.4	$\pm 1.8 \text{ kJ kg}^{-1}$
Std. enthalpy of Argon (vapor) at 298.15 K (25 ° C):	13 893	$\pm 72 \text{ J mol}^{-1}$
-----		

The changes in calorimetric (absolute) standard thermal enthalpy for  $\text{N}_2$  is computed by using the relationship (127) with the third-law hypothesis  $h = 0$  at 0 K for the solid state, with the specific heat  $c_p(T)$  given in the Table 9 and with the latent heats mentioned in the Fig. 14.

— — — — —  $\left[ H_{\text{x/calor.}} \right]$  of  $\text{N}_2$  at 1000 hPa. — — — — —

40

### 5.3 The calorimetric absolute thermal enthalpy for O<sub>2</sub>

The changes in calorimetric (absolute) standard thermal enthalpy for O<sub>2</sub> is computed by using the relationship (127) with the third-law hypothesis  $h = 0$  at 0 K for the solid state, with the specific heat  $c_p(T)$  given in the Table 10 and with the latent heats mentioned in the Fig. 15.

The corresponding changes in calorimetric (absolute) standard thermal enthalpy for O<sub>2</sub> are:

----- [ $H_{x/calor.}$ ] of O <sub>2</sub> at 1000 hPa. -----		
-----		
Std. enthalpy of O <sub>2</sub> (Solid- $\alpha$ ) at 0 K	0.0	kJ kg <sup>-1</sup>
-----		
The Debye region enthalpy for Solid- $\alpha$ O <sub>2</sub> (below 2 K):	+ 0.000 24	$\pm 0.000\,01$ kJ kg <sup>-1</sup>
The Solid- $\alpha$ region for O <sub>2</sub> (between 2 K and 23 K):	+ 4.16	$\pm 0.07$ kJ kg <sup>-1</sup>
The Solid $\alpha$ - $\beta$ (2nd order) transition for O <sub>2</sub> (between 23 K and 25 K):	+ 3.94	$\pm 0.10$ kJ kg <sup>-1</sup>
The Solid- $\beta$ region for O <sub>2</sub> (between 25 K and 43.8 K):	+ 19.80	$\pm 0.10$ kJ kg <sup>-1</sup>
The Solid $\beta$ - $\gamma$ transition for O <sub>2</sub> (at 43.8 K):	+ 23.20	$\pm 0.20$ kJ kg <sup>-1</sup>
The Solid- $\gamma$ region for O <sub>2</sub> (between 43.8 K and 54.4 K):	+ 15.20	$\pm 0.05$ kJ kg <sup>-1</sup>
Fusion (at 54.4 K):	+ 13.90	$\pm 0.2$ J kg <sup>-1</sup>
The liquid region of O <sub>2</sub> (between 54.4 K and 90.20 K):	+ 62.38	$\pm 0.18$ kJ kg <sup>-1</sup>
Vaporization (at 90.20 K):	+ 213.0	$\pm 0.5$ kJ kg <sup>-1</sup>
The vapour region of O <sub>2</sub> (between 90.20 K and 273.15 K):	+ 168.37	$\pm 0.10$ kJ kg <sup>-1</sup>
-----		
Std. enthalpy of O <sub>2</sub> (vapor) at 273.15 K (0 ° C):	524.0	$\pm 1.5$ kJ kg <sup>-1</sup>
Std. enthalpy of O <sub>2</sub> (vapor) at 273.15 K (0 ° C):	16 767	$\pm 48$ J mol <sup>-1</sup>
-----		
The vapour region of O <sub>2</sub> (between 273.15 K and 298.15 K):	+ 22.93	$\pm 0.01$ kJ kg <sup>-1</sup>
-----		
Std. enthalpy of O <sub>2</sub> (vapor) at 298.15 K (25 ° C):	546.9	$\pm 1.5$ kJ kg <sup>-1</sup>
Std. enthalpy of O <sub>2</sub> (vapor) at 298.15 K (25 ° C):	17 500	$\pm 48$ J mol <sup>-1</sup>
-----		

The special feature for the O<sub>2</sub> solid  $\alpha$ - $\beta$  second-order transition occurring at about 23.85 K (namely with a kind of Dirac's pulse in the Fig. 15, but without latent heat) is replaced here by a finite interval between 23 K and 25 K, with the large values of  $c_p(T)$  listed in the Table 10 with a threshold of 1000 J K<sup>-1</sup> kg<sup>-1</sup>, leading to a finite increase in thermal enthalpy of about  $3.94 \pm 0.10$  kJ kg<sup>-1</sup>.

If this second-order transition was replaced by a linear increase in  $c_p(T)$  between 718.8 J K<sup>-1</sup> kg<sup>-1</sup> at 23 K and 725 J K<sup>-1</sup> kg<sup>-1</sup> at 25 K, the increase in thermal enthalpy would be of about  $1.44 \pm 0.01$  kJ kg<sup>-1</sup>. The impact of the second-order transition is thus of about  $3.94 - 1.44 \approx 2.5$  kJ kg<sup>-1</sup>, which is larger than the retained uncertainty in the thermal enthalpy at 273.15 K ( $524.0 \pm 1.5$  kJ kg<sup>-1</sup>).

## 5.4 The calorimetric absolute thermal enthalpy for CO<sub>2</sub>

The changes in calorimetric (absolute) standard thermal enthalpy for CO<sub>2</sub> is computed by using the relationship (127) with the third-law hypothesis  $h = 0$  at 0 K for the solid state, with the specific heat  $c_p(T)$  given in the Table 11 and with the latent heats mentioned in the Fig. 16.

The corresponding changes in calorimetric (absolute) standard thermal enthalpy for CO<sub>2</sub> are:

[ $H_{x/\text{calor.}}$ ] of CO <sub>2</sub> at 1000 hPa.		
-----		
Std. enthalpy of CO <sub>2</sub> (Solid- $\alpha$ ) at 0 K	0.0	kJ kg <sup>-1</sup>
-----		
The Debye region enthalpy for Solid CO <sub>2</sub> (below 2.112 K):	+ 0.000 06	$\pm 0.000\,003$ kJ kg <sup>-1</sup>
The Solid region for CO <sub>2</sub> (between 2.112 K and 194.525 K):	+ 152.0	$\pm 0.7$ kJ kg <sup>-1</sup>
Sublimation (at 194.525 K):	+ 573.0	$\pm 0.5$ kJ kg <sup>-1</sup>
The vapour region of CO <sub>2</sub> (between 194.525 K and 273.15 K):	+ 62.4	$\pm 0.3$ kJ kg <sup>-1</sup>
-----		
Std. enthalpy of CO <sub>2</sub> (vapor) at 273.15 K (0° C):	787.4	$\pm 1.5$ kJ kg <sup>-1</sup>
Std. enthalpy of CO <sub>2</sub> (vapor) at 273.15 K (0° C):	34 653	$\pm 67$ J mol <sup>-1</sup>
-----		
The vapour region of CO <sub>2</sub> (between 273.15 K and 298.15 K):	+ 21.0	$\pm 0.1$ kJ kg <sup>-1</sup>
-----		
Std. enthalpy of CO <sub>2</sub> (vapor) at 298.15 K (25° C):	808.4	$\pm 1.6$ kJ kg <sup>-1</sup>
Std. enthalpy of CO <sub>2</sub> (vapor) at 298.15 K (25° C):	35 577	$\pm 71$ J mol <sup>-1</sup>
-----		

## 5.5 The calorimetric absolute thermal enthalpy for H<sub>2</sub>O

The calorimetric thermal enthalpy for H<sub>2</sub>O (Ice-Ih, liquid and vapour) is computed for the standard pressure of 1000 hPa and the standard temperatures of 273.15 K and 298.15 K by using the relationship (127) with the third-law hypothesis  $h = 0$  at 0 K for the solid state, with the specific heat  $c_p(T)$  given in the Table 12 and with the latent heats mentioned in the Fig. 17.

The changes in calorimetric (absolute) standard thermal enthalpy for H<sub>2</sub>O are:

----- [ $H_{x/calor.}$ ] of H <sub>2</sub> O at 1000 hPa. -----		
-----		
Std. enthalpy of H <sub>2</sub> O (Ice-Ih) at 0 K	0.0	kJ kg <sup>-1</sup>
-----		
The Debye region of (Ice-Ih) H <sub>2</sub> O enthalpy (below 2 K):	+ 0.000 04	± 0.00 ... kJ kg <sup>-1</sup>
The Ice (Ih) region for H <sub>2</sub> O (between 2 K and 273.15 K):	+ 298.63	± 0.10 kJ kg <sup>-1</sup>
-----		
Std. enthalpy of H <sub>2</sub> O (Ice-Ih) at 273.15 K (0 ° C):	298.63	± 0.10 kJ kg <sup>-1</sup>
Std. enthalpy of H <sub>2</sub> O (Ice-Ih) at 273.15 K (0 ° C):	5380	± 2 J mol <sup>-1</sup>
-----		
Fusion (at 273.15 K):	+ 333.7	± 0.25 J kg <sup>-1</sup>
-----		
Std. enthalpy of H <sub>2</sub> O (liquid) at 273.15 K (0 ° C):	632.33	± 0.35 J kg <sup>-1</sup>
Std. enthalpy of H <sub>2</sub> O (liquid) at 273.15 K (0 ° C):	11 392	± 6 J mol <sup>-1</sup>
-----		
Vaporization (at 273.15 K):	+ 2500.8	± 0.25 kJ kg <sup>-1</sup>
-----		
Std. enthalpy of H <sub>2</sub> O (vapor) at 273.15 K (0 ° C):	3 133.1	± 0.60 kJ kg <sup>-1</sup>
Std. enthalpy of H <sub>2</sub> O (vapor) at 273.15 K (0 ° C):	56 444	± 11 J mol <sup>-1</sup>
-----		
The vapour region (between 273.15 K and 298.15 K):	+ 25.1	± 0.01 kJ kg <sup>-1</sup>
-----		
Std. enthalpy of H <sub>2</sub> O (vapor) at 298.15 K (25 ° C):	3 179.3	± 0.61 kJ kg <sup>-1</sup>
Std. enthalpy of H <sub>2</sub> O (vapor) at 298.15 K (25 ° C):	57 276	± 11 J mol <sup>-1</sup>
-----		

The contribution to the water vapor enthalpy (3133.13 kJ kg kg<sup>-1</sup>) at 273.15 K due to the Debye region is very small (0.000 04 kJ kg kg<sup>-1</sup>) and the main contributions (about 80 %) is due to the vaporisation process, with smaller contributions (about 10 %) due to fusion and the integration of  $c_p(T) dT$  over the Ice-Ih region from 0 K to 273.15 K or 298.15 K.

The value  $H_{H_2O/calor.} \approx 298.63 \pm 0.10$  kJ kg<sup>-1</sup> for Ice-Ih at 273.15 K is very close to the difference in the “specific enthalpy”  $h(273.15 \text{ K}) - h(0 \text{ K}) \approx 298.658$  kJ kg<sup>-1</sup> and 298.662 kJ kg<sup>-1</sup> published in Feistel and Wagner (2006, Table. 14, p.1043) at the pressures of 1013.25 hPa and 0 hPa, respectively (with values at 273.15 K extrapolated from those given at 270 K and 273 K).

## 6 Detailed computations of the third-law statistical enthalpies

### 6.1 The general statistical-physics “difference in enthalpies”

The translational molar partition function of a gas is  $(Q_t)^{N_A}$ , where  $Q_t$  is given by (22) for a molecule of this gas. The difference in molar enthalpy

$$\Delta H_{\text{trans}}(T) = H_{\text{trans}}(T) - H_0$$

recalled in Atkins and de Paula (2014, Eq. 15F.4, p.646) can then be written in terms of derivative of  $T$  instead of  $\beta = 1/(kT)$ , leading to

$$\ln(Q_t) = \ln(V) + \frac{3}{2} \ln(T) + \ln \left[ \frac{(2\pi m k)^{3/2}}{h^3} \right], \quad (128)$$

$$H_{\text{trans}}(T) - H_0 = R_* T^2 \left[ \frac{\partial \ln(Q_t)}{\partial T} \right]_V + R_* T V \left[ \frac{\partial \ln(Q_t)}{\partial V} \right]_T, \quad (129)$$

$$H_{\text{trans}}(T) = H_0 + \frac{5}{2} R_* T = H_0 + \Delta H_{\text{trans}}(T), \quad (130)$$

where  $H_0$  is a constant to be determined and which (a priori) depends on the gas under consideration.

---

Differently from what happens with the molar entropy  $S_{\text{trans}}(T)$  given by (25) and which depends on  $\ln(Q_t)$  itself, the logarithm of the Sackur-Tetrode constant  $(2\pi m k)^{3/2}/h^3$  has no impact on the molar “difference in enthalpy”  $\Delta H_{\text{trans}}(T) = H_{\text{trans}}(T) - H_0 = (5/2) R_* T$ , because the two derivatives of this Sackur-Tetrode constant cancel out in (129).

This explains why, differently from the entropy where  $S_0$  can be determined by either the statistical method (via the Sackur-Tetrode constant) or the calorimetric method (via the Third law), the statistical method does not determine the value of the reference enthalpy  $H_0$ , which may not be the same for all atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , Argon,  $\text{H}_2\text{O}$ ).

The reference enthalpies  $H_0$  are thus set to arbitrary values, depending on the datasets and authors, where the choices may be to:

- compute  $H(T) - H_0(0 \text{ K})$ , or set  $H_0 = 0$  for all solid species at 0 K, like in CODATA-73 (1975), CODATA-77 (1978), Cox et al. (1989), Panasiti et al. (1999);
- compute  $H(T) - H_0(298.15 \text{ K})$ , or set  $H_0 = 0$  at 298.15 K for all gases, like in Stull and Prophet (1971, JANAF-2), Chase (1998, NIST-JANAF-4), Lemmon et al. (2000), Tegeler et al. (1999, for Argon);
- compute  $H(T) - H_0(273.15 \text{ K})$ , or set  $H_0 = 0$  at 273.15 K for dry air, like in IAPWS (2010) and Feistel et al. (2010a, TEOS10).

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To cope with so many formulations and presentations of the “enthalpy” or “difference in enthalpy” in the thermodynamic tables, with so many different zero-values at 0 K or 273.15 K or 298.15 K, I have tried to harmonize these data by adding, if necessary, the values at 0 K in order to obtain comparable values of enthalpies between 100 and 300 K. The table 5 shows these “rescaled” values for the main atmospheric gases  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , Argon and  $\text{H}_2\text{O}$ .

Since Argon is a mono-atomic gas with translational degrees of freedom only, it is possible to check in the corresponding line of the Table 5 for Argon (JANAF-4 / Chase, 1998, where  $R_* \approx 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ ) that “[  $H(T) - H(0 \text{ K})$  ] / ( $R_* T$ )” is indeed equal to  $5/2 = 2.5$ : this ratio



is indeed between 2.4993 and 2.4999 for temperatures from 100 K to 300 K. Differently, values for Argon from Tegeler et al. (1999, where  $R_* \approx 8.31451 \text{ J K}^{-1} \text{ mol}^{-1}$ ) show some discrepancies from the theoretical value of 2.5 (with values down to 2.4438 at 100 K) likely due to the fitting to observed (real gas?) thermodynamical values, or to experimental errors, or to the choice of  $+6204.1 \text{ J mol}^{-1}$  as global shift of data.

Table 5: The “difference in enthalpies”  $H(T) - H(0 \text{ K})$  in  $\text{J mol}^{-1}$  for the dry air and the main dry-air atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , Argon,  $\text{H}_2\text{O}$ ) given for some selected temperatures and by different Thermodynamical tables. The pressure is set to 1000 hPa, except for the (dry-air) first two lines, where it is set to 1013.25 hPa. The global shifts are:  $+7914.137 \text{ J mol}^{-1}$  for the TEOS10 software (McDougall et al., 2010; Feistel et al., 2010b; Feistel, 2012); “ $-H(0 \text{ K})$ ” for all JANAF-4 values from Chase (1998);  $+6204.1 \text{ J mol}^{-1}$  for Argon from Tegeler et al. (1999); and  $+9484.3 \text{ J mol}^{-1}$  for  $\text{CO}_2$  from Span and Wagner (1996). The Chase (JANAF-4 / 1998) dry-air enthalpy has been computed from enthalpies of  $\text{N}_2$ ,  $\text{O}_2$ , Argon and  $\text{CO}_2$  with the molar concentrations of Picard et al. (2008) rescaled given in the last line of the Table 26 (0.780 878, 0.209 390, 0.009 332 and 0.000 400  $\text{mol mol}^{-1}$ , respectively for “A”) and values used in Lemmon et al. (2000) from enthalpies of  $\text{N}_2$ ,  $\text{O}_2$  and Argon without  $\text{CO}_2$  (0.781 2, 0.209 6 and 0.009 2, respectively for “B”).

	0 K	100 K	150 K	200 K	250 K	298.15 K	300 K
Dry air / Lemmon et al. (2000)	—	2842.1	4321.8	5782.9	7239.9	8642.6	8696.5
Dry air / TEOS10 / 1013.25 hPa	—	2842.13	4321.83	5782.96	7239.86	8642.58	8696.50
Dry air / TEOS10 / 1000 hPa	—	2842.82	4322.14	5783.14	7239.98	8642.66	8696.59
Dry air / JANAF-4 Chase (1998) A	0	2894.73	—	5802.71	—	8649.92	8703.78
Dry air / JANAF-4 Chase (1998) B	0	2894.84	—	5802.87	7226.55	8649.97	8703.83
$\text{N}_2$ / JANAF-4 Chase (1998)	0	2902	—	5819	7268	8670	8724
$\text{N}_2$ / Span et al. (2000)	—	2854.7	4334.5	5798.9	7259.0	8663.7	8717.7
$\text{O}_2$ / JANAF-4 Chase (1998)	0	2904	—	5815	7273	8683	8737
$\text{O}_2$ / Stewart et al. (1991)	—	2849.4	4332.0	5798.3	7261.3	8674.1	8728.5
Argon / JANAF-4 Chase (1998)	0	2078	—	4157	5196	6197	6235
<b>Argon / (<math>2.5 \times 8.3144 \times T</math>)</b>	<b>0</b>	<b>2078.6</b>	<b>3117.9</b>	<b>4157.2</b>	<b>5196.5</b>	<b>6197.3</b>	<b>6235.8</b>
Argon / Tegeler et al. (1999)	—	2031.9	3099.3	4148.5	5192.7	6196.5	6235.0
$\text{CO}_2$ / JANAF-4 Chase (1998)	0	2908	—	5950	—	9364	9433
$\text{CO}_2$ / Span and Wagner (1996)	—	—	—	5916.7	7620.3	9364.3	9433.0
$\text{H}_2\text{O}$ / JANAF-4 Chase (1998)	0	3289	—	6622	—	9904	9966

## 6.2 The translational, rotational and vibrational “difference in enthalpies”

Since the enthalpy data from Chase (JANAF-4 / 1998) seem to be explained by the same translational partition function from statistical physics that is used to calculate absolute entropy of Argon, one can try to use the other partition functions to calculate the enthalpy contributions created by the rotational and vibrational degrees of freedom for  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

The translational part of the difference in enthalpy for atoms (Ar) and molecules ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$  and

$\text{H}_2\text{O}$ ) is given by (130), with therefore:

$$\Delta H_{\text{trans}}(T) = H_0 + \frac{5}{2} R_* T, \quad (131)$$


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The molar rotational enthalpy for diatomic molecules ( $\text{N}_2$ ,  $\text{O}_2$ ) corresponding to (45) for entropy and including the quadratic correction term is derived in Mayer and Mayer (1940, Eq.7.21, p.158) and recalled in Chase (1998, p.18):

$$\Delta H_{\text{rot./lin}} \approx R_* T \left[ 1 - \frac{u}{3} - \frac{u^2}{45} \right], \quad \text{where } u = \frac{\Theta_{\text{rot.}}}{T}. \quad (132)$$


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The molar vibrational enthalpy for diatomic molecules ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ) corresponding to (51) for entropy is derived in Mayer and Mayer (1940, Eq.7.16, p.155) and recalled in Chase (1998, p.18):

$$\Delta H_{\text{vibr./lin}} = R_* T \left[ \frac{u}{\exp(u) - 1} \right], \quad \text{where } u = \frac{\Theta_{\text{vib.}}}{T}. \quad (133)$$


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The molar anharmonic vibrational enthalpy for diatomic molecules ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ ) corresponding to (57) for entropy and recalled in Chase (1998, p.18, with however the exponent 3 missing in the last term  $\{\exp(u) - 1\}^3$ ) can be derived from the logarithm of the correction partition function  $\ln(Q_c)$  given by Eq. (7.42) in Mayer and Mayer (1940, p.164) where  $u = \Theta_{\text{vib.}}/T$  and with  $\Delta H = R_* T^2 d \ln(Q_c)/dT = -R_* T u d \ln(Q_c)/du$ , leading to:

$$\Delta H_{\text{v-an./lin}} = R_* T \left[ \frac{8 g_e}{u} + \frac{u [d_e \exp(u) - 2 x_e]}{[\exp(u) - 1]^2} + \frac{4 x_e u^2 \exp(u)}{[\exp(u) - 1]^3} \right]. \quad (134)$$


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The molar rotational enthalpy for polyatomic linear molecules like  $\text{CO}_2$  corresponds to the partition function (85) for entropy, but including the term  $\exp(u/3)$  present in McDowell (1988, Eq.5, p.357) and Martin et al. (1991, Eq.2, p.8375), leading to

$$Q_{\text{rot/CO}_2} \approx \frac{\exp(u/3)}{\sigma_r u} \left( 1 + \frac{u^2}{90} \right) \left( 1 + \frac{\tilde{\alpha}_e}{u} \right), \quad \text{where } u = \frac{\Theta_{\text{rot.}}}{T}, \quad (135)$$

$$\ln(Q_{\text{rot/CO}_2}) \approx -\ln(\sigma_r) - \ln(u) + \frac{u}{3} + \frac{u^2}{90} + \frac{\tilde{\alpha}_e}{u}, \quad (136)$$

$$\Delta H_{\text{rot/CO}_2} = -R_* T u \frac{d \ln(Q_{\text{rot}})}{du}, \quad (137)$$

$$\Delta H_{\text{rot/CO}_2} \approx R_* T \left[ 1 - \frac{u}{3} - \frac{u^2}{45} + \frac{\tilde{\alpha}_e}{u} \right], \quad (138)$$

where it is assumed that  $u < 1/10$  and  $\tilde{\alpha}_e/u < 1/10$  are small terms and  $\ln(1+b) \approx b$  for  $|b| \ll 1$ . The only difference with (132) is the last (small) term  $\tilde{\alpha}_e/u$  in (138).

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The rotational partition function for the non-linear molecule  $\text{H}_2\text{O}$  is given by (106), with the additional distortion term  $f_{\text{dist.}} \approx 1 + \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3$  given by (109), leading to

$$Q_{\text{rot}/\text{H}_2\text{O}} \approx \left[ \frac{\sqrt{\pi}}{\sigma_r (\Theta_{\text{rot}})^{3/2}} \right] T^{3/2} (1 + \rho_0 + \rho_1 T + \rho_2 T^2 + \rho_3 T^3), \quad (139)$$

$$\Delta H_{\text{rot}/\text{H}_2\text{O}} = R_* T^2 \frac{d \ln(Q_{\text{rot}/\text{H}_2\text{O}})}{dT} \approx \frac{3}{2} R_* T + (\rho_1 T + 2 \rho_2 T^2 + 3 \rho_3 T^3) R_* T. \quad (140)$$

The constants  $\rho_0 \approx -3.663 \cdot 10^{-5}$ ,  $\rho_1 \approx 2.0364 \cdot 10^{-5} \text{ K}^{-1}$ ,  $\rho_2 = \rho_{2D} + \rho_{2H} \approx -0.7534 \cdot 10^{-9} \text{ K}^{-2}$  and  $\rho_3 = \rho_{3D} + \rho_{3DH} \approx -4.3529 \cdot 10^{-13} \text{ K}^{-3}$  are given in table IV of Martin et al. (1991, p.8384) for  $\text{H}_2\text{O}$ . For  $T < 350 \text{ K}$ ,  $\rho_0 \ll 1$ ,  $\rho_1 T \ll 1$ ,  $\rho_2 T^2 \ll 1$  and  $\rho_3 T^3 \ll 1$  are used together with  $\ln(1+b) \approx b$  for  $|b| \ll 1$  to derive the leading order approximation (140). The term  $\rho_1 = 2.0364 \cdot 10^{-5}$  leads to a large impact on  $\Delta H_{\text{rot}/\text{H}_2\text{O}}$  in (140) of the order of  $15 \text{ J mol}^{-1}$  at  $300 \text{ K}$ , which is not small in comparison with  $1.5 R_* T \approx 3441 \text{ J mol}^{-1}$  at  $300 \text{ K}$ . The other quadratic and cubic correction terms lead to the smaller impacts of  $-0.34 \text{ J mol}^{-1}$  and  $-0.09 \text{ J mol}^{-1}$  at  $300 \text{ K}$ , respectively, which show that other terms with exponents larger than 3 are not mandatory in  $f_{\text{dist.}}$  and (140), because they must lead to corrections terms of less than  $\pm 0.001 \text{ J mol}^{-1}$  at  $300 \text{ K}$ .

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The molar vibration enthalpy for  $\text{H}_2\text{O}$  is the same as (133) for linear molecules, but with the three vibrational temperatures ( $\Theta_{\text{vib.A}/\text{H}_2\text{O}}$ ,  $\Theta_{\text{vib.B}/\text{H}_2\text{O}}$ ,  $\Theta_{\text{vib.C}/\text{H}_2\text{O}}$ ) and three vibrational corresponding parameters ( $u_A$ ,  $u_B$ ,  $u_C$ ) defined in (115) to (117), leading to

$$\Delta H_{\text{vibr.}/\text{H}_2\text{O}} = R_* T \left[ \frac{u_A}{\exp(u_A) - 1} + \frac{u_B}{\exp(u_C) - 1} + \frac{u_C}{\exp(u_C) - 1} \right]. \quad (141)$$

---

Finally, the electronic partition function for  $\text{O}_2$  gives no contribution on the molar enthalpy because  $Q_e = 3$  in (75) is a constant and thus:

$$\Delta H_{\text{elec.}/\text{O}_2} = R_* T^2 \frac{d \ln(Q_e)}{dT} = 0.$$

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I show in the Table (6) the corresponding “quantum-statistical-physics difference in enthalpies” noted  $H(298.15 \text{ K}) - H(0 \text{ K})$ , or simply the “enthalpy” in  $\text{J mol}^{-1}$  computed at  $298.15 \text{ K}$ , for the dry air and the main atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , Argon,  $\text{H}_2\text{O}$ ).

The value of  $(5/2) R_* T \approx 6197.35 \text{ J K}^{-1} \text{ mol}^{-1}$  for Argon in the last line of Table 6 for M25-Stat is computed with  $R_* \approx 8.31441 \text{ J K}^{-1} \text{ mol}^{-1}$ , at  $T = 298.15 \text{ K}$  and with the translational component (130) with  $H_0 = 0$ . Since no additional degree of freedom exists for Argon, this value is logically equal to the other published values of about  $6197 \text{ J K}^{-1} \text{ mol}^{-1}$  recalled in the first four lines of this Table 6.

The same agreement is shown between the M25-Stat values and the previous values for  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{CO}_2$  and thus for the dry-air value, with however a larger discrepancy for  $\text{H}_2\text{O}$ .

More precisely, values for  $\text{N}_2$  and  $\text{O}_2$  are close to the value  $(7/2) R_* T \approx 8676.3 \text{ J K}^{-1} \text{ mol}^{-1}$ , with  $(5/2) R_* T$  coming from the translational component (130) with  $H_0 = 0$  and an additional quantity  $R_* T$  coming from the (first-order) rotational component (132) without the (negative) impact of the additional terms  $-u/3$  and  $-u^2/45$  (about  $-8$  unit for  $\text{N}_2$  and  $-5.7$  units for  $\text{O}_2$ ). Contributions from

Table 6: The “difference in enthalpies”  $H(298.15\text{ K}) - H(0\text{ K})$ , or simply the “enthalpy” in  $\text{J mol}^{-1}$  computed at 298.15 K for the dry air and the main atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{CO}_2$ , Argon,  $\text{H}_2\text{O}$ ) given in different Thermodynamical tables. The pressure is 1000 hPa, but for Lemmon et al. (2000) where it was 1013.25 hPa. The dry-air enthalpy is only available in Lemmon et al. (2000) from  $\text{N}_2$ ,  $\text{O}_2$  and Argon with the molar concentrations of 0.7812, 0.2096 and 0.0092  $\text{mol mol}^{-1}$ , respectively. Other values of dry-air enthalpy (in parenthesis) are computed from enthalpies of  $\text{N}_2$ ,  $\text{O}_2$ , Argon and  $\text{CO}_2$  with the rescaled molar concentrations of Picard et al. (2008) given in the last line of the Table 26, namely 0.780878, 0.209390, 0.009332 and 0.000400  $\text{mol mol}^{-1}$ , respectively.

“ $H$ ” at 298.15 K and 1000 hPa	$\text{N}_2$	$\text{O}_2$	Argon	$\text{CO}_2$	Dry air	$\text{H}_2\text{O}$
CODATA-73 (1975)	$8669 \pm 3$	$8682 \pm 4$	$6197 \pm 2$	$9364 \pm 8$	$(8648.9 \pm 3.2)$	$9908 \pm 8$
Cox et al. (1989)	$8670 \pm 1$	$8680 \pm 2$	$6197 \pm 1$	$9365 \pm 3$	$(8649.3 \pm 1.2)$	$9905 \pm 5$
JANAF-4 (Chase, 1998)	8670	8683	6197	9364	(8649.9)	9904
Lemmon et al. (2000, p.334-335)	8670.0	8680.0	6197.0	—	8649.34	—
$H(298.15\text{ K})$ M25-Stat	8670.2	8683.3	6197.4	9360.6	(8650.2)	9939.1

vibrational and anharmonic contributions are smaller but cannot be neglected (about +1.8 units for  $\text{N}_2$  and +12.7 units for  $\text{O}_2$ ).

The values of  $H(298.15\text{ K})$  for  $\text{CO}_2$  (about 9360 to 9365  $\text{J K}^{-1} \text{mol}^{-1}$  up to  $\pm 0.05\%$ ) is logically much larger than  $(7/2) R_* T \approx 8676.3$  due to the impact of the large vibrational component (about +685 units).

Larger differences exist (about +33 units or +0.33 %) between the M25-Stat  $\text{H}_2\text{O}$  value 9939.1  $\text{kJ mol}^{-1}$  for  $H(298.15\text{ K})$  and the other published values from 9904 to 9908 unit. However, the sole translational and (first order) rotational components lead to  $4 R_* T \approx 9915.8 \text{ J K}^{-1} \text{mol}^{-1}$ , which is already larger than those smaller published values. Since all other terms lead to positive impacts on  $H(298.15\text{ K})$ , the explanation for this disagreement of about +0.33 % between values for  $\text{H}_2\text{O}$  is left unexplained to me.

### 6.3 Determination of $H_0$ ?

The values I have computed and labelled “M25-Stat” in the Table 6 are thus in agreement with the other datasets published in CODATA-73 (1975), Cox et al. (1989), JANAF-4 (Chase, 1998) and by Lemmon et al. (2000). This can likely be interpreted as a validation (up to +0.33 % for  $\text{H}_2\text{O}$  and better than +0.04 % for  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{CO}_2$  and dry air) of the computations made by summing the different contributions (130), (132), (133), (134), (138), (140) and (141), depending on the atmospheric species.

However, it is likely questionable whether the definition for statistical enthalpies  $H(T)$ , with the term  $H_0 = 0$  in (130), is the most relevant one. In fact the term  $H_0$  in (130) is left undetermined, and another possibility would be to seek for more relevant values for  $H_0$ .

To do so, I would be inclined to follow the conclusions of Richardson (1922), who explained in his “Digression on entropy” (p.159): “(...) the question then arise: what energy and entropy are to be ascribed to unit mass of the incoming substance?” especially when Richardson immediately added: “As there is a constant of integration in the entropy, we must ask what would be the effect of an increase in this constant (...) Approximations are not here permissible, for the constant might be made indefinitely large” (and the same need exists to determine the energy or enthalpy constant  $H_0$ ).

The conclusions of Richardson for entropy indeed apply for energy (or enthalpy) as well, because when it comes to calculating and studying the enthalpy for a mixture the constants  $H_{0x}$  do matter, and already for the simplest example of moist air composed of dry air and water vapor with the respective molar concentrations  $x_d$  and  $x_v$ , which are assumed to be variable but of constant sum  $x_d + x_v = 1$ . For

this simple system at  $T_0 = 298.15$ , according to the last line of the Table 6 and with a priori separate values for the “zero-enthalpies”  $H_{d0}$  and  $H_{v0}$ :

$$\text{for dry-air and water-vapour: } H_d(T_0) \approx 8650 + H_{d0} \text{ and } H_v(T_0) \approx 9939 + H_{v0}, \quad (142)$$

$$\text{and thus for the moist-air: } H(T_0) = x_d H_d(T_0) + x_v H_v(T_0), \quad (143)$$

$$\text{and thus: } H(T_0) \approx 8650 x_d + 9939 x_v + (x_d H_{d0} + x_v H_{v0}). \quad (144)$$

$$\text{and thus: } H(T_0) \approx 8650 x_d + 9939 x_v + (H_{v0} - H_{d0}) x_v + H_{d0}, \quad (145)$$

$$\text{and thus for turbulent fluxes: } \overline{w' H'(T_0)} \approx 8650 \overline{w' x'_d} + 9939 \overline{w' x'_v} + (H_{v0} - H_{d0}) \overline{w' x'_v}. \quad (146)$$

While the first two terms in (146) are not problematic (as far as the values 8650 and 9939 are relevant), those in parentheses made of the difference  $(H_{v0} - H_{d0})$  require the knowledge of the two reference values  $H_{d0}$  and  $H_{v0}$ , since both  $x_v$  (and  $x_d = 1 - x_v$ ) may vary with space and time.

Beyond the prophetic vision of Richardson (1922), this need to know absolute values  $H_{d0}$  and  $H_{v0}$  has been expressed more recently to calculate the turbulent surface energy fluxes  $\overline{w' h'}$  by Montgomery (1948) and above all Businger (1982). In this regard, we can paraphrase Richardson (1922) and say that: “*approximations are not here permissible,*” because enthalpy (like entropy) is a thermodynamic state function for which the computation of differences between two points  $A$  and  $B$  must be uniquely determined, with for instance the status of isenthalpic (and isentropic) processes, as well as increases or decreases in enthalpy (or entropy), which should not depend on arbitrary choices of  $H_{d0}$  or  $H_{v0}$  (and  $S_{d0}$  or  $S_{v0}$ ). And it turns out that the energy budget equation for the atmosphere ( $dE/dt = \dots$ ) depends on the surface enthalpy turbulent fluxes  $\overline{w' H'}$ , which in turn depends from (146) on  $(H_{v0} - H_{d0}) \overline{w' x'_v}$ , and thus on both  $H_{d0}$  and  $H_{v0}$  that must be known and determined independently from each other. One may dream of something different, but this is how atmospheric physics works.

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Therefore: what are the degrees of freedom in the definition of the partition functions, and thus the quantities that can leave the enthalpy or entropy unchanged?

On the one hand, only a constant term like  $Q_c$  has no impact on the enthalpy  $H(T)$ , but generates an increase in entropy of  $R_* \ln(Q_c)$  (for example the electronic partition function  $Q_e = 3$  in (75) for  $O_2$ ).

On the other hand, only the term  $Q_0 = \exp(-\alpha/T)$ , with  $\alpha$  an arbitrary constant, has no impact on the entropy  $S(T)$ , but generates an impact  $+\alpha R_*$  on the enthalpy  $H(T)$ . It is thus possible to add/remove such factors  $Q_0 = \exp(\pm\alpha/T)$  in the partition function, with a shift of the enthalpy  $H_0$  by  $\mp\alpha R_*$  and without changing the entropy  $S(T)$ .

This entropy-invariance corresponds for instance to the general definition of the partition function in terms of degeneracy factors ( $g_j$ ) and energy levels ( $E_j$ ), but with a possible undetermined global shift for all these energy levels (the same  $\Delta E$  for all  $j$ ), leading to

$$Q = \sum_{j \geq 0} g_j \exp\left(-\frac{E_j + \Delta E}{k T}\right) = Q_0 \times \left[ \sum_{j \geq 0} g_j \exp\left(-\frac{E_j}{k T}\right) \right], \quad (147)$$

$$\text{where } Q_0 = \exp\left(\frac{-\alpha}{T}\right) \text{ with } \alpha = \frac{\Delta E}{k}. \quad (148)$$

An example of such “entropy-invariance” term is the function  $\exp(u/3)$  recalled in (135) for  $Q_{\text{rot}/CO_2}$  with  $\alpha = -1/3$  corresponding to the terms  $-u/3$  in (132) for  $N_2$  and  $O_2$  and in (138) for  $CO_2$  where, however, the origin of these terms were not due to changes in energy levels like in (147), but to Euler-Maclaurin summation formulas (see Eqs. 7.1 to 7.13, p.149-153, of Mayer and Mayer, 1940).

## 6.4 Absolute calorimetric thermal enthalpies

The question is therefore: how to determine the statistical values of  $H(T)$ , and thus the undetermined constant  $H_0$  in (130), for each of the constituents ( $N_2$ ,  $O_2$ , Argon,  $CO_2$ ,  $H_2O$ ) of the atmosphere? Is it possible to freely choose the same, or different values, for  $H_0$  and for each of these constituents?

When all the degrees of freedom are taken into account via (130), (132), (133), (134), (138), (140) and (141), depending on the constituents, we can write the following general formulation for the statistical enthalpy:

$$H(T) = H_0 + \Delta H_{\text{trans}}(T) + \Delta H_{\text{rot}}(T) + \Delta H_{\text{vib}}(T) + \Delta H_{\text{vib/an}}(T). \quad (149)$$

A common way to answer the above question of choosing the value of  $H_0$  is to either cancel out  $H(0 \text{ K})$  or  $H(T_0)$  for all bodies for a standard room temperature (such as  $T_0 = 273.15 \text{ K}$  or  $298.15 \text{ K}$ ), leading to values recalled in Tables (5) and (6) for either the differences  $H(T) - H(0 \text{ K})$  or  $H(T) - H(T_0)$ .

These assumptions are commonly done for atmospheric gases at  $T_0 = 273.15 \text{ K}$  (Iribarne and Godson, 1973; Emanuel, 1994; Pauluis et al., 2010; Feistel et al., 2010a, among many others), for both water  $H_2O$  (mainly liquid, sometimes vapor) and the dry air (mainly made of  $N_2$ ,  $O_2$ , Argon and sometimes  $CO_2$ ). Interpreted in terms of the statistical physics and from (149), such cancellations at  $T_0 = 273.15 \text{ K}$  mean that  $H_0 = -[\Delta H_{\text{trans}}(T_0) + \Delta H_{\text{rot}}(T_0) + \Delta H_{\text{vib}}(T_0) + \Delta H_{\text{vib/an}}(T_0)]$ , which corresponds to a global extra partition function  $Q_0 = \exp(-\alpha/T)$  with  $\alpha = H_0/R_*$ .

However, these choices have impacts on the value of such enthalpies for dry air and water vapor, and thus on the enthalpy of moist air, its flux and its time derivative via the penultimate term of (146), which shows that flux and time derivative of  $H(T)$  depends on  $(H_{v0} - H_{d0})\overline{w'q'_v}$  and  $(H_{v0} - H_{d0})dq_v/dt$ . As the cancellations of both  $H_{v0}$  and  $H_{d0}$  have an impact on these flux and time derivative, they are problematic and we need to listen to what Richardson (1922) told us and try to determine these quantities in a more physical way.

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To answer differently these questions of determining the values of  $H_0$  or  $H(0 \text{ K})$  or  $H(T_0)$ , it is possible to rely on the good agreement between the two statistical and calorimetric definitions for entropies (see the whole section 3, the Tables 1 and 3 and the Figs. 1). It is then possible to hope to have the same agreement between the statistical and calorimetric definitions of enthalpies, provided that we are free for defining  $H_0$  in (130) via possible additional factors  $Q_0 = \exp(-\alpha/T)$ , with  $\alpha$  arbitrary constants depending on the constituents, and that the calorimetric thermal enthalpy is defined like in Marquet (2015a) as the exact counterpart of the entropy for a gas “ $x$ ” given by (12), but for the enthalpy, leading to

$$H_{x/\text{calor.}}(T_0) = H_{x/0}(0 \text{ K}) + \int_0^{T_0} c_{px}(T) dT + \sum_j L_x(T_j), \quad (150)$$

$$\text{with } H_{x/0}(0 \text{ K}) = 0 \text{ J kg}^{-1} \text{ for solid states of } N_2, O_2, \text{ Argon, } CO_2 \text{ and } H_2O. \quad (151)$$

By doing so, it would be the calorimetric “third-law” definition  $H_{x/0} = 0 \text{ J kg}^{-1}$  at  $0 \text{ K}$  in (151), valid for solid states of all species  $N_2$ ,  $O_2$ , Argon,  $CO_2$  and  $H_2O$ , that would define the corresponding values  $H_0$  in (130) via additional terms  $\ln(Q_0) = -\alpha/T$  in (129), with no impact in (25) for entropy and with corresponding constants  $\alpha$  different for each species  $N_2$ ,  $O_2$ , Argon,  $CO_2$  and  $H_2O$ .

By doing so, the resulting values of  $H_{x/\text{calor.}}$  in (151) can be called the “absolute thermal-calorimetric enthalpy” for all species  $N_2$ ,  $O_2$ , Argon,  $CO_2$  and  $H_2O$ , because they represent the enthalpy due to the thermal degree of freedom for heating the more stable solid states at  $0 \text{ K}$  toward the ideal gaseous states at the standard temperature  $T_0$  (say  $273.15 \text{ K}$  or  $298.15 \text{ K}$ ), with the enthalpy changes due to the other solid and liquid states taken into account.

The price to pay is the need to compute the integrals of  $c_{px}(T)$  and the sum of the  $L_x(T_j)$  in (150) from experimental values of these specific heats and latent heats for each species N<sub>2</sub>, O<sub>2</sub>, Argon, CO<sub>2</sub> and H<sub>2</sub>O. These computations has already been partly achieved in Marquet (2015a) for N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O. They have been redone and extended for the present note, with Argon and CO<sub>2</sub> added, with the new values of  $c_{px}(T)$  listed in Tables 12 to 8, and with the latent heats  $L_x(T_j)$  indicated in Figs. 14 to 17.

The Debye (1912) law  $c_{px} \approx a_x T^3$  is assumed between 0 K and the first available temperature  $T_1$ , leading to

$$\int_0^{T_1} c_{px}(T) dT = \int_0^{T_1} a_x T^3 dT = \frac{a_x T_1^4}{4} = c_{px}(T_1) \left( \frac{T_1}{4} \right), \quad (152)$$

where  $T_1 = 2$  K for N<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O,  $T_1 = 2.112$  K for CO<sub>2</sub> and  $T_1 = 3$  K for Argon. The integral of  $c_{px}(T)$  between  $T_1$  and  $T_0$  in (150) is then computed between each intervals  $T_i$  and  $T_{i+1} = T_i + \Delta T$  with linear variations of the specific heats between  $c_{px}(T_i)$  and  $c_{px}(T_{i+1}) = c_{px}(T_i) + \Delta c_{px}$ , leading to

$$c_{px}(T) = c_{px}(T_i) + (T - T_i) \left[ \frac{\Delta c_{px}}{\Delta T} \right], \quad (153)$$

$$\int_{T_i}^{T_i + \Delta T} c_{px}(T) dT = \Delta T \left[ \frac{c_{px}(T_{i+1}) + c_{px}(T_i)}{2} \right]. \quad (154)$$

The uncertainties of  $H_{x/calor.}(T_0)$  computed with (150) to (154) have been evaluated with the same method as for the calorimetric entropies in section 3, but with adaptation for the enthalpy computations. More precisely, the uncertainty of each terms are evaluated in the following ways:

- the uncertainty of the Debye's contribution " $a_x T_1^4/4$ " is  

$$\Delta[a_x] (T_1^4/4);$$
- the uncertainty of each integral of  $c_p(T)$  between the two limit temperatures  $T_p$  and  $T_{p+1}$  of a given phase " $p$ " (solid(s), liquid, vapour) is  

$$\Delta(c_p) [T_{p+1} - T_p] + \Delta T_{p+1} [c_p(T_{p+1})] - \Delta T_p [c_p(T_p)];$$
- the uncertainty of each term due to changes of phases  $L(T_j)$  is  

$$\Delta[L(T_j)];$$
- the uncertainty of the enthalpies " $H_{x/calor.} \times M_x$ " expressed in unit of kJ mol<sup>-1</sup> (with  $H_{x/calor.}(T_0)$  in units of kJ kg<sup>-1</sup>) is  

$$\Delta(H_{x/calor.}) \times [M_x] + \Delta(M_x) \times [H_{x/calor.}].$$

The absolute thermal enthalpies listed in the Table 7 are computed in the Sections 5 at both 273.15 K and 298.15 K by using the calorimetric method for three phases of water (Ice-Ih, liquid water and water vapour) and for the dry air made of the main gaseous components N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub> (see the Section 9.2).

The absolute thermal enthalpies are computed as the difference  $H(T) - H_0(0 \text{ K})$ , or equivalently by setting  $H_0 = 0$  at 0 K for all species. This hypotheses to set the origin of enthalpies at 0 K is the same as in CODATA-73 (1975), CODATA-77 (1978), Cox et al. (1989), Panasiti et al. (1999), but here with all latent heat of change of states taken into account, leading to (150) with (151).

The Ice-Ih enthalpy "FW06" of  $298.658 \approx 298.7 \pm 1.0$  kJ kg<sup>-1</sup> at 273.15 K and 1013.25 hPa in the second Table 7 is computed from the dataset of Feistel and Wagner (2006, Table 14, p.1043) extrapolated at 273.15 K from the differences  $-339.928 + 632.020 = 292.092$  (between 270 K and 0 K) and  $-333.675 + 632.020 = 298.345$  (between 273 K and 0 K). Note that the impact of pressure is very small, leading to the same rounded value  $298.662 \approx 298.7 \pm 1.0$  kJ kg<sup>-1</sup> at 0 hPa, which is only  $298.662 - 298.658 = 0.04$  kJ kg<sup>-1</sup> larger than at 1013.25 hPa.

Table 7: A synthesis of the standard “calorimetric” thermal enthalpies ( $H_{x/\text{calor.}}$ ) computed in the next sections at 1000 hPa and at both 273.15 K and 298.15 K. Values are provided in both units of  $\text{kJ kg}^{-1}$  and  $\text{J mol}^{-1}$ , for the four main atmospheric gases ( $\text{N}_2$ ,  $\text{O}_2$ , Argon,  $\text{CO}_2$ ), the dry air and the water (ice, liquid and vapour  $\text{H}_2\text{O}$ ) species. The enthalpy “FW06” for Ice-Ih is from Feistel and Wagner (2006) and values “M15” are from Marquet (2015a) and Marquet and Geleyn (2015). See additional explanations in the main text. The last lines in these Tables recall the values of  $H_0$  suggested in the Fig. 9.

$H_{x/\text{calor.}}$	$\text{N}_2$ (gas)	$\text{O}_2$ (gas)	Argon (gas)	$\text{CO}_2$ (gas)	Dry air (gas) (400 ppmv)	Dry air (gas) (440 ppmv)
M15 / 0 °C ( $\text{kJ kg}^{-1}$ )	532.4	525.6			530	
2025 / 0 °C ( $\text{kJ kg}^{-1}$ )	$530.9 \pm 1.3$	$524.0 \pm 1.5$	$335.3 \pm 1.7$	$787.4 \pm 1.5$	$526.95 \pm 1.3$	$526.96 \pm 1.3$
2025 / 25 °C ( $\text{kJ kg}^{-1}$ )	$556.9 \pm 1.4$	$546.9 \pm 1.5$	$348.4 \pm 1.8$	$808.4 \pm 1.6$	$552.06 \pm 1.4$	$552.08 \pm 1.4$
2025 / 0 °C ( $\text{J mol}^{-1}$ )	$14\,871 \pm 36$	$16\,766 \pm 48$	$13\,373 \pm 68$	$34\,653 \pm 67$	$15\,262 \pm 39$	$15\,263 \pm 39$
2025 / 25 °C ( $\text{J mol}^{-1}$ )	$15\,600 \pm 37$	$17\,500 \pm 48$	$13\,893 \pm 72$	$35\,577 \pm 71$	$15\,990 \pm 41$	$15\,991 \pm 41$
$H_0$ ( $\text{J mol}^{-1}$ )	$6\,930 \pm 37$	$8\,817 \pm 48$	$7\,700 \pm 72$	$26\,216 \pm 71$	$7\,340 \pm 41$	
$H_{x/\text{calor.}}$	$\text{H}_2\text{O}$ (ice-Ih)		$\text{H}_2\text{O}$ (liq.)		$\text{H}_2\text{O}$ (vap.)	
FW06 / 0 °C ( $\text{kJ kg}^{-1}$ )	$298.7 \pm 1.0$		$632.1 \pm 1.2$		$3\,133.1 \pm 1.5$	
M15 / 0 °C ( $\text{kJ kg}^{-1}$ )	298		632		3 133	
2025 / 0 °C ( $\text{kJ kg}^{-1}$ )	$298.63 \pm 0.10$		$632.33 \pm 0.35$		$3\,133.1 \pm 0.6$	
2025 / 25 °C ( $\text{kJ kg}^{-1}$ )			$737.78 \pm 0.36$		$3\,179.3 \pm 0.6$	
2025 / 0 °C ( $\text{J mol}^{-1}$ )	$5\,380 \pm 2$		$11\,392 \pm 6$		$56\,444 \pm 11$	
2025 / 25 °C ( $\text{J mol}^{-1}$ )			$13\,291 \pm 7$		$57\,276 \pm 11$	
$H_0$ ( $\text{J mol}^{-1}$ )					$47\,337 \pm 11$	

- The enthalpies “M15” at 273.15 K indicated in the table 7 for  $\text{N}_2$ ,  $\text{O}_2$ , dry air and  $\text{H}_2\text{O}$  (Ice-Ih, liquid and vapour) are from the previous 2015 computations published in Marquet (2015a, Eqs.43-46) and Marquet and Geleyn (2015, Eqs.2.17-2.20), with the dry air only made of the main gaseous components  $\text{N}_2$  and  $\text{O}_2$  (and thus with Ar and  $\text{CO}_2$  neglected as a first guess).

- The molar values of  $H_0$  have been computed by subtracting the molar statistical values in the last line of the Table 6 (noted  $H(298.15\text{ K})$  M25-Stat) from the last line of the molar calorimetric values in the Table 7 noted: 2025 / 25 °C ( $\text{J mol}^{-1}$ ). The uncertainties of the statistical values must be lower than  $\pm 0.3\text{ J mol}^{-1}$ , with therefore the same (large) uncertainties retained for  $H_0$  as those for the calorimetric values.



Figure 9: The “calorimetric” (solid red) and “shifted-statistical” (dashed black) enthalpies for  $N_2$ ,  $O_2$ , Ar,  $CO_2$ ,  $H_2O$  and dry air (units in  $\text{kJ mol}^{-1}$ ). The vertical shifts at 0 K (blue line and numbers) are the starting points for the linear theoretical laws (thin blue solid lines proportional to  $R_* \times T$ ). For the dry air, the molar enthalpies are computed with the concentrations rescaled from values of Picard et al. (2008) and given in the last line of the Table 26, with the molar concentrations 0.780878, 0.209390, 0.009332 and 0.000400  $\text{mol mol}^{-1}$  for  $N_2$ ,  $O_2$ , Ar and  $CO_2$ , respectively. The green dashed line corresponds to values from 200 K to 300 K (see the vertical limits) listed in the Table A2 in Lemmon et al. (2000, “L00”, p.366-367), where the impact of  $CO_2$  was not taken into account and with the molar concentrations 0.7812, 0.2096 and 0.0092 for  $N_2$ ,  $O_2$  and Ar, respectively.

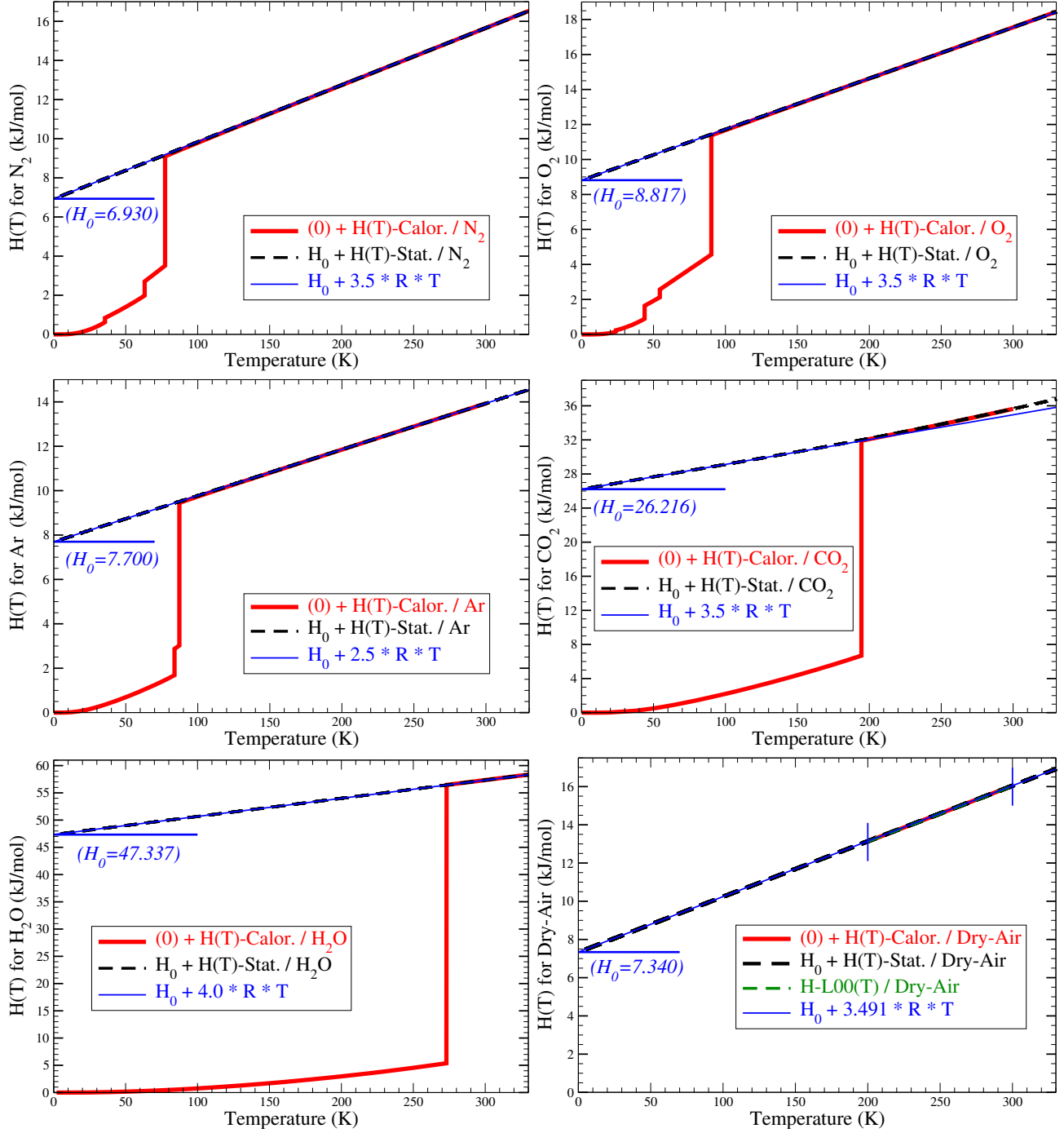
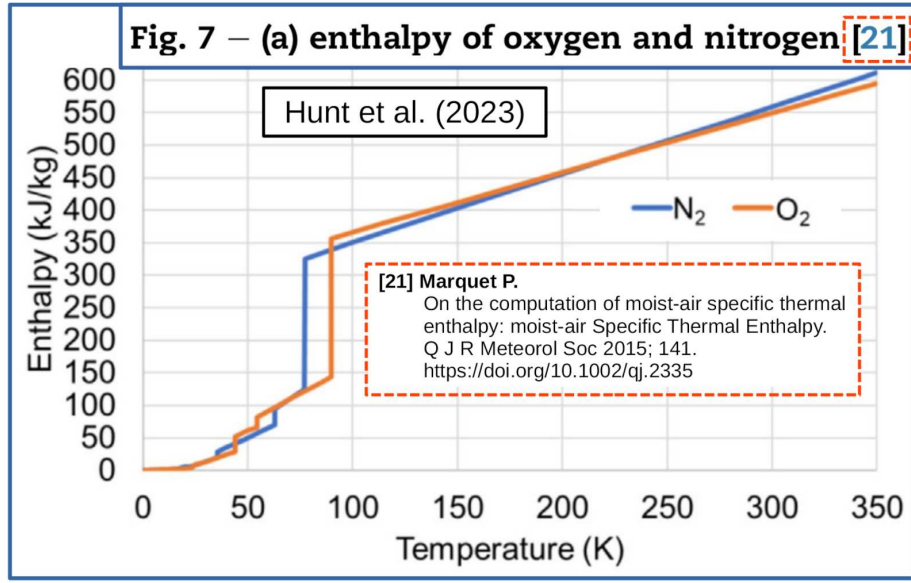


Figure 10: The Fig. 7(a) published in Hunt et al. (2023, p.6).



- In the Figs. 9 only the CO<sub>2</sub> curve shows significant and increasing departures from the linear law  $26.216 + 3.5 \times R_* \times T$  above about 150 K, where one of the vibrational mode starts to be activated. This CO<sub>2</sub> mode with the vibrational temperature of about 960.2 K and a degeneracy of 2 leads to a contribution of about  $0.3 \times R_* \times T$  at 300 K, see Eqs. (93) and (94) in the section 4.5.

- According to the Fig. 10, the Figure 7(a) published in Hunt et al. (2023, p.6)<sup>3</sup> is made of the same red curves I show in the two top panels of Figs. 9 for N<sub>2</sub> and O<sub>2</sub>, with the same hypothesis that the (thermal) enthalpy is to be computed with the calorimetric method from 0 K up to 300 K by integrating  $c_p(T)$  and by adding all latent heats  $L_k(T_k)$  due to changes of states, but based on my previous dataset published in Marquet (2015a).

<sup>3</sup> Where the authors study the possibility to use “solid nitrogen or oxygen as a medium for recycling cold energy across the hydrogen liquefaction supply chain” for the development of the “green hydrogen economy” and to challenge the “long-distance transportation” problem.

## 7 Figures of $c_p(T)$ for atmospheric gases

The aim of next subsections is to plot the specific heats  $c_p(T)$  against the absolute temperature  $T$  (from about 2 K up to about 300 K) for the 5 main atmospheric species  $N_2$ ,  $O_2$ , Ar,  $CO_2$  and  $H_2O$ , in a way similar to the figures shown by Giauque (1949) in his Nobel lecture for  $N_2$ ,  $O_2$ , and  $CO_2$  recalled in the Fig. 11, and in a way similar to the Fig. 11-6 of Lewis and Randall (1961, p.126) recalled in the Fig. 12.

To plot these figures all the Tables for  $c_p(T)$  listed in the Section 8 for the 5 main atmospheric species  $N_2$ ,  $O_2$ , Ar,  $CO_2$  and  $H_2O$  are used.

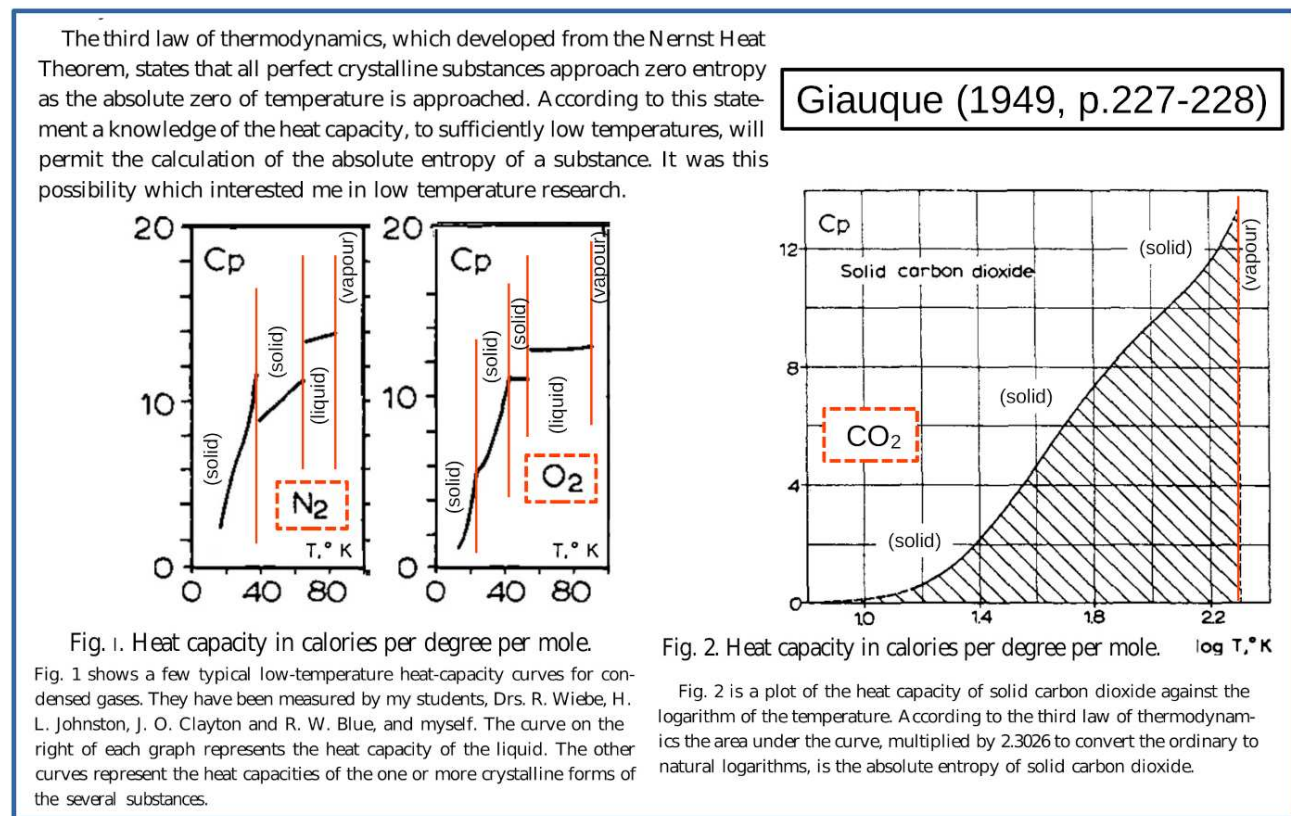


Figure 11: Parts of the text and of the Fig. 1 and Fig. 2 from Giauque (1949, p.227-228). I have enlarged the original figures and added the red vertical lines for indicating the changes of phases for  $N_2$  and  $O_2$  (between different solid phases on the left, then between solid and liquid phases, and then between liquid and vapour on the very right). The temperatures axes  $T$  are with a linear scale (labelled from 0 K to 100 K for  $N_2$  and  $O_2$ ), whereas the temperatures axis  $\log_{10}(T) = \ln(T)/\ln(10)$  is a (decimal) logarithmic scale for solid  $CO_2$  plotted (solid curve) from about  $\log_{10}(15\text{ K}) = 1.18$  up to about  $\log_{10}(195\text{ K}) \approx 2.29$  (with the labels 1.0, 1.4, 1.8, 2.2).

The Fig. 1 of Giauque (1949) plotted for the solids and liquid phases regions for  $c_p(T)$  and  $O_2$  (reproduced in the Fig. 11) is similar to the Fig. 15 I have plotted for  $O_2$  (but with the gaseous region included), and is similar to the Fig. 2 of Lewis and Randall (1923, p.153) and Fig. 11-6 of Lewis and Randall (1961, p.126) reproduced in the Fig. 12, but with the gaseous region included and with a logarithmic  $x$ -scale for  $\ln(T)$ .

The Fig. 1 of Giauque (1949) plotted for the solids and liquid phases regions for  $c_p(T)$  and  $N_2$  (reproduced in the Fig. 11) is similar to the Fig. 14 I have plotted for  $N_2$  (with the same linear  $x$ -scale for  $T$  but with the gaseous region included).

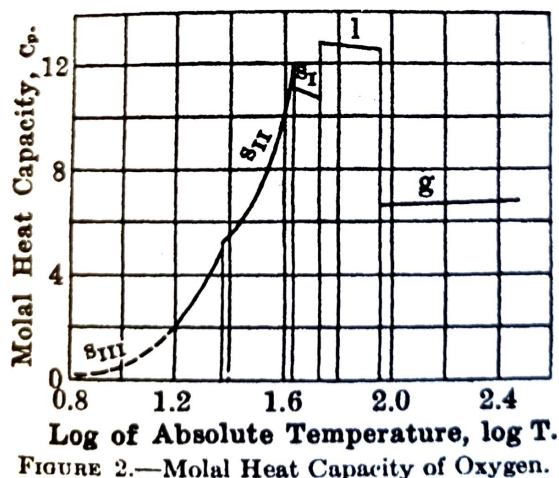


TABLE 11-1. THE ENTROPY OF OXYGEN	
0–14°K, extrapolation.....	0.54
14–23.66°K, solid III, graphical.....	1.500
Transition, $22.42/23.66$ .....	0.948
23.66–43.76°K, solid II, graphical.....	4.661
Transition, $177.6/43.76$ .....	4.058
43.76–54.39°K, solid I, graphical.....	2.397
Fusion, $106.3/54.39$ .....	1.954
54.39–90.13°K, liquid, graphical.....	6.462
Vaporization $1628.8/90.13$ .....	18.07
Total, $s_{90.13}$ (gas, 1 atm), cal/deg.....	40.59

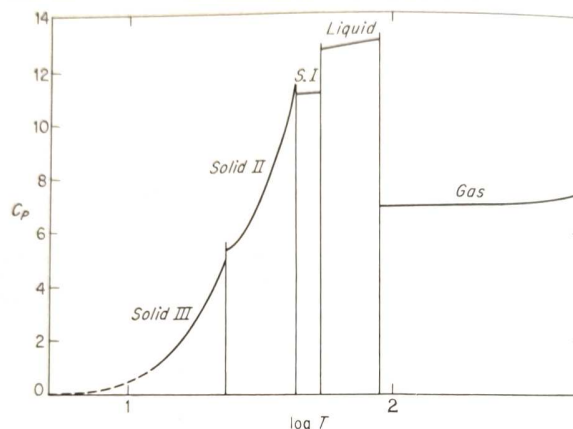


Figure 12: **Bottom left:** The Fig. 2 of Lewis and Randall (1923, p.153) for  $O_2$ , with  $c_p(T)$  plotted against  $\ln(T)$  with  $T$  the absolute temperature, and the (calorimetric) entropy to be computed via the integrals of  $dS = c_p(T) dT/T = c_p(T) d\log(T)$ . This figure is similar to the one I have plotted in the Fig. 15. **Bottom right:** The same Fig. 11-6 of Lewis and Randall (1961, p.126) for  $O_2$ , with  $c_p(T)$  plotted against  $\ln(T)$ . **Top:** The Table 11-1 of Lewis and Randall (1961, p.126) showing the computations of the (calorimetric) saturation entropy of gaseous  $O_2$ , with a value of about  $40.59 \text{ cal K}^{-1} \text{ mol}^{-1}$  at 90.13 K.

The Fig. 2 of Giauque (1949) (reproduced in the Fig. 11) with  $c_p(T)$  plotted for the solid phase of  $CO_2$  is similar to the Fig. 16 I have plotted for  $CO_2$  (but with a linear  $x$ -scale for  $T$  and with the gaseous region included).

The advantage of plotting  $c_p(T)$  versus the logarithmic scales  $\ln(T)$  or  $\log_{10}(T) = \ln(T)/\ln(10)$  (like in the Fig. 11 for  $CO_2$  and in the Fig. 12 for  $O_2$ ) is the possibility to compute graphically the entropy as the integrals of either  $dS = c_p(T) dT/T = c_p(T) d\log(T)$  or  $dS = \ln(10) c_p(T) d\log_{10}(T) \approx 2.3026 c_p(T) d\log_{10}(T)$ , as clearly indicated by the dashed area for solid  $CO_2$  in the Fig. 11.

I have chosen to plot in the next figures  $c_p(T)$  for the 5 substances  $N_2$ ,  $O_2$ ,  $CO_2$ , Ar and  $H_2O$  with linear  $x$ -axes expressed in terms of the absolute temperature  $T$ .

I have also plotted for these 5 substances the “Debye” coefficients “ $a$ ” corresponding to the Debye’s limit law  $C_p(T) \approx a T^3$ , and thus:  $a \approx C_p(T)/T^3$  (also plotted in terms of the absolute temperature  $T$ , but up to 20 K or 30 K and for the more stable solid- $\alpha$  phase only).

## 7.1 Figures of $c_p(T)$ for Argon

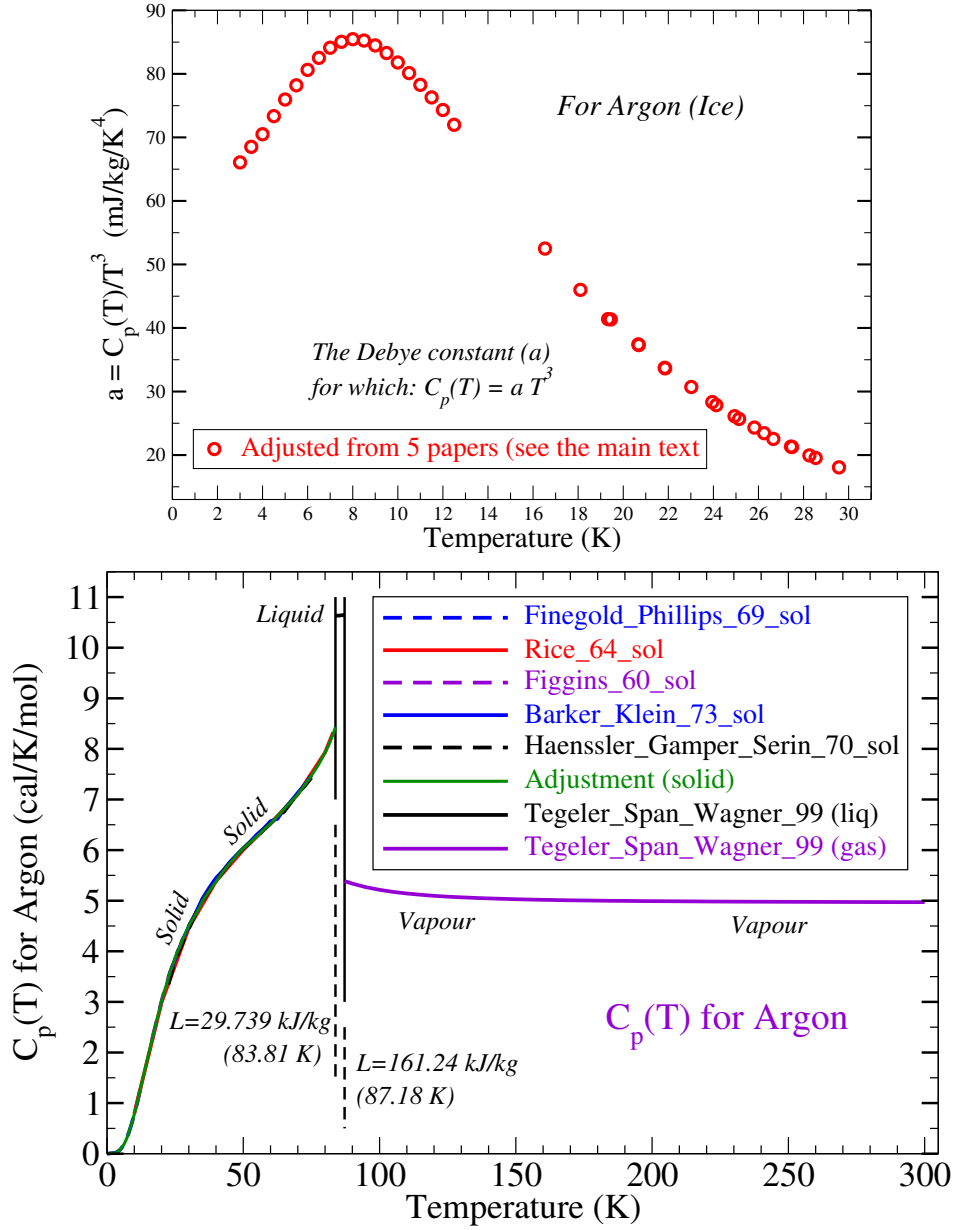


Figure 13: *Top: the Debye's constant for Argon. Bottom: the specific heat at constant pressure  $c_p(T)$  (in cal/K/mol) and the latent heats (in kJ/kg) for the solid, liquid and vapor states of Argon.*

## 7.2 Figures of $c_p(T)$ for $N_2$

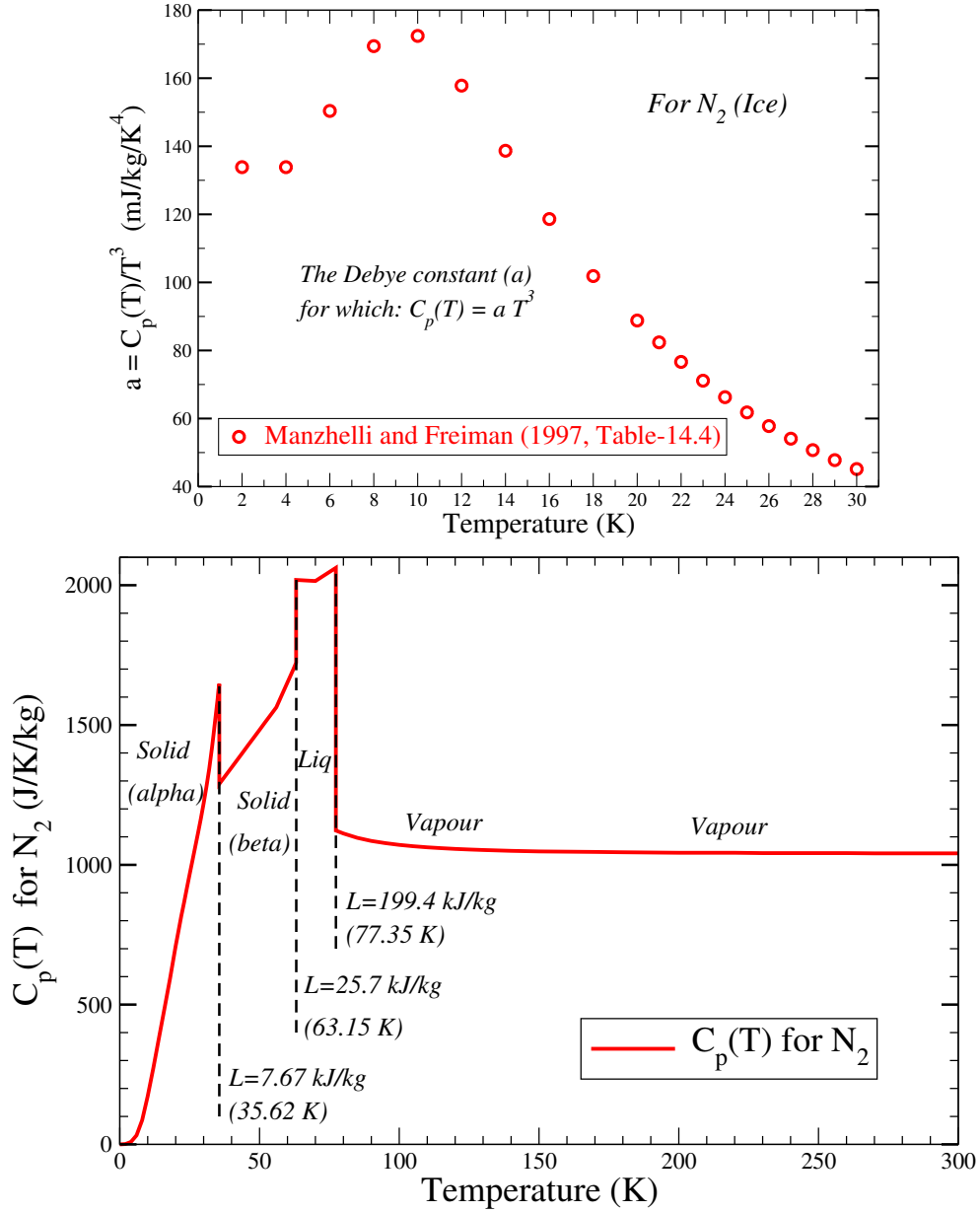


Figure 14: Top: the Debye's constant for  $N_2$ . Bottom: the specific heat at constant pressure  $c_p(T)$  (in J/K/kg) and the latent heats (in kJ/kg) for the two solid ( $\alpha, \beta$ ), liquid and vapor states of  $N_2$ .

### 7.3 Figures of $c_p(T)$ for $O_2$

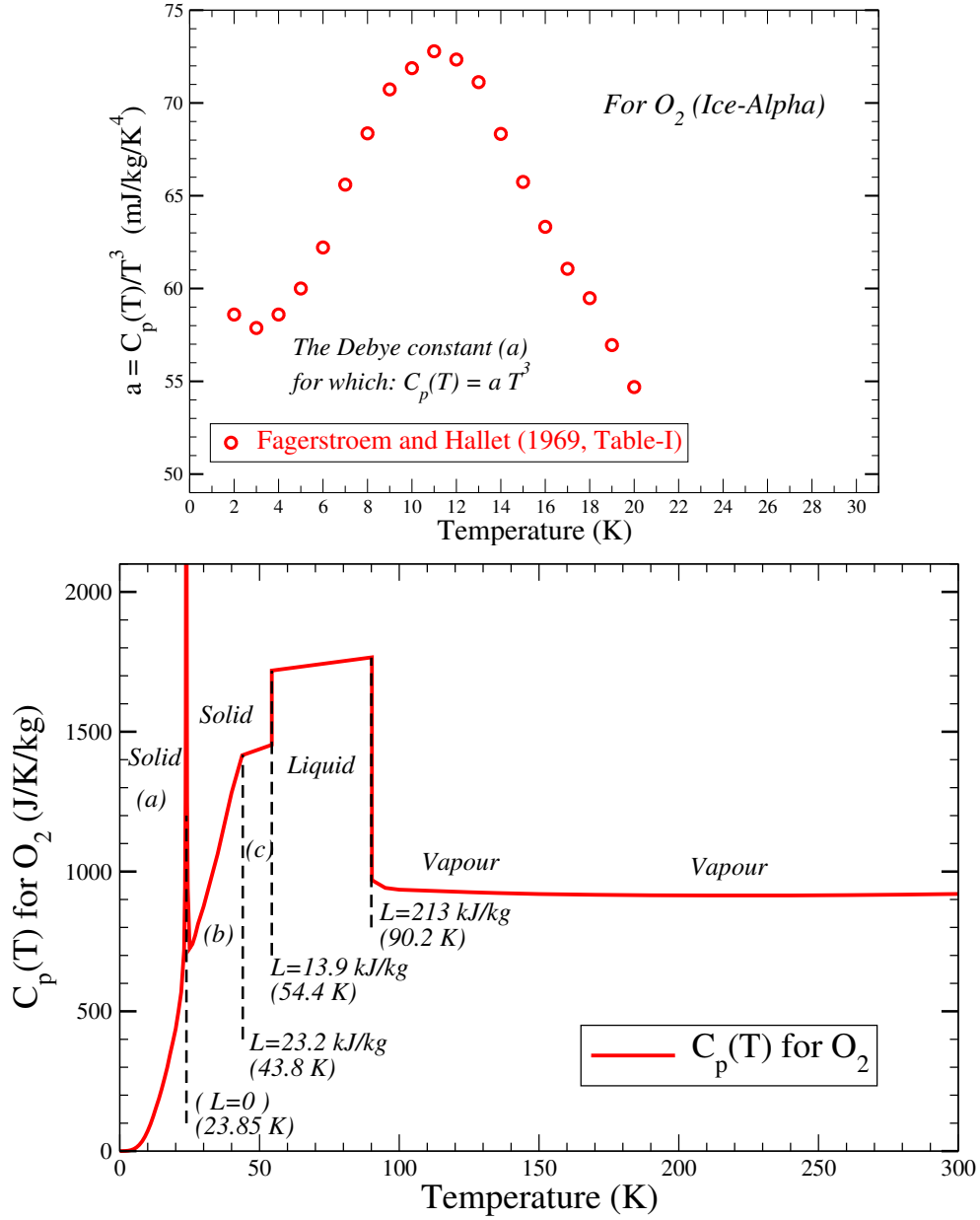


Figure 15: Top: the Debye's constant for  $O_2$ . Bottom: the specific heat at constant pressure  $c_p(T)$  (in J/K/kg) and the latent heats (in kJ/kg) for the three solid (a,b,c), liquid and vapor states of  $O_2$ .

#### 7.4 Figures of $c_p(T)$ for $\text{CO}_2$

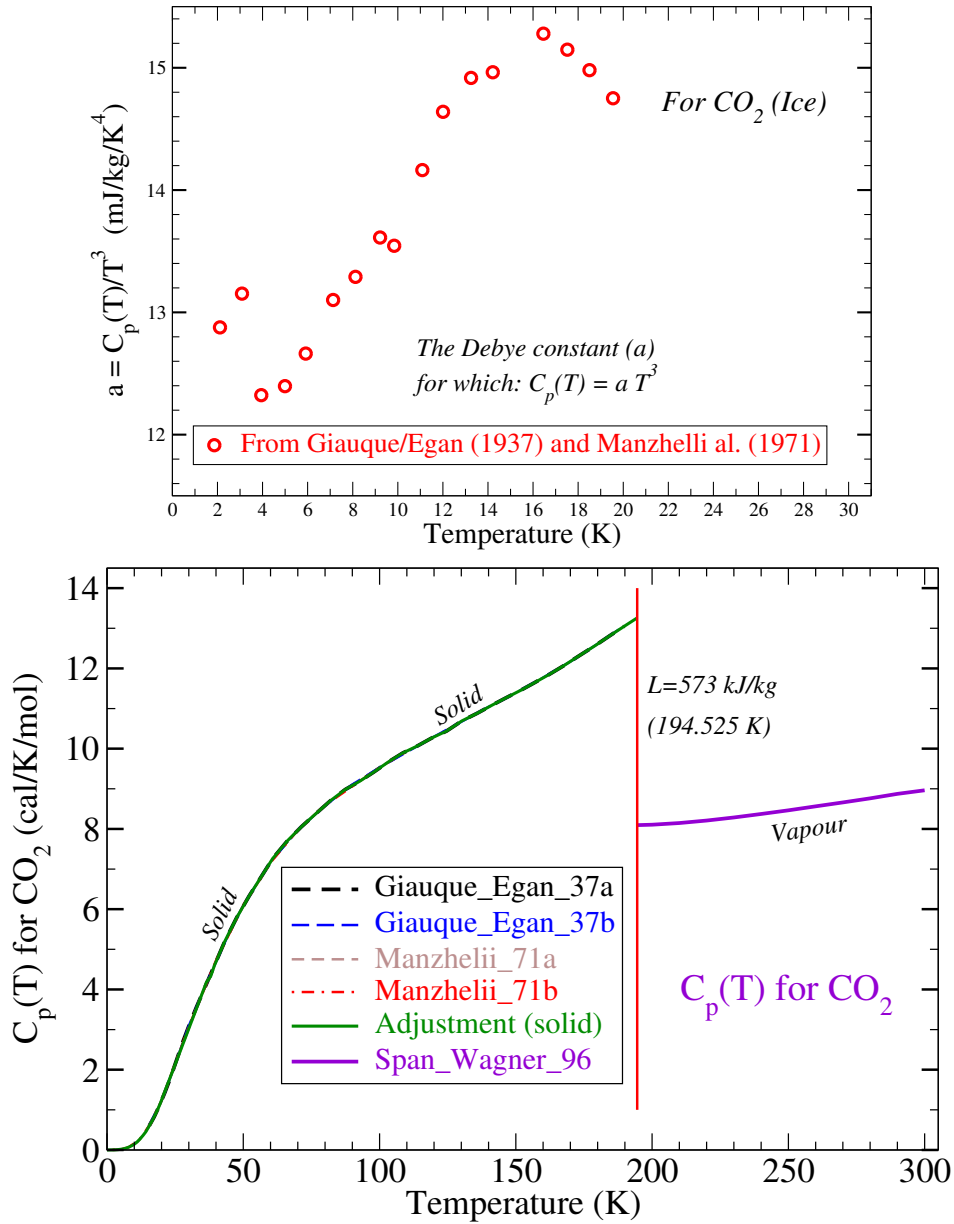


Figure 16: Top: the Debye's constant for  $\text{CO}_2$ . Bottom: the specific heat at constant pressure  $c_p(T)$  (in cal/K/mol) and the latent heats (in kJ/kg) for the solid, liquid and vapor states of  $\text{CO}_2$ .



## 7.5 Figures of $c_p(T)$ for $H_2O$ (Ice-Ih)

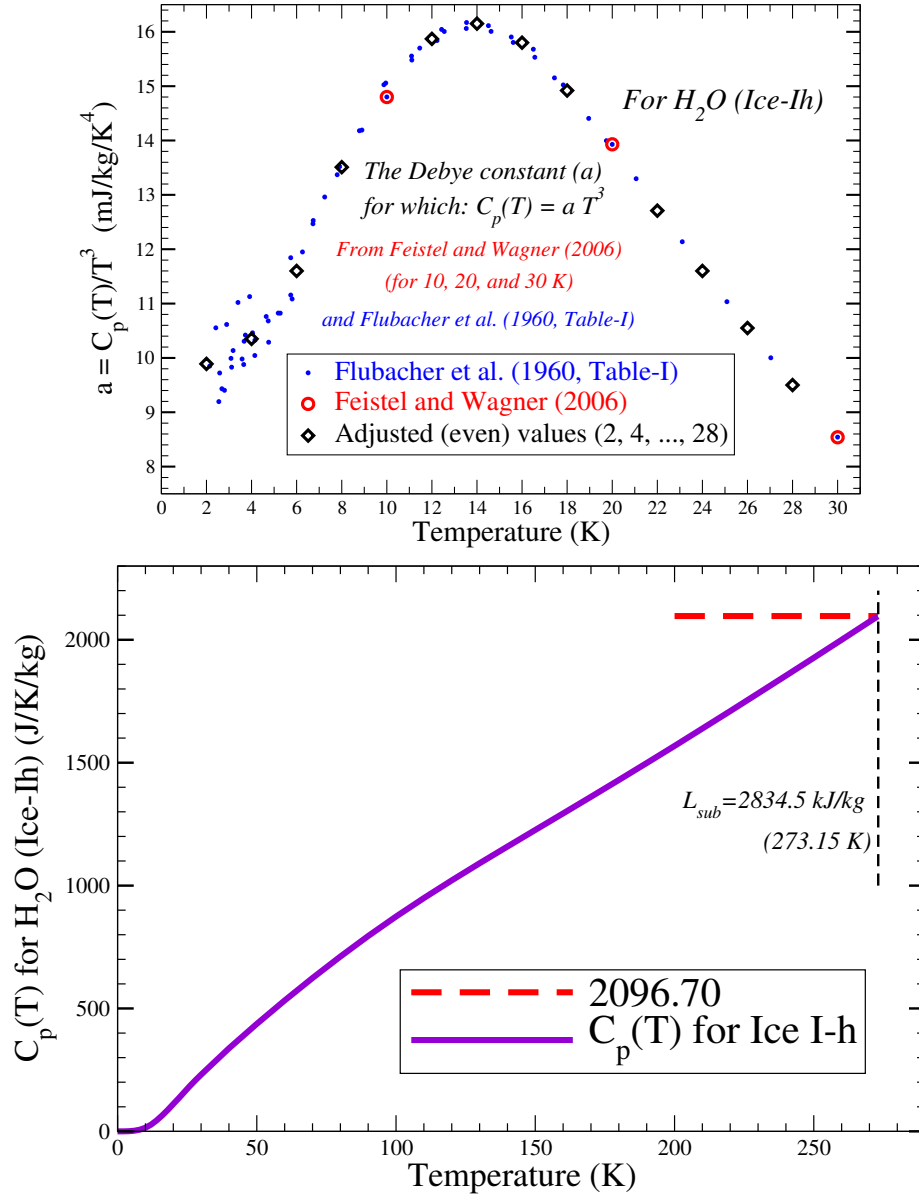


Figure 17: *Top: the Debye's constant for  $H_2O$  (Ice-Ih). Bottom: the specific heat at constant pressure  $c_p(T)$  (in J/K/kg) for  $H_2O$  (Ice-Ih) and corresponding to the Table 12.*

## 8 Tables of $c_p(T)$ for atmospheric species

### 8.1 Tables of $c_p(T)$ for Argon

Table 8: The specific heat (at constant pressure) for Argon given from  $T = 0$  K to 300 K. The first table corresponds to adjusted values for the ice (solid) state obtained from Figgins (1960), Rice (1964), Finegold and Phillips (1969), Barker and Klein (1973) and Haenssler et al. (1970) datasets. Units are K for  $T$  and  $\text{cal K}^{-1} \text{mol}^{-1}$  for  $c_p$  (to be multiplied by  $4.184 \text{ J cal}^{-1}$  and divided by  $0.039948 \text{ kg mol}^{-1}$  to obtain units of  $\text{J K}^{-1} \text{kg}^{-1}$ ). The second and third tables correspond to the liquid and gaseous states, with data obtained from Tegeler et al. (1999) in unit of  $\text{J K}^{-1} \text{kg}^{-1}$ .

$c_p(T)$  for Argon (ice) - Unit of  $\text{cal K}^{-1} \text{mol}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
0.0	0.0	18.10	2.60	32.40	4.720
3.0	0.0170	19.33	2.85	33.26	4.800
3.5	0.0280	19.45	2.90	34.07	4.880
4.0	0.0430	20.67	3.15	35.00	4.993
4.5	0.0637	20.69	3.15	37.50	5.197
5.0	0.0905	21.84	3.35	40.00	5.376
5.5	0.1240	21.86	3.35	42.50	5.567
6.0	0.1660	23.02	3.57	45.00	5.734
6.5	0.2160	23.95	3.71	47.50	5.889
7.0	0.2750	24.13	3.73	50.00	6.033
7.5	0.3420	24.94	3.86	52.50	6.152
8.0	0.4170	25.14	3.89	55.00	6.271
8.5	0.4990	25.82	3.99	57.50	6.403
9.0	0.5870	26.25	4.04	60.00	6.523
9.5	0.6805	26.66	4.07	70.00	7.100
10.0	0.7796	27.44	4.20	75.00	7.470
10.5	0.8840	27.49	4.21	77.50	7.680
11.0	0.9930	28.26	4.29	80.00	7.928
11.5	1.1060	28.54	4.33	81.50	8.100
12.0	1.2240	29.57	4.45	83.00	8.300
12.5	1.3400	30.56	4.56	83.81	8.430
16.53	2.2600	31.51	4.64		

$c_p(T)$  for Argon (liquid) - Unit of  $\text{J K}^{-1} \text{kg}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
83.81	1115.6	85.00	1115.7	87.18	1117.1

$c_p(T)$  for Argon (vapour) - Unit of  $\text{J K}^{-1} \text{kg}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
87.18	565.41	120	534.72	155	526.98	190	524.12	250	522.20
90	560.00	125	532.98	160	526.41	195	523.87	260	522.02
95	552.56	130	531.53	165	525.91	200	523.64	270	521.87
100	547.02	135	530.31	170	525.46	210	523.24	280	521.74
105	542.79	140	529.28	175	525.07	220	522.91	290	521.62
110	539.48	145	528.40	180	524.72	230	522.64	300	521.52
115	536.85	150	527.64	185	524.41	240	522.40		

## 8.2 Tables of $c_p(T)$ for $N_2$

Table 9: *The specific heat (at constant pressure) for  $N_2$  from  $T = 0$  K to 300 K. The first table corresponds to the solid- $\alpha$  state, with data obtained up to 35.62 K from Table 14.4 of Manzhelii and Freiman (1997). Units are K for  $T$  and  $J K^{-1} \text{ mol}^{-1}$  for  $c_p$  (to be divided by  $0.0280134 \text{ kg mol}^{-1}$  to obtain units of  $J K^{-1} \text{ kg}^{-1}$ ). The second table corresponds to the solid- $\beta$  state, with data obtained up to 56 K directly from Table 14.4 of Manzhelii and Freiman (1997) and in the range 56 to 63.15 K obtained from the measured values depicted on Figure 1 of Kudryavtsev and Nemchenko (2001), with a change in the slope of the curve  $c_p(T)$ . The third table corresponds to the liquid state, with  $c_p$  (at 1000 hPa) expressed in  $J K^{-1} \text{ kg}^{-1}$  in the Table 5.73 of Jacobsen et al. (1997). The fourth table corresponds to the vapour state, with  $c_p$  (at 1000 hPa) expressed in  $J K^{-1} \text{ kg}^{-1}$  in the table page 1410 of Span et al. (2000).*

$c_p(T)$  for  $N_2$  (solid- $\alpha$ ) - Unit of  $J K^{-1} \text{ mol}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
0	0	20	19.9	30	34.16
2	0.03	21	21.37	31	35.80
4	0.24	22	22.86	32	37.64
6	0.91	23	24.24	33	39.77
8	2.43	24	25.67	33.5	40.97
10	4.83	25	27.05	34	42.16
12	7.64	26	28.45	34.5	43.38
14	10.66	27	29.82	35	44.63
16	13.61	28	31.19	35.3	45.53
18	16.64	29	32.64	35.62	46.14

$c_p(T)$  for  $N_2$  (solid- $\beta$ ) - Unit of  $J K^{-1} \text{ mol}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
35.62	36.12	44	39.27	56	43.79
36	36.26	46	40.03	58	45.04
38	37.02	48	40.78	60	46.29
39	37.39	50	41.53	62	47.54
40	37.76	52	42.29	63.15	48.26
42	38.52	54	43.04		

$c_p(T)$  for  $N_2$  (liquid) - Unit of  $J K^{-1} \text{ kg}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
63.15	2018.9	70.00	2015	77.35	2062.3

$c_p(T)$  for  $N_2$  (vapour) - Unit of  $J K^{-1} \text{ kg}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
77.35	1122.6	125	1054.8	220	1043
80	1112.0	130	1053	230	1042
85	1096.6	140	1050	240	1042
90	1085.5	150	1048	250	1042
95	1077.7	160	1047	260	1042
100	1071.3	170	1046	270	1041
105	1066.6	180	1045	280	1041
110	1062.7	190	1044	290	1041
115	1059.5	200	1043	300	1041
120	1057.0	210	1043		

### 8.3 Tables of $c_p(T)$ for $O_2$

Table 10: *The specific heat (at constant pressure) for  $O_2$  from  $T = 0$  K to 300 K. The first table corresponds to the solid- $\alpha$  state. Units are K for  $T$  and  $J K^{-1} mol^{-1}$  for  $c_p$  (to be divided by  $0.0319988 kg mol^{-1}$  to get unit of  $J K^{-1} kg^{-1}$ ). Data were obtained up to 20 K from Table I of Fagerstroem and Hallet (1969), with some interpolation performed from their Figures 1 and 2 for the range 21 to 23.84 K. The second table corresponds to the solid- $\beta$  state from Table I of Fagerstroem and Hallet (1969) for the range 30 to 43.8 K, with interpolation performed from their Figures 1 and 2 for the range 23.855 to 28 K. The third table corresponds to the solid- $\gamma$  state (43.8 to 54.4 K) and the fourth table to the liquid form (54.4 to 90.2 K), with data obtained from Fagerstroem and Hallet (1969) with linear interpolation from their Figure 1. The fifth table corresponds to the vapour form at 1013.25 hPa (above 90.2 K) and with  $c_p$  expressed in  $J K^{-1} kg^{-1}$  in Table 5.79 of Jacobsen et al. (1997).*

$c_p(T)$ for $O_2$ (solid- $\alpha$ ) - Unit of $J K^{-1} mol^{-1}$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
	0	0	9	1.65	17	9.6	23.52	40
	2	0.015	10	2.30	18	11.1	23.6	50
	3	0.05	11	3.10	19	12.5	23.68	70
	4	0.12	12	4	20	14	23.71	100
	5	0.24	13	5	21	16	23.76	150
	6	0.43	14	6	22	18.2	23.80	300
	7	0.72	15	7.1	23	23	23.82	500
	8	1.12	16	8.3	23.35	30	23.84	1000

$c_p(T)$ for $O_2$ (solid- $\beta$ ) - Unit of $J K^{-1} mol^{-1}$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
	23.855	1000	24.03	50	28	26
	23.860	500	24.10	40	30	28
	23.865	300	24.32	30	35	34
	23.87	150	25	23.2	40	41
	23.88	100	26	23.7	43.8	45.3
	23.91	70	27	24.7		

$c_p(T)$ for $O_2$ (solid- $\gamma$ ) - Unit of $J K^{-1} mol^{-1}$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
	43.8	45.3	50	46	54.4	46.5

$c_p(T)$ for $O_2$ (liquid) - Unit of $J K^{-1} mol^{-1}$	$T$	$c_p$	$T$	$c_p$
	54.4	55	90.2	56.5

$c_p(T)$ for $O_2$ (vapour) - Unit of $J K^{-1} kg^{-1}$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
	90.2	969.3	125	926.2	190	915.1	270	916.4
	95	941.3	130	924.6	210	914.3	280	917.4
	100	935.2	135	923.1	230	914.3	290	918.5
	105	933.2	140	921.8	235	914.4	300	919.9
	110	931.6	145	920.7	240	914.5		
	115	929.8	150	919.6	250	915.0		
	120	928.0	170	916.7	260	915.6		

## 8.4 Tables of $c_p(T)$ for $\text{CO}_2$

Table 11: *The specific heat (at constant pressure) for  $\text{CO}_2$  from  $T = 0 \text{ K}$  to  $300 \text{ K}$ . Units are  $\text{K}$  for  $T$  and  $\text{cal K}^{-1} \text{ mol}^{-1}$  for  $c_p$  (to be multiplied by  $4.184 \text{ J}$  and divided by  $0.0440098 \text{ kg mol}^{-1}$  to obtain units of  $\text{J K}^{-1} \text{ kg}^{-1}$ ). The first table corresponds to adjust values for the ice (solid) state obtained from Giauque and Egan (1937) and Manzhelii et al. (1971) datasets. The second table corresponds to the gaseous state, with data obtained from Span and Wagner (1996).*

$c_p(T)$  for  $\text{CO}_2$  (ice) - Unit of  $\text{cal K}^{-1} \text{ mol}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
0.0	0.0	36.517	4.185	113.91	10.07
2.112	0.001276	37.988	4.323	119.24	10.27
3.087	0.00407	39.43	4.603	124.58	10.44
3.942	0.00794	43.19	5.195	130.18	10.69
4.995	0.01625	47.62	5.794	135.74	10.88
5.914	0.02755	52.11	6.326	141.14	11.08
7.130	0.04995	56.17	6.765	146.48	11.27
8.121	0.07487	60.86	7.269	151.67	11.45
9.214	0.1120	61.26	7.302	156.72	11.64
9.839	0.1357	66.24	7.707	162.00	11.84
11.090	0.2032	71.22	8.047	167.62	12.07
12.006	0.2665	76.47	8.370	173.36	12.32
13.250	0.3650	81.94	8.703	179.12	12.57
14.215	0.4521	87.45	8.984	184.58	12.82
16.457	0.7163	92.71	9.189	189.78	13.05
17.521	0.8570	97.93	9.421	194.525	13.26
18.505	0.9985	103.26	9.671		
19.548	1.1590	108.56	9.893		

$c_p(T)$  for  $\text{CO}_2$  (vapour) - Unit of  $\text{cal K}^{-1} \text{ mol}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
194.525	8.096	230	8.285	270	8.661
200	8.106	240	8.372	280	8.762
210	8.146	250	8.464	290	8.874
220	8.209	260	8.564	300	8.964

## 8.5 Tables of $c_p(T)$ for $\text{H}_2\text{O}$

Table 12: *The specific heat (at constant pressure) for the solid (ice-Ih) state of  $\text{H}_2\text{O}$  from  $T = 0 \text{ K}$  to  $273 \text{ K}$ . Data were obtained from Table 13 of Feistel and Wagner (2006) for  $10 \text{ K}$ ,  $20 \text{ K}$  and above  $30 \text{ K}$ . Other data below  $28 \text{ K}$  are from interpolated and smoothed measured values given in Table I of Flubacher et al. (1960), according to the top of Fig. 17. Units are  $\text{K}$  for  $T$  and  $\text{J K}^{-1} \text{ kg}^{-1}$  for  $c_p$  (with  $4.184 \text{ J cal}^{-1}$  and a molar mass of  $0.01801528 \text{ kg mol}^{-1}$  to transform values of Flubacher et al. (1960) into unit of  $\text{J K}^{-1} \text{ kg}^{-1}$ ). The value at  $273.15 \text{ K}$  (2096.70) is linearly extrapolated from those at  $270$  and  $273 \text{ K}$ .*

$c_p(T)$  for  $\text{H}_2\text{O}$  (ice-Ih) - Unit of  $\text{J K}^{-1} \text{ kg}^{-1}$

$T$	$c_p$	$T$	$c_p$	$T$	$c_p$
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)

## 9 The absolute dry-air entropies and enthalpies

### 9.1 The absolute dry-air entropies

It may seem surprising at first sight that the dry-air entropies  $s_{d0}$  in the second line of the Table 1 are larger than each of the standard entropies  $s_0(T_0, p_0)$  of  $N_2$ ,  $O_2$ , Argon, and  $CO_2$  in the last four lines of this Table.

The explanation for this feature is the need to compute and take into account the impacts on entropy of the partial pressure of these gases, with a sum  $p_{N_2} + p_{O_2} + p_{CO_2} + p_{Ar}$  which must be equal to the standard pressure  $p_0$ . To do so, it is needed to define the standard specific entropy of dry air ( $s_{d0}$ ) in terms of its molar entropy ( $S_{d0}$ ) as two sums over the standard entropies computed at  $T_0$  and  $p_0$  for the four ( $j = 1, 2, 3, 4$ ) main dry-air components ( $N_2$ ,  $O_2$ , Argon and  $CO_2$ ), leading to

$$s_{d0} = \frac{S_{d0}}{M_d} = \sum_j \left( \frac{S_{j0}}{M_j} \right) q_j - \left( \frac{R_*}{M_d} \right) \sum_j [x_j \ln(x_j)] . \quad (155)$$

The first sum is the usual weighted sum of the specific values with the specific contents  $q_j = x_j(M_j/M_d)$ , whereas the second sum represents the impact of the partial pressures expressed in terms of the molar masses  $M_j$  recalled in the Table 25, the molar concentrations  $x_j$  recalled in the Table 26 and the dry air value  $M_d = \sum_j M_j x_j$ . This impact of partial pressures is called the “entropy of mixing” and corresponds to the last term in the equation

$$s_v = s_{v0}(T_0, p_0) + c_{pv} \ln\left(\frac{T}{T_0}\right) - R_v \ln\left(\frac{p_v}{p_0}\right)$$

written for the water vapour, but also for  $N_2$ ,  $O_2$ , Argon and  $CO_2$ .

As an example, the dry-air value  $s_{d0}$  of Lemmon et al. (2000, LEM00) in the Table 1 is the sum of the contributions for  $N_2$ ,  $O_2$  and Argon (without  $CO_2$ ), according to:

$$6776.6 \approx 6748.7 \times 0.7557 + 6330.8 \times 0.2316 + 3830.5 \times 0.0127 \\ - \left( \frac{8.31451}{0.0289586} \right) [0.7812 \times \ln(0.7812) + 0.2096 \times \ln(0.2096) + 0.0092 \times \ln(0.0092)] , \quad (156)$$

with the dry-air value  $6776.6 \text{ J K}^{-1} \text{ kg}^{-1}$  indeed larger than both 6748.7 for  $N_2$ , 6330.8 for  $O_2$  and 6614.9 according to the first line of (156).

More precisely, the M25 statistical and calorimetric dry-air entropies  $s_{d0}$  listed in the last two columns of the Table 1 has been computed with Eq. (155) and for the four gases  $N_2$ ,  $O_2$ , Argon and 400 ppmv of  $CO_2$ , the “Picard et al. (2008) rescaled” concentrations of dry-air components (see the last line of the Table 26) and the IUPAC-2017 (Meija, 2017) molar masses (see the last line of the Table 25). These datasets are recalled in the Table 13, together with the M25 statistical and calorimetric uncertainties in  $s_j$ .

Since the dry-air molar mass is  $M_d = \sum_j M_j x_j$  and because all  $\Delta x_j \approx \Delta x = 5 \cdot 10^{-6}$  are assumed to be the same for all gases, the uncertainty on  $M_d$  is:

$$\Delta M_d \approx \left( \sum_{j=1}^4 M_j \right) \Delta x + \sum_{j=1}^4 (x_j \Delta M_j) \approx (7 + 12) \cdot 10^{-4} \approx 0.002 \text{ g/mol} , \quad (157)$$

thus leading to  $M_d \approx 28.965 \pm 0.002 \text{ J K}^{-1} \text{ kg}^{-1}$  and  $\Delta M_d/M_d \approx 6.9 \cdot 10^{-5}$ .

Table 13: *The molar concentrations  $x_j$  (Picard et al., 2008, rescaled) from the Table 26, the specific contents  $q_j = x_j (M_j/M_d)$ , the molar masses  $M_j$  (Meija, 2017, IUPAC-2017) from the Table 25 and uncertainties in specific standard entropy from the Table 1, listed for the four main dry-air components ( $j = 1, 2, 3, 4$  for  $N_2$ ,  $O_2$ ,  $CO_2$  and Argon). The last lines is for the dry-air value  $M_d = \sum_j M_j x_j$ . Values in parentheses represent the last-digits uncertainties.*

	$x_j$ (mol/mol)	$q_j$ (kg/kg)	$M_j$ (g/mol)	$\Delta(s_j)_{400ppmv}$ M25-stat	$\Delta(s_j)_{400ppmv}$ M25-calor
$N_2$	0.780 878(5)	0.755 225(5)	28.013 71(63)	0.34	19
$O_2$	0.209 390(5)	0.231 319(5)	31.998 80(54)	0.33	37
Argon	0.009 332(5)	0.012 848(5)	39.878 00(6300)	0.30	2.5
$CO_2$	0.000 400(5)	0.000 608(5)	44.009 40(130)	0.24	12
Dry air	1.000 000	1.000 000	28.965 30(200)	0.49	23

Table 14: **First line:** *The same dry-air standard entropies  $s_{d0}$  shown in the Table 14 and computed at  $T_0 = 273.15$  K,  $p_0 = 1000$  hPa and for 400 ppmv of  $CO_2$ .* **Second line:** *The same values for  $s_{d0}$  but for 440 ppmv of  $CO_2$ . In the last column  $\Delta = (M25-Calor) - (M25-Stat)$  are the absolute and relative differences between the calorimetric method compared to the more accurate statistical-physics formulation.*

	HH87	LEM00	M11	SS20	M25-Stat	M25-Calor ( $\Delta$ )
Dry air ( $s_{d0}$ ) <sub>400ppmv</sub>	6775	6776.6	6775	6783	$6776.34 \pm 0.49$	$6783.04 \pm 23$ (+6.6 or 0.10 %)
Dry air ( $s_{d0}$ ) <sub>440ppmv</sub>					$6776.31 \pm 0.49$	$6783.01 \pm 23$ (+6.6 or 0.10 %)

The uncertainty of  $s_{d0}$  can then be computed from the differential of (155), leading to

$$\Delta s_{d0} = \Delta \left( \frac{s_{d0}}{M_d} \right) \approx \left\{ \sum_{j=1}^4 q_j \Delta \left( \frac{S_{j0}}{M_j} \right) \right\} + \left\{ \sum_{j=1}^4 \left( \frac{S_{j0}}{M_j} \right) \right\} \Delta q + \left( \frac{R_*}{M_d} \right) \left\{ \sum_{j=1}^4 |1 + \ln(x_j)| \right\} \Delta x + \left\{ \sum_{j=1}^4 |x_j \ln(x_j)| \right\} \Delta \left( \frac{R_*}{M_d} \right). \quad (158)$$

The uncertainties of M25-statistical and M25-calorimetric dry-air entropies  $s_{d0}$  given in the last two columns of the Table 1 can be computed with (158) and the molar concentrations  $x_j$ 's recalled in the Table 13. The other numerical values are  $\Delta q = \Delta x = 5 \cdot 10^{-6}$ ,  $\Delta R_*/R_* \approx 3.6 \cdot 10^{-5}$ ,  $\Delta(R_*/M_d) = (R_*/M_d)(\Delta R_*/R_* + \Delta M_d/M_d) \approx 0.03 \text{ J K}^{-1} \text{ kg}^{-1}$ ,  $R_*/M_d \approx 287.050 \pm 0.008 \text{ J K}^{-1} \text{ kg}^{-1}$ ,  $\sum_j |1 + \ln(x_j)| \approx 11.8$ ,  $\sum_j |x_j \ln(x_j)| \approx 0.567$  and  $\sum_j (S_{j0}/M_j) \approx 21700 \text{ J K}^{-1} \text{ kg}^{-1}$  leading to

$$\Delta s_{d0} \approx \left\{ \sum_{j=1}^4 q_j \Delta \left( \frac{S_{j0}}{M_j} \right) \right\} + 0.109 + 0.017 + 0.0008 \approx 0.13 + \left\{ \sum_{j=1}^4 q_j \Delta \left( \frac{S_{j0}}{M_j} \right) \right\}. \quad (159)$$

The last sum must be evaluated differently with the uncertainties recalled in the last columns of Table 13 for the M25-stat and M25-calor formulations, leading to

$$(\Delta s_{d0})_{Stat} \approx 0.49 \text{ J K}^{-1} \text{ kg}^{-1}, \quad (160)$$

$$(\Delta s_{d0})_{Calor} \approx 23 \text{ J K}^{-1} \text{ kg}^{-1}, \quad (161)$$



which are the uncertainties of dry-air entropies in the last lines of the Table 13, where the small term 0.13 in (159) only impact the (smaller) uncertainty of the statistical value.

I recall in the Table 14 the absolute dry-air entropy show in the Table 1, but with more digits for the dry-air entropies and with the two sets of concentrations for both 400 ppmv and 440 ppmv of CO<sub>2</sub>.

## 9.2 The absolute dry-air enthalpies

In about the same way as the dry-air entropy is computed via the weighted sum (155), including the entropy of mixing terms, the dry-air enthalpy can be computed via the weighted sum

$$h_{d0} = \frac{H_{d0}}{M_d} = \sum_j \left( \frac{H_{j0}}{M_j} \right) q_j, \quad (162)$$

with the sum over the standard enthalpies computed at  $T_0$  (and  $p_0$ ) for the same four ( $j = 1, 2, 3, 4$ ) main dry-air components (N<sub>2</sub>, O<sub>2</sub>, Argon and CO<sub>2</sub>), but without “enthalpy of mixing” terms.

The dry-air enthalpy is computed from the enthalpies of N<sub>2</sub>, O<sub>2</sub>, Argon and 400 ppmv of CO<sub>2</sub>, with the 2015 rescaled molar concentrations of Picard et al. (2008) given in the last line of the Table 26

$$(0.780\,878, 0.209\,390, 0.009\,332 \text{ and } 0.000\,400 \text{ mol mol}^{-1})$$

with the corresponding 2015 mass concentrations

$$(0.755\,225, 0.231\,319, 0.012\,848 \text{ and } 0.000\,608 \text{ kg kg}^{-1})$$

for N<sub>2</sub>, O<sub>2</sub>, Argon and CO<sub>2</sub>, respectively.

Table 15: *The calorimetric values of the vapour thermal enthalpies (in units of kJ kg<sup>-1</sup>) computed with the formula (8) for N<sub>2</sub>, O<sub>2</sub>, Argon, CO<sub>2</sub> and H<sub>2</sub>O. The first line were computed by Marquet (2015a) at 0°C, with the dry air made of about 0.79 % of N<sub>2</sub> and 0.21 % O<sub>2</sub> gases. The second and third lines are for new, more accurate computations at both 0°C and 25°C including Argon and CO<sub>2</sub> gases, with the dry-air value computed with the two sets of molar concentrations (0.780 878, 0.209 390, 0.009 332 and 0.000 400 mol mol<sup>-1</sup>) and (0.780 847, 0.209 381, 0.009 332 and 0.000 440 mol mol<sup>-1</sup>) for N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub>, respectively, with moreover the accuracy information included for all gases.*

(Standard Enthalpies)	N <sub>2</sub> (vap)	O <sub>2</sub> (vap)	Ar(vap)	CO <sub>2</sub> (vap)	Dry-air(vap)
Marquet (2015a) (0°C):	532.4	525.6			530
Marquet-2025 (0°C, 400 ppmv):	530.9 ± 1.3	524.0 ± 1.5	335.3 ± 1.7	787.4 ± 1.5	526.94 ± 1.3
Marquet-2025 (25°C, 400 ppmv):	556.9 ± 1.4	546.9 ± 1.5	348.4 ± 1.8	808.4 ± 1.6	552.06 ± 1.4
Marquet-2025 (0°C, 440 ppmv):	530.9 ± 1.3	524.0 ± 1.5	335.3 ± 1.7	787.4 ± 1.5	526.96 ± 1.3
Marquet-2025 (25°C, 440 ppmv):	556.9 ± 1.4	546.9 ± 1.5	348.4 ± 1.8	808.4 ± 1.6	552.08 ± 1.4

Another computation is made for the future 2030 concentrations of about 440 ppmv of CO<sub>2</sub>, with the rescaled molar concentrations

$$(0.780\,847, 0.209\,381, 0.009\,332 \text{ and } 0.000\,440 \text{ mol mol}^{-1})$$

and the corresponding mass concentrations

$$(0.755\,179, 0.231\,305, 0.012\,847 \text{ and } 0.000\,669 \text{ kg kg}^{-1})$$

for N<sub>2</sub>, O<sub>2</sub>, Argon and CO<sub>2</sub>, respectively.

I show in the Table 15 more detailed computations for the dry-air calorimetric enthalpies than those summarized in the Table 4, with both 400 ppmv and 440 ppmv of CO<sub>2</sub>.

### 9.3 Changes with CO<sub>2</sub> of absolute dry-air entropies and enthalpies

In the same way as the enthalpy and entropy for the moist-air atmosphere and the seawater oceans depend on the concentrations of water species and sea salts, respectively, according to the Tables 14 and 15, the dry-air enthalpy and entropy also depend on the concentration of CO<sub>2</sub>.

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• More precisely, I explain in the Section 11 and in the Figs.27(a)-(c) that the changes in the concentration of CO<sub>2</sub> correspond to two possible processes, due to the fact that the relationship (170) of Glueckauf (1951), Jones (1978) and Keeling (1988) may not be valid for all location on earth:

- (A) The case where the concentration of CO<sub>2</sub> increases at the expense of the simultaneous and proportional decrease in the concentrations of the other three species, and thus the sum of N<sub>2</sub>+O<sub>2</sub>+Ar ;
  - (B) The case where the molar concentration of CO<sub>2</sub> increases at the expense of the only decrease in that of O<sub>2</sub>, in accordance with the relationship (170) of Glueckauf (1951), Jones (1978) and Keeling (1988).
- 

• The impacts on the dry-air mass  $M_d$  and the dry-air constant  $R_d$  due to the changes in CO<sub>2</sub> concentrations measured at Mauna Loa between 1958 and 2021 are shown in the Fig. 18. In particular, the larger impacts of changes in O<sub>2</sub> at the expense of N<sub>2</sub>+O<sub>2</sub>+Ar (case A) correspond to the values in the Table 16:

Table 16: *Changes in dry-air molar mass and gas constant at Mauna-Loa from 1958 to 2021 (case A).*

	1958	2021	2021 – 1958	seasonal changes
$x_{\text{CO}_2}$ (concentration in CO <sub>2</sub> , ppmv)	315	415	100 (+ 30 %)	±5
$M_d$ (molar mass, g/kg)	28.964 0	28.965 5	+0.001 5 (+ 0.005 %)	±0.000 05
$R_d$ (gas “constant”, J/K/kg)	287.062 0	287.047 3	– 0.015 (– 0.005 %)	±0.000 5

Clearly, both the dry-air molar mass  $M_d$  and the dry-air gas constant  $R_d$  are not constant with time, with similar changes in latitudes (not shown). According to the Figures 18 and the Table 16 it is not possible to use constant values for

$$M_d \approx 28.965 \pm 0.001 \text{ g/mol} \quad \text{and} \quad R_d = R_*/M_d \approx 287.05 \pm 0.01 \text{ J/K/kg}, \quad (163)$$

with more than 3 and 2 decimal digits, respectively, with between 1958 and 2021:

- an increase in  $M_d$  of +0.0015 g/mol, with seasonal changes of ±0.000 05 g/mol;
- a decrease in  $R_d$  of about – 0.015 g/mol, with seasonal changes of ±0.000 5 g/mol.

Note that Jones (1978) evaluated the same order of magnitude for the uncertainty due to seasonal changes: ±0.000 06 g/mol for  $M_d$  and ±0.000 26 J/K/kg for  $R_d$ ,

This means that both  $R_d$  and  $M_d$  should vary with space and time in NWP models and GCMs:  $R_d$  and  $M_d$  cannot remain constant (on average) for more than 20 years (or so) in time, and latitudinal and seasonal variations appear to be non-negligible (especially at high latitudes).

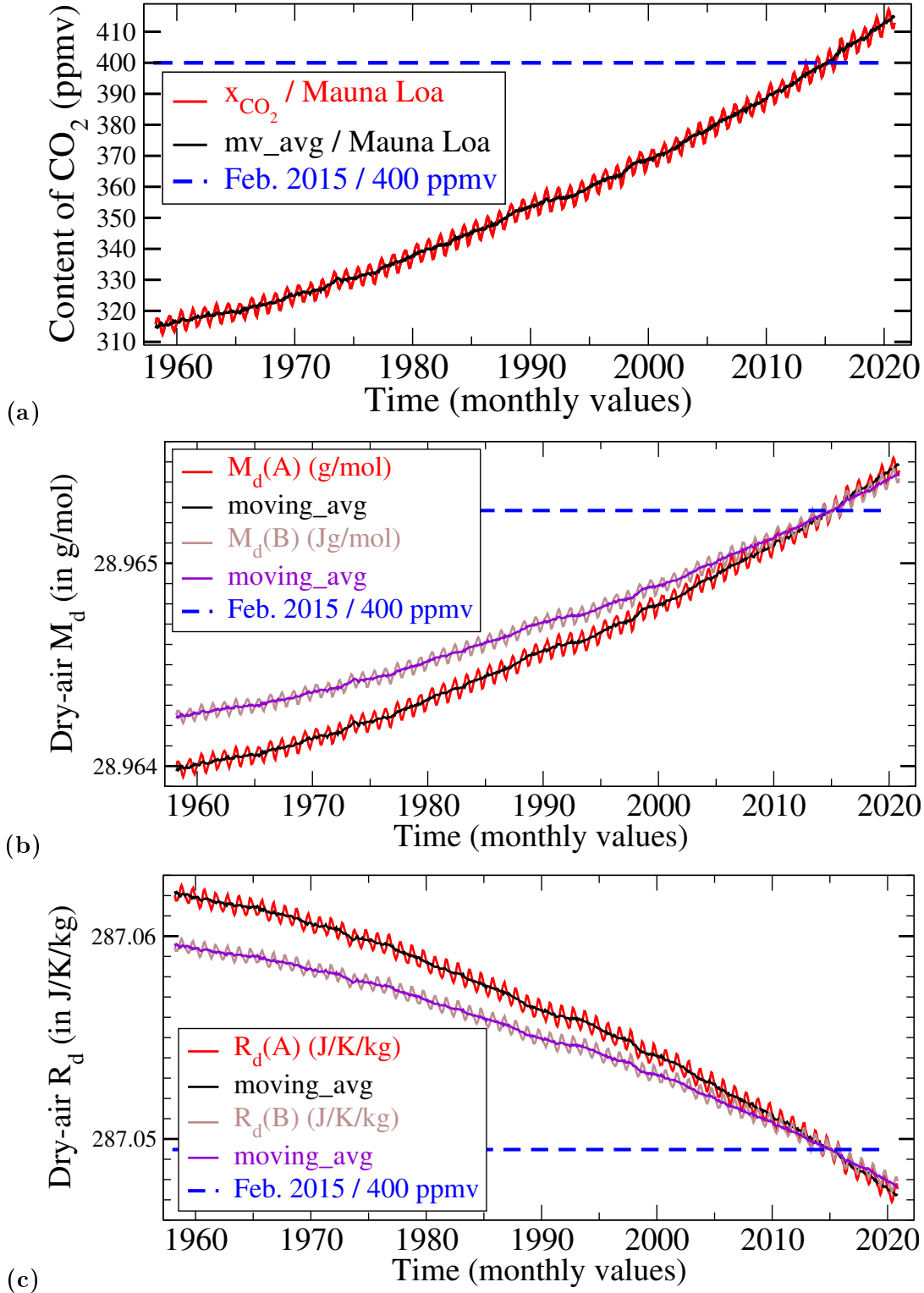


Figure 18: The same examples as those published in Marquet (2021) for the change in dry-air physical properties at Mauna Loa (monthly means and de-seasonalized values from 1958 to 2020), but for the two cases (A) and (B). **(a)**: the variable global concentration in  $\text{CO}_2$  (ppmv); **(b)**: the (variable) dry-air molar mass (g/mol); **(c)**: the (variable) dry-air gas “constant” (J/K/kg). The blue dashed lines represent the February 2015 values for 400 ppmv close to values retained in IAPWS-TEOS10 (Feistel et al., 2010a). These figures correspond to those of Marquet (2021).

Note that, differently, the values retained in IAPWS or TEOS10 (McDougall et al., 2010, Table J.1) are defined with too many digits in the setup of constants made in the subroutine `Constants_0.F90` in the SIA Seawater-Ice-Air software:

$$M_d \approx 28.965\,46 \pm 0.000\,33 \text{ g/mol}$$

corresponding to  $R_d = \frac{R_*}{M_d} \approx 287.048\,41 \pm 0.000\,38 \text{ J/K/kg}$ ,

where  $R_* \approx 8.314\,472 \pm 0.000\,015 \text{ J/K/kg}$ . These (too accurate) values seems to be only valid close to the years from 2017 to 2020.

- 
- The change with  $\text{CO}_2$  in the absolute dry-air entropy at  $0^\circ\text{C}$  is shown in the Fig. 19(a)-(b) and in the Table 17:

Table 17: *Changes in absolute dry-air entropy at  $0^\circ\text{C}$  and 1000 hPa with the  $\text{CO}_2$  concentrations at Mauna-Loa from 1958 to 2021 (case A).*

	1958	2021	2021 – 1958	seasonal changes
$s_{d0}$ (dry-air entropy, $\text{J K}^{-1} \text{ kg}^{-1}$ )	6776.403	6776.333	$-0.070$ ( $-0.001\%$ )	$\pm 0.003$

The Fig. 19(a) and the Table 17 show that both the decrease in dry-air entropy of  $-0.070 \text{ J K}^{-1} \text{ kg}^{-1}$  between 1958 and 2021 and the seasonal changes of  $\pm 0.003 \text{ J K}^{-1} \text{ kg}^{-1}$  are much smaller than the uncertainties in the dry-air entropies  $s_{d0}(T_0, p_0)$  recalled in the Tables 1 and 14:

$$6776.34 \pm 0.49 \text{ J K}^{-1} \text{ kg}^{-1} \text{ for the statistical value ;}$$

$$6783.0 \pm 23 \text{ J K}^{-1} \text{ kg}^{-1} \text{ for the calorimetric value.}$$

This explain why the impact the impact of the concentration in  $\text{CO}_2$  may likely been discarded.

However, this also explains that the arbitrary cancellation of  $s_{d0}(T_0, p_0)$ , as done in atmospheric and oceanographic sciences (in particular in IAPWS and TEOS10 software), cannot be exact and should be able to vary (in time and in place) at least up to about  $\pm 0.05 \text{ J K}^{-1} \text{ kg}^{-1}$ .

The Fig. 19(b) show that, except for the oldest values of dry-air entropy computed from the dataset published by Kelley (1932, in black), all other more recent values (in blue and green) published since 1958 almost superimpose. Even the more uncertain calorimetric values of Gokcen and Reddy (1996, GR96-calor, in red) remain very close to the blue and green values.

- 
- The change with  $\text{CO}_2$  in the dry-air enthalpy is shown in the Fig. 20 and the Table 18:

Table 18: *Changes in dry-air enthalpy at  $0^\circ\text{C}$  with the  $\text{CO}_2$  concentrations at Mauna-Loa from 1958 to 2021 (case A).*

	1958	2021	2021 – 1958	seasonal changes
$h_{d0}$ (dry-air enthalpy, $\text{kJ kg}^{-1}$ )	526.913	526.952	$+0.039$ ( $+0.007\%$ )	$\pm 0.002$

Like for the dry-air entropy, the uncertainty in the calorimetric value of the dry-air enthalpy recalled in the Tables 4 and 15 ( $527.0 \pm 1.3 \text{ kJ kg}^{-1}$ ) show that the impact of the concentration in  $\text{CO}_2$  may likely been discarded (i.e. with a trend of about  $-0.04$  and seasonal variations of about  $\pm 0.002$  with even larger variations close to the north pole).

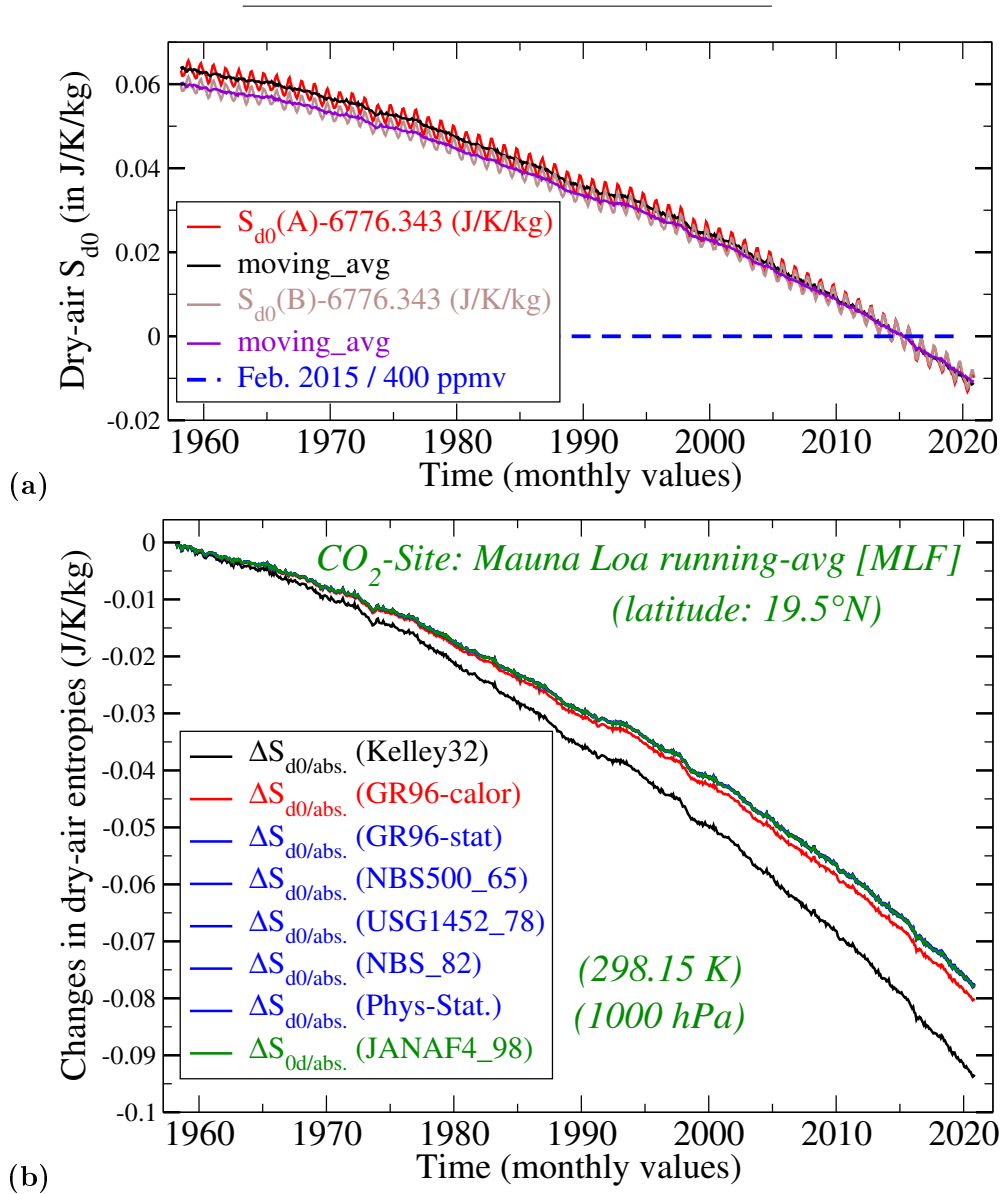


Figure 19: (a) The same as in Fig. 18 but for the change in the reference absolute dry-air entropy ( $s_{d0}$ ) computed for the Mauna Loa dataset (monthly means and de-seasonalized values from 1958 to 2020), with the same two methods (A) and (B) for the impacts of changes in  $CO_2$  concentrations. (b) The changes in  $s_{d0}$  computed for the Mauna Loa dataset for several definitions of absolute reference entropies for  $N_2$ ,  $O_2$ , Argon and  $CO_2$ . The black line is for the entropy values by Kelley (1932); the red line for the calorimetric values by Gokcen and Reddy (1996, GR96-calor); the blue lines for entropy values by Gokcen and Reddy (1996, GR96-statistical), Rossini et al. (1952, NBS500), Wagman et al. (1965, 270-1), Robie et al. (1978, USG1452\_78), Wagman et al. (1982, NBS\_82) and the statistical (Phys-Stat.) values I have computed in 2025; with the last green line for Chase (1998, NIST-JANAF4\_98).

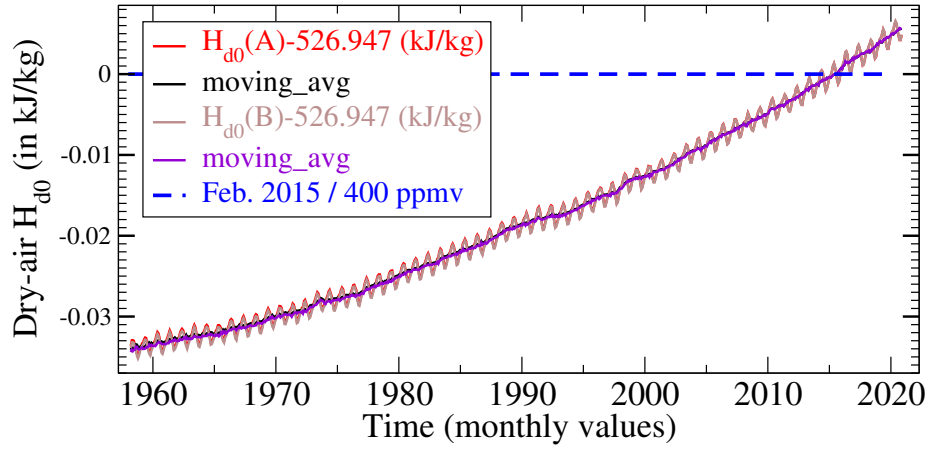


Figure 20: *Change in the dry-air reference enthalpy  $h_d(T_0) - 526.947 \text{ kJ kg}^{-1}$  at  $T_0 = 273.15 \text{ K}$  due to changes in the  $\text{CO}_2$  content and computed at the Mauna Loa observatory, with the monthly means and de-seasonalized values from 1958 to 2020. The value  $526.947 \text{ kJ kg}^{-1}$  was reached in February 2015 for 400 ppmv of  $\text{CO}_2$  content. This figure is similar to those published by Marquet (2021) for the changes in the dry-air molar mass ( $M_d$ ), specific heat at constant pressure ( $c_p$ ) and entropy ( $s_d$ ). The two hypotheses A and B lead to almost similar results.*

## 10 Entropies of seawater cations and anions

### 10.1 Entropies of ions: the first vision of Latimer (1921,1951,1952)

According to Grenthe et al. (2020a, Appendix D, p.1279-1282) “*Latimer (1951)’s method for entropy estimation is based on the additivity principle, where cations give constant contributions to the entropy values, while the contributions of anions depend on the charge of the cation in the solid compounds under consideration.*”

In fact, results published in Latimer (1951) and recalled in Latimer (1952) are based on the first paper of Latimer (1921), who accepted several general results of thermodynamics but made several ad-hoc assumptions.

- He first explained that “*The Third Law of Thermodynamics, by means of which the entropy of a substance may be calculated from specific heats, has made possible the determination of free energy changes in chemical reactions from thermal data alone. However, the difficulties involved in the accurate measurements of specific heats at low temperatures are so great as to make highly desirable some method of calculating the entropy of a substance from other physical quantities.*”
- He then added that “*Many attempts in this direction have been made. A large number of these, including the determination of Nernst’s chemical constants, have been based wholly or in part, upon the quantum theory. Gratifying as have been the results from the specific heat formulas of Einstein, Nernst and Lindemann, and Debye, these formulas do not as yet offer a reliable method of estimating the entropy of solids.*” This is why Latimer (1921) trusted: “*the value of  $S_{298} = 19.70$  for potassium chloride (KCl), as calculated by Lewis and Gibson (1917)*” (at 298 K and in  $\text{cal K}^{-1} \text{mol}^{-1}$ , with  $4.184 \text{ cal J}^{-1}$  and thus  $S_{298} = 82.43 \text{ J K}^{-1} \text{mol}^{-1}$ , which is close to the modern value of  $82.55 \text{ J K}^{-1} \text{mol}^{-1}$  given in Chase, 1998).
- Then Latimer (1921) also trusted the Sackur (1911, 1913a,b) and Tetrode (1912a,b) equation “*for the entropy of a perfect monoatomic gas*” written as  $S = (3/2)R \ln(M) + (5/2)R \ln(T) - R \ln(P) + S_0$  in terms of the molar mass, absolute temperature and pressure, where  $S_0$  is “*a constant independent of the nature of the substance,*” namely like in  $S_{\text{trans}}(T, p, M)$  given by (35) with  $S_0 = R (5/2 + K_{\text{ST}})$  and  $K_{\text{ST}} \approx 18.22285 \text{ J K}^{-1} \text{mol}^{-1}$  given by (36).
- Moreover, Latimer (1921) assumed that “*From a critical study of the data now at hand it seems possible to go further and state that the entropy of large classes of substances at a given temperature and pressure approaches a limiting value which is determined solely by the mass and by the number of degrees of freedom of the molecules composing the substance.*”
- This is why Latimer (1921) assumed that “*at a given temperature the entropy of an atom in a solid depends both upon the mass of the atom and the constraint by which it is held. However, a postulate will be made, namely, that there is a limiting value of the constraint, below which the effect upon the entropy is negligible*” (...) leading to the main hypothesis that “*since an atom in a solid has three degrees of freedom of motion, we will write for the entropy of each element*”  $S_{298} = (3/2)R \ln(M) + S'_0$  “*where  $S'_0$  is the same for all elements in which the condition postulated in regard to the constraints is fulfilled.*”
- It was moreover assumed as “*a second postulate (...) that the entropy of a compound is the sum of the entropies of the elements in the compound as given by Equation*” for  $S_{298}$  above. This allowed Latimer (1921) to write for the compound KCl, with K and Cl of molar mass 35.45 and 39.1, respectively:  $19.70 = (3/2)R \ln(35.45) + (3/2)R \ln(39.1) + 2S'_0$ , leading to  $S'_0 = -0.94 \text{ cal K}^{-1} \text{mol}^{-1}$  and thus to the final formula

$$S_{298} = \frac{3}{2} R \ln(M) - 0.94 \text{ cal K}^{-1} \text{mol}^{-1} . \quad (164)$$

Figure 21: Figs. 7 and 8 of Latimer (1952, p.360 and 366). See comments in the main text.

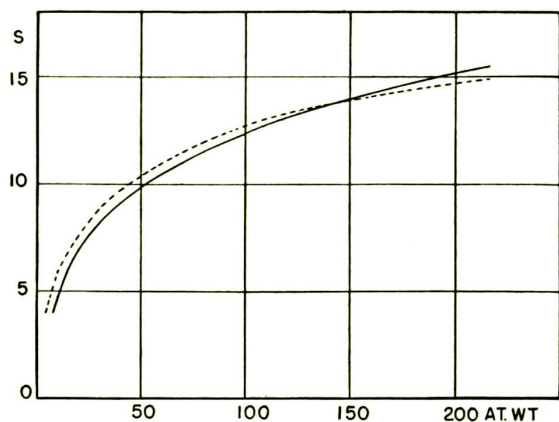


FIG. 7. Entropies of elements in solid compounds as a function of atomic weight.

(a)

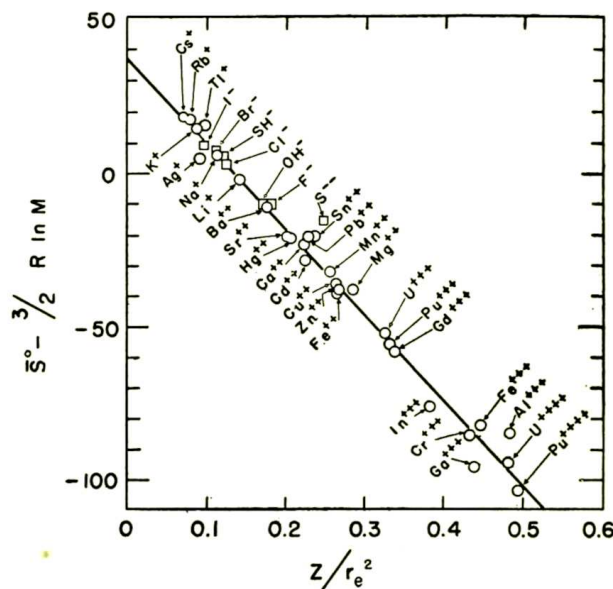


FIG. 8. Corrected entropy in aqueous solution versus  $Z/r_e^2$  for various ions.

(b)

- It is however explained in Latimer (1952, p.359) that this relationship is modified “to increase slightly the entropies of the heavier elements and increase slightly the entropies of the lighter elements (...) and by their use the entropies of solid salts may be estimated with somewhat greater accuracy.” An explanation can be found in Latimer (1951), where it is explained (p.1480) that “For simple salts, such as the alkali halides, the entropy may be estimated with fair accuracy as the sum of the entropies of the constituent elements as given by this equation (164). However, the forces in solid salts are largely ionic attractions, and the effect of the ionic radii upon the force constants and the vibrational frequencies is appreciable: in general the entropy of a large ion is increased and the entropy of a small ion is decreased over the values given by equation (164). Since there is enough correlation between size and weight, the full line in Fig. 1 has been drawn to increase slightly the entropies of the heavier elements and decrease slightly the entropies of the lighter elements.” The original relationship is plotted in dashed line in the Fig. 1 (p.1480) of Latimer (1951) or Fig. 7 (p.360) of Latimer (1952), reproduced here in the Fig. 21(a), whereas the modified formulation is plotted in solid line. Comparisons of these original and modified numerical values are shown in the Table 19.
- Latimer (1951) also explained that:  
 “In line with the argument just presented, it may be expected that the entropy of an ionic solid will also depend upon the magnitude of the ionic charges. To illustrate this effect, the apparent contribution of the chloride ion in combination with +1, +2 and +3 ions has been calculated (Table II in the 1951 paper and Table 88 in the 1952 book) by subtracting from the experimental entropy of the salt, the entropy of the positive ion as given in Table I (in the 1951 paper, partly recalled in the Table 19). The agreement of the calculated Cl values for each type of salt is remarkably good, and the average values 10.0, 8.1 and 6.9 for the positive ions  $M^+$ ,  $M^{2+}$  and  $M^{3+}$  decrease with increasing positive charge as is to be expected.  
 The value for Cl from Table I (see the line (b) in the Table 19) is 8.8 and it may be seen from Table II (88) that this is a fair approximation, but that much better agreement is obtained if the average values for the salt types  $M^+$ ,  $M^{2+}$  and  $M^{3+}$  are employed. An examination of the data for a large number of negative ions shows that a similar charge effect exists in all cases.”
- Latimer (1951) added that: “It is proposed, then, to arbitrarily assign all the variation with charge



Table 19: Values of “Atomic weight” (in fact the molar mass  $M$  in  $\text{g mol}^{-1}$ ) and entropies (in  $\text{cal K}^{-1} \text{mol}^{-1}$ , with  $4.184 \text{ J cal}^{-1}$  and  $R = 2.981 \text{ cal K}^{-1} \text{mol}^{-1}$ ) for several sea-salt elements in solid compounds at 298 K (cations and anions), from:

(a) the original relationship  $S_{298} = (3/2) R \ln(M) - 0.94$  leading to the values partly listed in the Table I (p. 820) of Latimer (1921, L21), and computed by me if not available (into parentheses), both corresponding to the dashed line in the Fig. 1 (p.1480) of Latimer (1951) and Fig. 7 (p.360) of Latimer (1952, L52), reproduced here in the Fig. 21-a;

(b) the updated and modified version corresponding to the solid curve of Fig. 7 (p.360), listed in the Table 87 (p.361) of Latimer (1952, L52) and still in the more recent Table D.1 (p.1281) of Grenthe et al. (2020a, for the cations Na, Mg, K, Ca and Sr).

(c) The difference  $\Delta(\text{b})-(\text{a})$  shows the modifications made to the original relationship.

	F <sup>(-)</sup>	Na <sup>(+)</sup>	Mg <sup>(2+)</sup>	Cl <sup>(-)</sup>	K <sup>(+)</sup>	Ca <sup>(2+)</sup>	Br <sup>(-)</sup>	Sr <sup>(2+)</sup>
$M$	19.0	22.99	24.31	35.45	39.1	40.08	79.9	87.62
(a): $S_{298}$ L21	(7.8)	(8.4)	(8.6)	9.7	10.0	(10.0)	12.1	(12.4)
(b): $S_{298}$ L52	6.9	7.5	7.6	8.8	9.2	9.3	11.7	12.0
(c): $\Delta(\text{b})-(\text{a})$	0.9	0.9	1.0	0.9	0.8	0.7	0.4	0.4

to the negative ion and to prepare from the experimental entropies a table for the negative ions in which the value is modified by-the charge on the positive ion. The entropy of any salt may then be estimated by combining the values in this summary for negative ions, Table V, with the values in Table I for the positive ions.” This Table V of Latimer (1951) is the same as the Table 90 of Latimer (1952) and is recalled in the the right part of the Fig. 22. Moreover: “In addition to the simple negative ions, the summary includes values for the oxygen complex” (in particular for the sea-salts ions  $\text{CO}_3^{2-}$  and  $\text{SO}_4^{2-}$ ).

- Additional comments of Latimer (1951) are: “It is not possible to complete Table V from experimental data. For example, there are no data on fluorides (...) It will be noted that in some cases the values for the +4 ions are slightly larger than those for the +3 ions. There are sufficient data to establish this as a real effect, and it is doubtless due to the anion repulsion which exists with four large negative ions about a small positive ion. This repulsion tends to weaken the bond energies and increase the entropy.”

Figure 22: Tables 88 to 90 of Latimer (1952, p.362-363), corresponding to the Table II, III and IV of Latimer (1951, p.1481-1482). See comments in the main text.

TABLE 88

CONTRIBUTION OF Cl TO THE ENTROPY OF MCl, MCl<sub>2</sub> AND MCl<sub>3</sub> COMPOUNDS.

(Calculated by subtracting entropy of positive ion, Table 87, from the entropy of the salt.)

Salt	Entropy of Salt	Entropy of Cl	Salt	Entropy of Salt	Entropy of Cl	Salt	Entropy of Salt	Entropy of Cl
NaCl	17.3	9.9	PbCl <sub>2</sub>	32.6	8.5	CrCl <sub>3</sub>	31.0	6.7
KCl	19.75	10.6	ZnCl <sub>2</sub>	25.9	7.6	VCl <sub>3</sub>	31.3	7.1
TlCl	24.8	9.3	CdCl <sub>2</sub>	28.3	7.7	Aver.		6.9
AgCl	22.97	10.2	Hg <sub>2</sub> Cl <sub>2</sub>	46.8	8.0			
	Aver.	10.0	NiCl <sub>2</sub>	25.6	7.8			
			CoCl <sub>2</sub>	25.4	7.5			
			FeCl <sub>2</sub>	28.6	9.0			
			MnCl <sub>2</sub>	28.0	8.8			
			CrCl <sub>2</sub>	27.4	8.7			
			VCl <sub>2</sub>	23.2	6.6			
			Aver.		8.1			

TABLE 89

CONTRIBUTION OF SULFATE TO THE ENTROPY OF M<sub>2</sub>SO<sub>4</sub>, MSO<sub>4</sub>, AND M<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> TYPE OF COMPOUND

(Calculated by subtracting entropy of positive ion, Table 87, from the entropy of the salt.)

Salt	Entropy of Salt	Entropy of SO <sub>4</sub>	Salt	Entropy of Salt	Entropy of SO <sub>4</sub>	Salt	Entropy of Salt	Entropy of SO <sub>4</sub>
Ag <sub>2</sub> SO <sub>4</sub>	47.8	22.2	CuSO <sub>4</sub>	27.1	16.3	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	57.2	13.7
K <sub>2</sub> SO <sub>4</sub>	42.0	23.6	MnSO <sub>4</sub>	26.8	16.5	Aver.		13.7
Na <sub>2</sub> SO <sub>4</sub>	35.7	20.7	BaSO <sub>4</sub>	31.6	17.8			
	Aver.	22.0	CaSO <sub>4</sub>	25.6	16.3			
			PbSO <sub>4</sub>	35.2	19.7			
			ZnSO <sub>4</sub>	29.8	18.9			
			CdSO <sub>4</sub>	32.8	19.9			
			MgSO <sub>4</sub>	21.9	14.4			
			FeSO <sub>4</sub>	25.7	15.3			
			Hg <sub>2</sub> SO <sub>4</sub>	48.0	17.2			
			Aver.		17.2			

TABLE 90

SUMMARY OF ENTROPY CONTRIBUTION OF NEGATIVE IONS IN SOLID COMPOUNDS AT 298° K.

(Values in cal./deg. per mole.)

Negative Ion	Charge on Positive Ion			
	+1	+2	+3	+4
F <sup>-</sup>	(5.5)	4.7	(4.0)	5.0
Cl <sup>-</sup>	10.0	8.1	6.9	8.1
Br <sup>-</sup>	13.0	10.9	(9.)	(10.)
I <sup>-</sup>	14.6	13.6	12.5	13.0
CN <sup>-</sup>	7.2	(6.)		
OH <sup>-</sup>	(5.0)	4.5	3.0	
ClO <sup>-</sup>	(14.)	(10.)	(8.)	
ClO <sub>2</sub> <sup>-</sup>	19.2	(17.)	(14.)	
ClO <sub>3</sub> <sup>-</sup>	24.9	(20.)		
ClO <sub>4</sub> <sup>-</sup>	26.0	(22.)		
BrO <sub>3</sub> <sup>-</sup>	26.5	22.9	(19.)	
IO <sub>3</sub> <sup>-</sup>	25.5	(22.)		
H <sub>4</sub> IO <sub>6</sub> <sup>-</sup>	33.9	(30.)		
NO <sub>2</sub> <sup>-</sup>	17.8	(15.)		
NO <sub>3</sub> <sup>-</sup>	21.7	17.7	(15.)	(14.)
VO <sub>3</sub> <sup>-</sup>	20.0	(18.)		
MnO <sub>4</sub> <sup>-</sup>	31.8	(28.)		
O <sup>-</sup>	2.4	0.5	0.5	1.0
S <sup>-</sup>	8.2	5.0	1.3	2.5
Se <sup>-</sup>	(16.)	11.4	(8.)	
Te <sup>-</sup>	(16.5)	12.1	(9.)	
CO <sub>3</sub> <sup>-</sup>	15.2	11.4	(8.)	
SO <sub>3</sub> <sup>-</sup>	(19.)	14.9	(11.)	
C <sub>2</sub> O <sub>4</sub> <sup>-</sup>	(22.)	17.7	(14.)	
SO <sub>4</sub> <sup>-</sup>	22.	17.2	13.7	(12.)
CrO <sub>4</sub> <sup>-</sup>	26.2	(21.)		
SiO <sub>4</sub> <sup>-</sup>	(19.)	13.8	(9.)	7.9
SiO <sub>3</sub> <sup>-</sup>	16.8	10.5	(7.)	
PO <sub>4</sub> <sup>-</sup>	(24.)	17.0	(12.)	
HCO <sub>3</sub> <sup>-</sup>	17.4	(13.)	(10.)	
H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	22.8	(18.)		
H <sub>2</sub> ASO <sub>4</sub> <sup>-</sup>	25.1	(21.)		

## 10.2 Entropies of ions: Latimer (1926)

Latimer (1921)'s earlier study of the entropy of anions and cations in aqueous solution was followed by a series of other studies, again by Latimer, but with different paradigms.

First Born (1920, p.46-47) imagined “*the  $z$ -valent ion as a positively or negatively charged sphere of charge “ $z e$ ” and radius “ $r_i$ ” (... leading to ...) the heat of hydration per mole of ions  $W \propto (1 - 1/\epsilon) (e^2 z^2)/(2 r_i)$  (...) where “ $\epsilon$ ” is the dielectric constant.*”

Latimer (1926, p.1234) started with the same result of Born (1920) for the “*energy of solution given by the expression,*” but rewritten as the equality  $\Delta E = (1 - 1/D) (e^2)/(2 r_i)$  for ions of charge “ $e$ ” (with thus “ $z$ ” included in “ $e$ ”).

Latimer (1926, p.1235) then considered that, since both the energy of solution  $\Delta E$  and free energy of solution  $\Delta F = \Delta E - T \Delta S$  are known, “*in order to complete our calculation of  $\Delta E$  we must know  $\Delta S$ , the entropy change. For this calculation the difficulty exists that in general we have no values for the absolute entropies of ions in solutions. (...) The simple calculation of the sum of the entropies of the ions of a salt in solution shows that these values are less than the corresponding values from the Sackur equation for the ions as gases by a quantity which is roughly proportional to the heats of solution of the ions.*”

As a summary, Latimer (1926, p.1239) computed “*Approximate values for the entropies of ions in aqueous solution*” given (p.1235) by

$$S_{1\text{ mol}} = \frac{3}{2} R \ln(M) - 0.014 \times \Delta E + 25.7 \text{ cal K}^{-1} \text{ mol}^{-1} \quad (165)$$

$$\text{(and thus (?) with } S_{1\text{ mol}} = \frac{3}{2} R \ln(M) - 0.014 \times \left(1 - \frac{1}{D}\right) \frac{e^2 z^2}{2 r_i} + 25.7 \text{ cal K}^{-1} \text{ mol}^{-1}) \quad (166)$$

where “*approximate value of the proportionality factor has been chosen from a large number of different salts.*” This relationship is at the basis of the (nearly) linear law tested in the Figs. 8 (p.366) of Latimer (1952, recalled in the Fig. 21-(b) above) for  $S_{1\text{ mol}} - (3/2) \ln(M)$  plotted against the Born (1920) value  $\Delta E \propto z^2/r_i$ , where however the  $x$ -axis is  $z/r_e$  instead (without explanation) with  $r_e = r + 2$  for cations and  $r_e = r + 1$  for anions (see the next paper of Powell and Latimer, 1951).

In a next paper, and using another approach, Latimer and Buffington (1926) explained that “*A knowledge of the values of the entropies of aqueous ions would place at our command a powerful tool for the direct solution of a large number of thermodynamical problems, many of which otherwise are open only to the most roundabout methods of attack. The treatment of these fundamental entropies has long been deferred by workers in the field of thermodynamics, in part because of the large discrepancies existing in the experimental reaction heats that are involved in their calculation, and in part because of the general lack of information in regard to the entropies of compounds. It would seem, however, that a profitable start may now be made, using as a guide the approximate proportionality pointed out by Latimer (1926) between the entropy of solution and the heat of solution of gaseous ions. It is the purpose of this paper to investigate this relation and to give from a survey of existing data a table of values for the entropies of the more important ions.*”

As an example, Latimer and Buffington (1926) explained that “*The sum of the entropies of  $H^+$  and  $Cl^-$  is equal to the entropy of hydrogen chloride ( $HCl$ ) plus the the entropy of solution of hydrogen chloride. This latter quantity is obtained from the relation  $\Delta S = (\Delta H - \Delta F)/T$ , where  $\Delta H$  is the heat of solution of hydrogen chloride in an infinitely dilute solution,  $\Delta F$  is the free energy of solution at a concentration of hypothetical one molal hydrogen and chloride ions, and  $T$  is the absolute temperature.*”

In the Tables III (p.2299), IV (p.2300) and V (p.2305) Latimer and Buffington (1926) computed the “*Relative entropies of aqueous ions at 25° C*” defined with the hypothesis of zero relative entropy for

the cation  $H^+$  (thus with  $S_{H^+} = 0$ ), or equivalently and more precisely corresponding to the “*Entropy changes in the replacement of  $H^+$  by other ions at 25° C*” and computed by the sum and difference “ $(S_{M^{n+}}) - n(S_{H^+})$ ” for the cations  $M^{n+}$  and “ $(S_{M^{n-}}) + n(S_{H^+})$ ” for the anions  $M^{n-}$ .

The corresponding “relative entropies of ions” of Latimer and Buffington (1926, with  $S_{H^+} = 0$ ) listed in the Table 20 are very different from the previous values computed in Latimer (1921) and listed in the previous Table 19: there was clearly a change of paradigm.

The “relative entropies” in the first two lines of the Table 20 published in Latimer and Buffington (1926) suffered from a lack of precision, but those in (a) published shortly afterwards in Latimer et al. (1938) were already in agreement with the values in (b) listed in Lewis and Randall (1961) and retained in Millero and Leung (1976) and Millero (1983), and also with those available in the more recent Tables in (c). Note that the other “relative entropies” for the missing sea salts  $B(OH)_4^-$ ,  $HCO_3^-$ ,  $B(OH)_3^{aq}$  and  $CO_2^{aq}$  in other papers and books are listed in the next Table 22, including uncertainties in last digits for some entries.

Table 20: **In the first two lines:** *the old relative entropies of most of the sea salts (except  $B(OH)_4^-$ ,  $HCO_3^-$ ,  $B(OH)_3^{aq}$  and  $CO_2^{aq}$ ) given in the Table V (p.2305) of Latimer and Buffington (1926) in units of cal K<sup>-1</sup> mol<sup>-1</sup> in the first line (in red), and translated in units of J K<sup>-1</sup> mol<sup>-1</sup> in the second line (in blue) with 4.184 J cal<sup>-1</sup>. In the third to fifth lines:* *the more recent “relative entropies of ions” (in J K<sup>-1</sup> mol<sup>-1</sup>) published in:*

- (a) *the improved values of Latimer et al. (1938, Table II, p.1831);*
- (b) *the main book of Lewis and Randall (1961, Table 25-7, p.400 for ions) retained in Millero and Leung (1976, Table 32, p.1071) and Millero (1983, Table X, p.35);*
- (c) *the synthesis of Wolery and Jové-Colón (2017, Tables 4, 5, 8 p.29-32,36-37) derived from Robie et al. (1978, for USG-1452), Wagman et al. (1982, for NBS-82) and Grenthe et al. (1992, for NEA-TDB).*

	$H^+$	$Na^+$	$Mg^{2+}$	$Ca^{2+}$	$K^+$	$Cl^-$	$SO_4^{2-}$	$Br^-$	$CO_3^{2-}$	$F^-$	$OH^-$
<i><math>S</math> (cal K<sup>-1</sup> mol<sup>-1</sup>)</i>	0	15	-19	-9	22	15.5	9	20.5	-14	-5	-2
<i><math>S</math> (J K<sup>-1</sup> mol<sup>-1</sup>)</i>	0	62.8	-79.5	-37.7	92	64.9	37.7	85.8	-58.6	-21	-8.4
(a) (J K <sup>-1</sup> mol <sup>-1</sup> )	0	58.6	-132.2	-47.7	101.3	56.5	18.4	82.4	-54.4	-9.6	-10.4
(b) (J K <sup>-1</sup> mol <sup>-1</sup> )	0	60.2	-118	-55.2	102.5	55.2	17.2	80.8	-51.3	-9.6	-10.5
(c) (J K <sup>-1</sup> mol <sup>-1</sup> )	0	58.45	-137	-56.2	101.2	56.6	18.5	82.55	-50	-13.8	-10.9

### 10.3 Entropies of ions: Latimer (1934, ..., 1951)

Similar values of “relative entropies” first determined in Latimer and Buffington (1926) for most of aqueous ions were then improved in Latimer et al. (1934) with some uncertainty interval, and then completed in Latimer et al. (1938) for almost all sea-salt ions and with generalized and improved uncertainty intervals (see the line (a) in the Table 20 and the first column in the Table 22).

Moreover, Latimer (1952, p.365) wrote that: “*Powell and Latimer (1951) have given the general equation for the entropies of the monoatomic ions in water solution*

$$S_{298.16}^\circ = \frac{3}{2} R \ln(M) - \frac{270 Z}{(r+x)^2} + 0.94 \text{ cal } K^{-1} \text{ mol}^{-1}. \quad (167)$$

where  $Z$  is the numerical value of the charge,  $r$  is the crystal radius and  $x$  has the value 2.00 for positive ions and 1.00 for negative ions. A comparison of the experimental values with the equation is shown in Figure 8” (recalled in the Fig.21(b) above). “*The equation (167) should include a term  $R \ln(Q)$ , where*

$Q$  is the multiplicity of the ground state, but, since  $Q$  is zero for the most ions and generally unknown for the others, this term has been omitted in the comparison (...) In view of the large variation in the values for  $Z$ ,  $r$ , and  $S^0$ , the agreements are remarkable and the equation may be employed to estimate unknown entropies with an accuracy which is comparable to most of the experimental values.”

## 10.4 Entropies of ions: Latimer (1952)

According to Latimer (1952, p.10-11), to compute the standard free energy  $\Delta F^0 = \Delta H^0 - T^0 \Delta S^0$  (at  $T_0 = 273.15$  K) it is needed to know the standard entropy at  $T_0 = 273.15$  K, with for instance for pure solids  $S^0 = \int_0^{T_0} C_p(T) d \ln(T) + R \ln(g)$ , “where  $C_p(T)$  is the specific heat at constant pressure and  $g$  the number of detailed states or the multiplicity of the solid when cooled to absolute zero. For all substances,  $C_p(T)$  becomes zero at very low temperatures and if the substances in its lowest energy level has but a single configuration,  $g$  then equal to unity and “the entropy of the substance at the absolute zero is zero.” This “(…)” clause is a statement of the third law of thermodynamics. The validity of this law, which has been the subject of much controversy during the past two decades, can no longer be doubted. Its application has made possible the experimental evaluation of the absolute entropies from specific-heat measurements and thus the calculation of  $\Delta F^0$  from thermal data by equation (for  $\Delta F^0$  recalled above). At least half of the free energies which we shall employ have been computed by this method.”

Then Latimer (1952, p.11) recalled the Sackur-Tetrode equation (for the translational energy) and that “if the gas has rotation, vibration, and electronic contributions, the additional entropy from molecules in the various excited states may be computed from a knowledge of the various states. These spectroscopic entropies have been a very valuable check on the corresponding values calculated from the specific-heat data (...) Extensive use has been made of the entropies of the aqueous ions which have been (...) obtained from the entropies of compounds at 25° C and their entropies of solution as calculated from the heats and free energies of solution by equation (for  $\Delta F^0$  recalled above).”

Finally, Latimer (1952, p.11) mentioned that “The heats of formation are known for many substances in solution for which it has been impossible to determined the free energies by electromotive force or equilibrium methods because of the slowness or irreversibility of the reactions. A knowledge of the (third-law, absolute) entropy values has thus made available these thermal data for the calculation of the reaction potentials.”

According to Latimer (1952, p.359), “The entropy of a solid compound is a function of the masses of the constituent atoms and the forces acting between these atoms: the greater the mass and the lower the force, the larger is the entropy.”

According to the values in the Table 87 of Latimer (1952, p.361), values retained and completed in the Table D.1 of Grenthe et al. (2020a, p.1281), a selected set of the resulting entropies of (cations and anions) elements in solid compounds at 298 K is given in the Table 19.

According to Latimer (1952, p.366-367), “The estimation of the entropy of a neutral molecule in aqueous solution is a difficult problem. From the work of Frank and Evans,<sup>4</sup> it may be concluded that the entropy of solution, i.e., the entropy of the molecule  $M$  solution minus the entropy of the gas, is negative and roughly proportional to the heat of solution.”

## 10.5 An “Absolute” definition for the Entropies of ions?

An attempt is made in Gurney (1953, see the Chapter 10) to get rid of the arbitrary choice “ $S_{H^+} = 0$  for the cation  $H^+$ ” used to compute the “relative entropy” introduced in Latimer and Buffington (1926) and valid for all lines of the Table 20. The aim would be to derive some “absolute” definitions for all the

<sup>4</sup> See Frank (1945b,a) and Frank and Evans (1945).

sea-salt anions and cations.

To do so, Gurney (1953, Table. 25, p.173) first recalled the results of Latimer et al. (1938) before to study in the Fig. 54 (p.174) the “*Correlation between Ionic Entropy and Viscosity (..) to see whether a decrease in viscosity is, in fact, accompanied by an increase in entropy, and vice versa.*” Both the Table. 25 and the Fig. 54 of Gurney (1953) recalled in the left parts of the Fig. 23 correspond to “*conventional partial molar entropies*” or “*relative entropies*” computed with the hypothesis  $S_{H^+} = 0$ .

Figure 23: The figures 54 and 55 plotted from the Tables 25 and 26 of Gurney (1953, p.173-176). Entropies are in  $\text{cal K}^{-1} \text{mol}^{-1}$  (with  $1 \text{ cal} = 4.184 \text{ J}$ ).

### IONIC PROCESSES IN SOLUTION

by RONALD W. GURNEY

1953

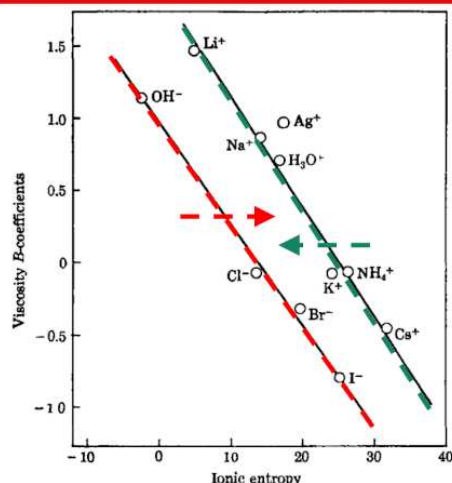


FIG. 54. Viscosity B-coefficients from Table 24 plotted against partial molar entropies from Table 25 (on scale of 0.0 for  $H^+$ )

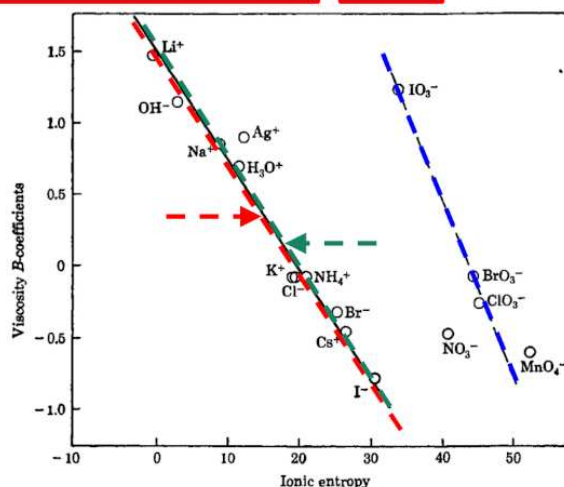


FIG. 55. Viscosity B-coefficients plotted against partial molar entropies from Table 26 (on scale of  $-5.5$  for  $H^+$ ).

Ion	e.u.	Ion	e.u.
$H^+$	(0.00)	$NH_4^+$	26.4
$Li^+$	4.7	$Cl^-$	13.5
$Na^+$	14.0	$Br^-$	19.7
$K^+$	24.2	$I^-$	25.3
$Cs^+$	31.8	$OH^-$	-2.49
$Ag^+$	17.54		

W. M. Latimer, K. S. Pitzer, and W. V. Smith,  
*J. Am. Chem. Soc.*, **60**, 1831 (1938)

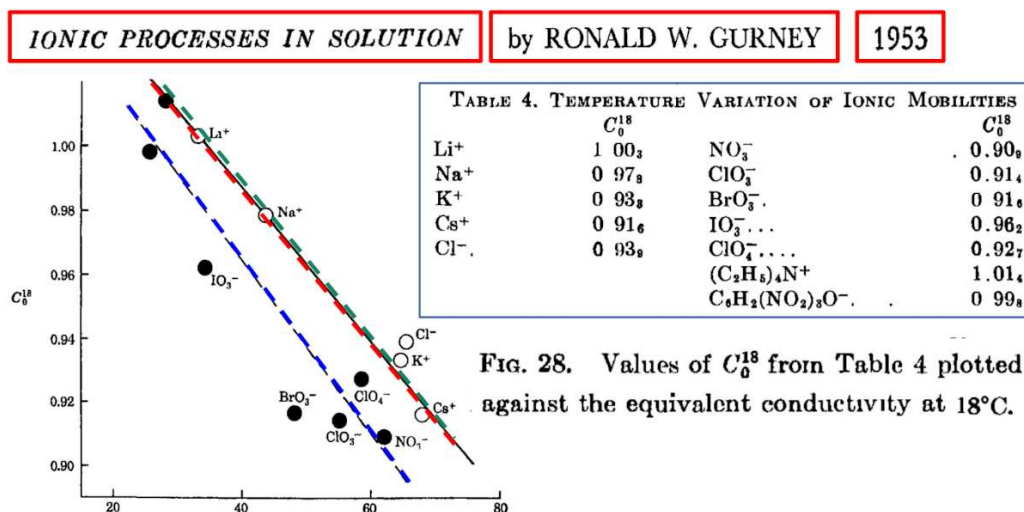
Ion	e.u.	Ion	e.u.
$H^+$	(-5.5)	$Br^-$	25.1
$Li^+$	-0.8	$I^-$	30.8
$Na^+$	8.5	$OH^-$	3.01
$K^+$	18.7	$MnO_4^-$	52.2
$Cs^+$	26.3	$NO_3^-$	40.5
$Ag^+$	12.04	$ClO_3^-$	44.9
$NH_4^+$	20.9	$BrO_3^-$	44.0
$Cl^-$	19.0	$IO_3^-$	33.5

Clearly, with the hypothesis  $S_{H^+} = 0$  all the plotted anions and cations are roughly aligned along straight lines in the Fig. 54, but along two different straight lines (in green for cations with  $Z = +1$  and in red for anions with  $Z = -1$ ) with an horizontal gap of about 11 “*entropy unit (eu)*” in  $\text{cal K}^{-1} \text{mol}^{-1}$ .

For Gurney (1953, p.175): “*In view of the fact that the entropy values are all based on the arbitrary choice of zero for the  $H^+$  ion, it is not surprising that the points for the positive and negative ions lie on separate straight lines; this fact is of no significance. If, instead of zero, we were to assign the value  $-5.0$  (namely half of 11) to the  $H^+$  ion, we should obtain the set of values shown in Table 26 (see the right parts of the Fig. 23) where the value for each positive ion has been diminished by 5.5 entropy unit, while at the same time the value for each negative ion has been increased by the same amount, so that the sum for any ion pair retains the same value, namely, the value derived from the experimental data. Table 26 also includes entropy values for five of the larger molecular ions. When the values of Table 26 are plotted (...) the result shown in Fig. 55 is obtained. The points for atomic ions of both signs now lie about a single straight line.*” Gurney (1953, p.176) further explained that “*It is difficult to resist the*

conclusion that (...) the ionic properties that are involved in these diagrams depend largely on the (...) degree of order or disorder in the ionic co-sphere.”

Figure 24: The figure 28 plotted from the Table 4 of Gurney (1953, p.70).



An important feature about the Fig. 55 is noticed by Gurney (1953, p.175): “there is a striking resemblance to Fig. 28 in Chapter 4, where the temperature coefficient of the ionic mobility was plotted against the mobility itself. This resemblance is more interesting when it is recalled that the experimental values plotted in Fig. 28 are obtained for each species of positive and each species of negative ion separately and do not contain any arbitrary factor (like the assignment of  $-5.5$  to the  $H^+$  ion).” More precisely, Gurney (1953, p.176) explained that “Six features of Fig. 28 may be enumerated as follows:

- (1) the values for  $K^+$  and  $Cl^-$  lie close together;
- (2) the values for  $Cs^+$  and  $I^-$  lie below;
- (3) the values for  $Na^+$  and  $Ag^+$  lie above;
- (4) the value for  $Li^+$  lies still higher;
- (5) the values for the large molecular ions lie about a nearly parallel line (n.b. in blue);
- (6) their order is  $(NO_3)^-$ ,  $(ClO_3)^-$  and  $(IO_3)^-$ .

On comparing Fig. 55 with Fig. 28, it will be seen that all these six features are reproduced in Fig. 55.”

In order to more clearly understand the method to add  $-S_{H+} = +5.5$  entropy unit for anions and remove the same amount for cations, it must be recalled that the “relative entropies” are computed by the relationships “ $(S_{Mz-}) - Z(-S_{H+})$ ” for the anions and “ $(S_{Mz+}) + Z(-S_{H+})$ ” for the cations. This means, moreover, that for an ion of charge  $\pm Z$  greater than  $+1$  (or smaller than  $-1$ ), it is the value “ $-Z \times S_{H+}$ ” that should be added/removed to the “relative entropy” of ions.

Conway (1978, Table. II, p.736) published a revue of 11 different values<sup>5</sup> of “Absolute Standard Partial Molal Entropies of the Hydrogen Ion in Water at 298 K” with three mean values for  $\bar{S}^\circ(H^+, aq.)$  of about  $-22.2 \pm 1.4$ ,  $-19.6 \pm 2.9$  and  $-22.15 \text{ J K}^{-1} \text{ mol}^{-1}$  (depending on the chosen values to make the average), to be compared with the value of  $-5.5 \text{ cal K}^{-1} \text{ mol}^{-1} = -23 \text{ J K}^{-1} \text{ mol}^{-1}$  of Gurney (1953).

Previously Goodrich et al. (1950) wrote a special section dealing with “The Absolute Partial Molal Entropy of Hydrogen Ion” establishing a value of about  $-2.1$  to  $-3.3 \text{ cal K}^{-1} \text{ mol}^{-1}$  “as the absolute

<sup>5</sup> Namely the homogeneous set of values:  $-20.9$  (Eastman, 1928),  $-19.6$  (Lange and Hesse, 1933),  $-22.6$  (Lee and Tai, 1941),  $-26.3$  (Crockford and Hall, 1950),  $-23.0$  (Gurney, 1953),  $-20.0$  (Criss and Cobble, 1964b),  $-23.0$  (Breck and Lin, 1965),  $-21.3$  (Ikeda, 1965) and  $-22.6 \text{ J K}^{-1} \text{ mol}^{-1}$  (Ikeda, 1965), with also the slightly different values of  $-13.8$  (Noyes, 1962) and  $-8.8$  to  $-14.2 \text{ J K}^{-1} \text{ mol}^{-1}$  (Goodrich et al., 1950), or equivalently  $-5.0$ ,  $-4.7$ ,  $-5.4$ ,  $-6.3$ ,  $-5.5$ ,  $-4.8$ ,  $-5.5$ ,  $-5.1$  and  $-5.4$ , with also  $-3.3$  and  $-2.1$  to  $-3.4 \text{ cal K}^{-1} \text{ mol}^{-1}$ .

entropy of hydrogen ion” (or equivalently  $-8.8$  to  $-14.2$  J K<sup>-1</sup> mol<sup>-1</sup>). Scott and Hugus Jr. (1957, p.1422) mentioned that “If the Powell and Latimer (1951) equation fits the conventional partial molar entropies (based on  $S_{H^+} = 0$ ), then it is functionally incapable of also fitting the absolute partial molar entropy (based on  $S_{H^+} = -5.5$  entropy unit) of Gurney (1953).” Laidler (1956, Table. II, p.110) called “Absolute entropy” those computed with the definition  $S_{H^+} = -5.5$  cal K<sup>-1</sup> mol<sup>-1</sup>. In the discussion section of Criss and Cobble (1964b, p.5387) it was mentioned that “It is important to note that the choice of standard states (...) corresponds to an ionic entropy of  $-5.0$  cal K<sup>-1</sup> mol<sup>-1</sup> for the hydrogen ion at 25°C. This falls within the range of values ( $-2.1$  to  $-6.3$ ) suggested by others for the “absolute” ionic entropy of  $H^+(aq)$ . Consequently, for consistency, the values of ionic entropy in use here will be assumed to be on the “absolute” scale.”

The paper of Ikeda (1965, p.3412) entitled “Absolute value of the partial molar standard entropy of the hydrogen ion in aqueous solutions” considered that “It is of great importance to determine the absolute value of  $S_{H^+}$ , the partial molar standard entropy of the hydrogen ion in water, and various attempts have been made to determine it. The methods reported so far are of necessity nonthermodynamic and involve various assumptions, giving values of great varieties falling in the range between  $-1$  and  $-7$  cal K<sup>-1</sup> mol<sup>-1</sup> at 25°C: i.e.  $-1.5$ ,  $-2.1$ ,  $-3.3$ ,  $-4.6$ ,  $-4.7$ ,  $-5.0$ ,  $-5.4$ ,  $-5.5$  and  $-6.4$  cal K<sup>-1</sup> mol<sup>-1</sup>.<sup>6</sup> This is why Ikeda (1965, p.3412) searched for an “(...) alternative new method of estimating this important quantity (...)” and considered that (...) “the transport of the hydrogen ion causes “structural diffusion” of the whole complex, i.e., by the formation and decomposition of H bonds at its periphery by proton transfer, not by the migration of  $H_3O^+$  entity.” The mean value  $S_{H^+}^0(abs) = -5.3$  cal K<sup>-1</sup> mol<sup>-1</sup> is an average of the two values  $-5.1$  (for  $H^+$ ) and  $-5.4$  (for  $OH^-$ ) listed in the Table I (p.3413), which “is in close agreement with  $-5.5$  eu estimated by Gurney (1953), with  $-5.4$  eu given by Lee and Tai (1941)<sup>7</sup>, and with  $-5.0$  eu assigned by Criss and Cobble (1964a).”

The same is true in the paper of Marcus and Loewenschuss (1984, Table. 4, p.107) in the Section 5 entitled “Absolute Entropies of Hydration,” where they wrote: “The conventional entropies of hydration are based (...) on the convention that  $\bar{S}_{i,conv}^0(aq) = 0$  for  $H^+(aq)$  at all temperatures. An assignment of an absolute value to this ion at some temperature permits, therefore, the calculation of absolute entropies of hydration for all ions at this particular temperature.”

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Does this mean that this value of about  $-5.5$  cal K<sup>-1</sup> mol<sup>-1</sup> entropy unit really corresponds to the “absolute” value of the entropy of  $H^+$  in (aqueous) solution? This is doubtful, as there is nothing to link this choice  $S_{H^+}$  to the third-law definition of entropies (for the calorimetric method), or equivalently to calculations based on quantum mechanics and statistical physics.

The important feature is that, since the seawater has a neutral electronic charge, the value of  $S_{H^+}$  has no impact on the sea-salts part of the seawater entropy, because the impact is given by the weighted sum  $-\sum_j (Z_j S_{H^+}) = -S_{H^+} \left( \sum_j Z_j \right)$ , where the valence  $Z_i$ ’s are given by the Table 21, and with the property  $\sum_j Z_j \equiv 0$  explaining a null impact of  $S_{H^+}$ .

## 10.6 Entropies of elements and ions: Lewis and Randall (1961)

Lewis and Randall (1961) already published complete datasets for:

- the (third-law and statistical+quantum physic) absolute entropies for all atmospheric basic elements (p.137, 421 and 672) computed at 298.15 K and 1000 hPa = 0.1 MPa and expressed in cal K<sup>-1</sup> mol<sup>-1</sup> (45.77 for N<sub>2</sub>, 49.01 for O<sub>2</sub>, 36.95 for Ar and 51.08 for CO<sub>2</sub>), leading to the dry-air

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<sup>6</sup> Or equivalently  $-6.3$ ,  $-8.8$ ,  $-13.8$ ,  $-19.2$ ,  $-19.7$ ,  $-20.9$ ,  $-22.6$ ,  $-23$  and  $-26.8$  J K<sup>-1</sup> mol<sup>-1</sup>.

<sup>7</sup> Note that I have not been able to found a copy of this paper of Lee and Tai (1941) and it is needed to rely on the result published in Gurney (1953).



absolute entropy of about  $47.509 \text{ cal K}^{-1} \text{ mol}^{-1} \approx 198.776 \text{ J K}^{-1} \text{ mol}^{-1} \approx 6864.05 \text{ J K}^{-1} \text{ kg}^{-1}$  computed by Lemmon et al. (2000)<sup>8</sup>, which is very close to the values of about  $6864.29 \text{ J K}^{-1} \text{ kg}^{-1} \approx 47.510 \text{ cal K}^{-1} \text{ mol}^{-1} \approx 198.783 \text{ J K}^{-1} \text{ mol}^{-1}$  recomputed by me in 2022 for 400 ppmv of  $\text{CO}_2$  from statistic+quantum physics results;

- the liquid-water absolute entropy at 298.15 K (p.137) of about  $16.73 \text{ cal K}^{-1} \text{ mol}^{-1}$  or about  $70.00 \text{ J K}^{-1} \text{ mol}^{-1} \approx 3885.5 \text{ J K}^{-1} \text{ kg}^{-1}$  retained in both Millero and Leung (1976, p.1070) and Millero (1983, p.34), and with a close value of about  $3883.7 \text{ J K}^{-1} \text{ kg}^{-1} \approx 69.97 \text{ J K}^{-1} \text{ mol}^{-1} \approx 16.722 \text{ cal K}^{-1} \text{ mol}^{-1}$  re-computed but considered as a mere remark in Feistel and Wagner (2006, p.1032), and not as a true option for IAPWS or TEOS10 software;
- the relative values for all sea-salt ions in the Table 25-7 (p.400-401) with values retained in both Millero and Leung (1976, Table 32, p.1071) and Millero (1983, Table X, p.35).

I show in the Figs. 25 the entropies of sea-salt ions were already available in the book of Lewis and Randall (1961, Table 25-7, p.400-401) cited in all IAPWS and TEOS10 documentations written by Rainer Feistel.

TABLE 25-7. THERMODYNAMIC DATA FOR AQUEOUS IONS AT 298.15°K,  
CAL/DEG MOLE OR KCAL/MOLE

Ion	$\bar{c}_p$	$\bar{s}^\circ$	$\Delta \bar{H}_f^\circ$	$\Delta \bar{F}_f^\circ$
• $\text{H}^+$ .....	0	0	0	0
$\text{OH}^-$ .....	-32.0	-2.52	-54.96	-37.59
$\text{F}^-$ .....	-29.5	-2.3	-78.66	-66.08
• $\text{Cl}^-$ .....	-30.0	13.2	-40.02	-31.35
$\text{ClO}_2^-$ .....		24.1	-17.18	2.74
$\text{ClO}_3^-$ .....	-18	39	-23.5	0.6
$\text{ClO}_4^-$ .....		43.2	-31.41	-2.47
• $\text{Br}^-$ .....	-31	19.29	-28.90	-24.57
$\text{I}^-$ .....	-31	26.14	-13.37	-12.35
$\text{I}_3^-$ .....		57.1	-12.4	-12.31
$\text{S}^{2-}$ .....		-4	7.8	20.6
$\text{HS}^-$ .....		15.0	-4.10	3.00
• $\text{SO}_4^{2-}$ .....	-66	4.1	-216.90	-177.34
$\text{HSO}_4^-$ .....		30.52	-211.70	-179.94
$\text{SeO}_3^{2-}$ .....		3.9	-122.39	-89.33
$\text{SeO}_4^{2-}$ .....		5.7	-145.3	-105.42
$\text{HSeO}_4^-$ .....		22.0	-143.1	-108.2
$\text{NH}_4^+$ .....	16.9	26.97	-31.74	-19.00
$\text{N}_2\text{H}_6^{4+}$ .....		19	-4	22.5
$\text{N}_2\text{H}_5^+$ .....		31	-1.7	21.0
$\text{NH}_2\text{OH}_2^+$ .....		37	-30.7	-13.54
$\text{NO}_2^-$ .....		29.9	-25.4	-8.25
$\text{NO}_3^-$ .....	-18	35.0	-49.37	-26.43
$\text{PO}_4^{3-}$ .....		-52	-306.9	-245.1
$\text{HPO}_4^{2-}$ .....		-8.6	-310.4	-261.5
$\text{H}_2\text{PO}_4^-$ .....		21.3	-311.3	-271.3
$\text{HAsO}_4^{2-}$ .....		0.9	-214.8	-169
$\text{H}_2\text{AsO}_4^-$ .....		28	-216.2	-178.9
$\text{HCOO}^-$ .....		21.9	-98.0	-80.0
• $\text{HCO}_3^-$ .....		22.7	-165.18	-140.31
$\text{CO}_3^{2-}$ .....		-12.7	-161.63	-126.22
$\text{CH}_3\text{COO}^-$ .....				

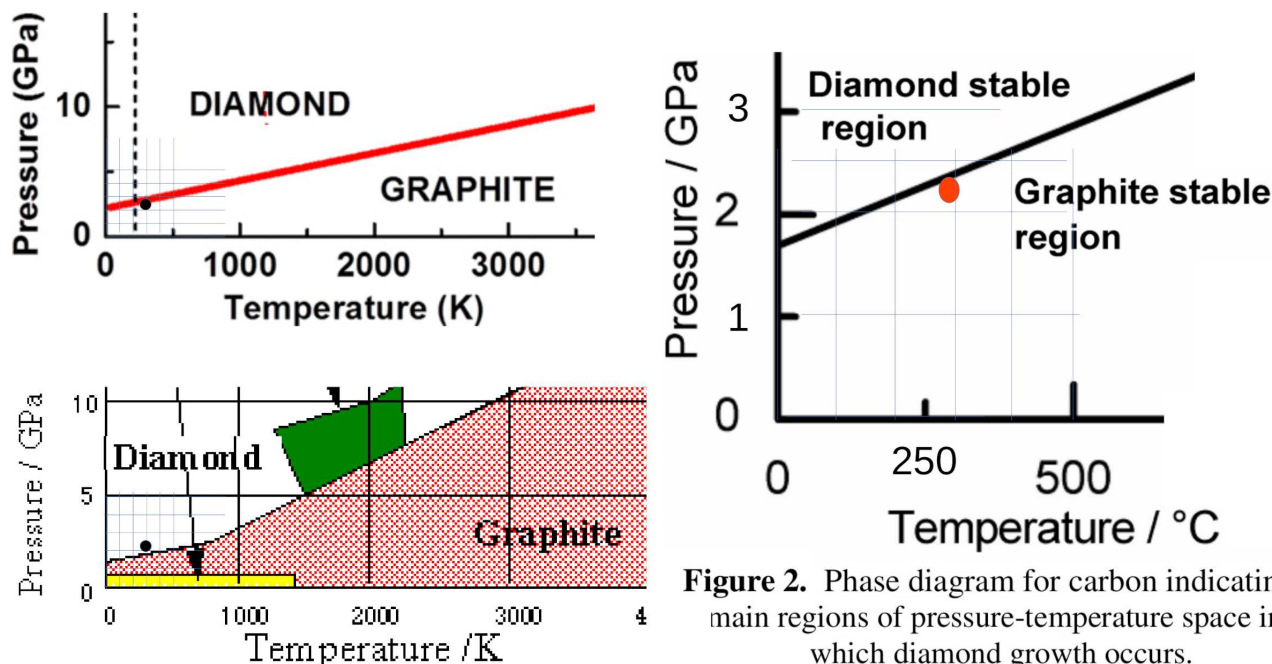
TABLE 25-7. THERMODYNAMIC DATA FOR AQUEOUS IONS AT 298.15°K,  
CAL/DEG MOLE OR KCAL/MOLE (Continued)

Ion	$\bar{c}_p$	$\bar{s}^\circ$	$\Delta \bar{H}_f^\circ$	$\Delta \bar{F}_f^\circ$
$\text{PtCl}_4^{2-}$ .....		42	-123.4	-91.9
$\text{PtCl}_6^{4-}$ .....		52.6	-167.4	-123.1
$\text{Fe}^{2+}$ .....		-27.1	-21.0	-20.30
$\text{Fe}^{3+}$ .....		-70.1	-11.4	-2.53
$\text{Fe}(\text{OH})^{++}$ .....		-23.2	-67.4	-55.91
$\text{FeNO}^{++}$ .....		-10.6	-9.7	1.5
$\text{Mn}^{2+}$ .....		-20	-53.3	-54.4
$\text{MnO}_4^-$ .....		45.4	-129.7	-107.4
$\text{H}_2\text{BO}_3^-$ .....		7.3	-251.8	-217.6
$\text{BF}_4^-$ .....		40	-365	-343
$\text{Al}^{3+}$ .....		-74.9	-125.4	-115
$\text{Gd}^{3+}$ .....		-43	-168.8	-165.8
• $\text{Mg}^{2+}$ .....	4	-28.2	-110.41	-108.99
• $\text{Ca}^{2+}$ .....	-9	-13.2	-129.77	-132.18
• $\text{Sr}^{2+}$ .....		-9.4	-130.38	-133.2
$\text{Ba}^{2+}$ .....	-11	3	-128.67	-134.0
$\text{Li}^+$ .....	14.2	3.4	-66.55	-70.22
• $\text{Na}^+$ .....	7.9	14.4	-57.28	-62.59
• $\text{K}^+$ .....	2.3	24.5	-60.04	-67.46
• $\text{Rb}^+$ .....	-8.7	28.7	-59.4	-67.65
$\text{Cs}^+$ .....	-18.7	31.8	-62.6	-70.8
$\text{UO}_2^{++}$ .....		-17	-250.4	-236.4

Figure 25: The molar entropy  $\bar{S}^\circ$  and specific heat at constant pressure  $\bar{C}_p^\circ$  for ions listed in the Table 25-7 of Lewis and Randall (1961, p.400-401).

<sup>8</sup> Obtained from the value  $198.776 \text{ J K}^{-1} \text{ mol}^{-1}$  interpolated between the values 197.86 at 290 K and 198.85 at 300 K given in the Table A2 (p.367), with the additional value of  $-287.05 \times \ln(1000/1013.25) \approx 3.78 \text{ J K}^{-1} \text{ kg}^{-1} \approx 0.0109 \text{ J K}^{-1} \text{ mol}^{-1}$  due to the change of pressure from 1013.25 hPa to 1000 hPa.

Figure 26: Three “phase diagrams for carbon” (graphite-diamond), where I have added (black and red bullets) the predicted point 298.15 K / 2.2 GPa. **Upper left:** a zoom adapted from Narayan and Bhaumik (2015) and Bundy (1980); **Lower left:** a zoom adapted from a coloured version of the Fig. 10 of Bundy (1980) available at [https://www.ch.ic.ac.uk/rzepa/mim/century/html/diamond\\_text.htm](https://www.ch.ic.ac.uk/rzepa/mim/century/html/diamond_text.htm); **On the right:** a zoom adapted from a coloured version of the Fig. 2 of Balmer et al. (2009).



**Figure 2.** Phase diagram for carbon indicating main regions of pressure-temperature space in which diamond growth occurs.

The fact is Lewis and Randall (1961) trusted the third-law and statistical+quantum physics values for the absolute entropy computed for elements, molecules.

As an example of the predictive power of the third-law and absolute values of entropies, the transition from graphite to diamond state at ambient temperature is predicted by Lewis and Randall (1961, p.162-163) to occur at a threshold pressure of about 22 000 atm or about 2.2 GPa (with 1 atm  $\approx$  0.1 MPa) computed from the value of  $\Delta F_{298}^0 \approx -685$  cal/mole obtained with the use of the calorimetric and third-law (i.e. with integrations of  $C_p(T) d\ln(T)$  and with zero entropies at 0 K) absolute standard entropies  $S^0$  of about 1.37 cal/deg/mole for graphite and about 0.58 cal/deg/mole for diamond at 298.15 K.

As a matter of fact, the points of coordinates (298.15 K / 2.2 GPa) predicted by Lewis and Randall (1961) are in agreement with the black and red bullets located in the modern phase diagrams plotted in the three Figs. 26.

Here lies all the power of the possibility to compute the absolute values of entropies, in accordance with the prophetic vision of Le Chatelier (1888), who first described the need to know the absolute values of entropy of reactants and products in order to be able to predict the stability of all chemical processes, this idea being at the origin of the seminal works of Nernst (1906, 1907, 1910, 1912), which eventually led to the expression of the third law of thermodynamics by Planck (1914, 1917) for radiation and matter.

## 10.7 A synthesis of reference entropies for liquid water and sea-salt ions

According to the Table 25 (for the molar masses) and the Table 22 (for the molar entropies), the absolute value of the reference entropy for pure liquid water derived from SG92 (NEA-TDB) is  $69.95 \pm 0.03 \text{ J K}^{-1} \text{ mol}^{-1}$  at  $25^\circ\text{C}$  with a molar mass of about  $18.0153 \pm 0.0005 \text{ g mol}^{-1}$ , leading to the absolute pure liquid-water entropy at  $25^\circ\text{C}$  (and  $298.15 \text{ K}$ ) of about

$$\eta_{w0} \approx \frac{69.95 \pm 0.03}{0.00180153 \pm 0.0005} \approx 3882.8 \pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1} \text{ at } 25^\circ\text{C}.$$

With a specific heat at constant pressure for pure liquid water of about  $4218 \pm 1 \text{ J K}^{-1} \text{ kg}^{-1}$ , the absolute value of the reference entropy for pure liquid water at  $0^\circ\text{C}$  (and  $273.15 \text{ K}$ ) is

$$\eta_{w0} \approx (3882.8 \pm 1.7) + (4218 \pm 1) \times \ln\left(\frac{273.15}{298.15}\right) \approx 3513.4 \pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1} \text{ at } 0^\circ\text{C}.$$

The sea-salts molar mass and molar reference entropy (relative to zero value for  $\text{H}^+$ ) given in bold in the Tables 21 and 22 are  $31.404 \pm 0.001 \text{ g mol}^{-1}$  and  $44.74 \pm 0.4 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively, leading to a specific entropy of sea salts at  $25^\circ\text{C}$  ( $298.15 \text{ K}$ ) of

$$\eta_{s0} \approx \frac{44.74 \pm 0.4}{0.031404 \pm 0.001} \approx 1488.3 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1} \text{ at } 25^\circ\text{C}.$$

The specific heats at constant pressure  $\bar{C}_p$  recalled in the Table 23 are only available for the 4 major sea salts ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ , in blue) from the Table 25-7 (p.400-401) of Lewis and Randall (1961, “LR61”). Moreover, when available the values from NBS82 roughly agree with those of LR61 (same sign and same order of magnitude) The average specific heat at constant pressure for sea salt computed from the blue values of the Table 23 is  $-52 \pm 1 \text{ J K}^{-1} \text{ mol}^{-1}$  or  $-52/0.031404 \approx 1656 \pm 30 \text{ J K}^{-1} \text{ kg}^{-1}$ . The specific entropy of sea salts at  $0^\circ\text{C}$  (and  $273.15 \text{ K}$ ) is therefore

$$\eta_{s0} \approx (1488.3 \pm 13) - (1656 \pm 30) \times \ln\left(\frac{273.15}{298.15}\right) \approx 1633.3 \pm 15 \text{ J K}^{-1} \text{ kg}^{-1} \text{ at } 0^\circ\text{C}.$$

The synthesis of the previous computation of reference values of entropies of pure liquid water ( $s_{w0}$ ) and sea salts ( $s_{s0}$ ) is:

$$s_{w0} \approx 3882.8 \pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1} \text{ (at } 25^\circ\text{C}) \text{ and } s_{w0} \approx \boxed{3513.4 \pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1}} \text{ (at } 0^\circ\text{C}), \quad (168)$$

$$s_{s0} \approx 1488.3 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1} \text{ (at } 25^\circ\text{C}) \text{ and } s_{s0} \approx \boxed{1633.3 \pm 15 \text{ J K}^{-1} \text{ kg}^{-1}} \text{ (at } 0^\circ\text{C}). \quad (169)$$

The same “*Reference Salinity molar mass*” of  $31.4038218 \text{ g}^{-1} \text{ mol}^{-1}$  is found as in the Table D.4 (p.145) of Feistel and TEOS10 (2010). This value of about  $31.404 \text{ g}^{-1} \text{ mol}^{-1}$  is computed with the same relationship ( $M_s = \sum_j X_j M_j$ ) and with the same molar masses ( $M_j$ ) given for all species in the Table D.3 (p.144) of Feistel and TEOS10 (2010) and retained in the Table 22 above.

Differently, Millero and Leung (1976, p.1039) found about twice this value by using the same relationship  $M_s = \sum_i N_i M_i$ , namely  $62.793 \approx 2 \times 31.4 \text{ g}^{-1} \text{ mol}^{-1}$ , due to about double values for all molal fractions ( $N_i$ ) listed in the Table 32 of Millero and Leung (1976, p.1071) and retained as such in the Table X of Millero (1983, p.35), with a global sum  $\sum_i N_i$  very close to 2 (i.e. 1.99944). Similarly, the mean molal sea-salt entropy computed by Millero and Leung (1976) and retained as such in Millero (1983) was about twice the values retained in (169), namely  $95.01 \approx 2 \times 47.5 \text{ J K}^{-1} \text{ mol}^{-1}$  at  $25^\circ\text{C}$ . However, these double values do not impact the mean sea-salt entropy express in units of  $95.01/0.062793 \approx 1513 \text{ J K}^{-1} \text{ kg}^{-1}$  at  $25^\circ\text{C}$ , which is indeed larger but close to the value  $1488.3 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$  at  $25^\circ\text{C}$ , retained in (169).

Table 21: Values of  $Z$  (valance, electric charge),  $M$  (molar mass, in  $\text{g mol}^{-1}$ ),  $X$  (mole fraction, in  $\text{mol mol}^{-1}$ ) and  $W$  (mass fraction, in  $\text{g g}^{-1}$ ) for the main sea-salt cations and anions.

- The oldest values of  $M_{(M74)}$  and  $X_{(M74)}$  are from Millero (1974, Table III, p.21). The mole fractions  $X_{(M74)}$  are computed from the “Weight Fractions” and normalized to a sum of 1, with as a result half of the “Mole fractions”  $X_{*(M74)}$  indicated by Millero (1974), i.e. with  $X_{(M74)} = X_{*(M74)}/2$ .
- The next values of  $M_{(M82)}$  and  $X_{(M82)}$  are from Millero (1982, Table IV, p.428) and  $M_{(M83)}$  and  $X_{(M83)}$  are from Millero (1983, Table X, p.35), with  $X_{(M83)} = X_{*(M83)}/2$  and  $X_{(M83)} = X_{*(M83)}/2$  normalized to a sum of 1.
- The more recent (complete set of) values for  $M$ ,  $X$  and  $W$  are from Feistel and TEOS10 (2010, Table D.3, p.144), where the molar fractions are from the rounded values of Millero et al. (2008, Table 3, p.60).
- As usual for these datasets, the numbers in parentheses refer to the uncertainty in the corresponding last digits, with for instance 24.305 0(6) meaning  $24.305 0 \pm 0.000 6$  and 96.062 6(50) meaning  $96.062 6 \pm 0.005 0$ .

Solute	$Z$ (-)	$M_{(M74)}$ ( $\text{g mol}^{-1}$ )	$X_{(M74)}$ ( $\text{mol mol}^{-1}$ )	$M_{(M82)}$ ( $\text{g mol}^{-1}$ )	$X_{(M82)}$ ( $\text{mol mol}^{-1}$ )	$X_{(M83)}$ ( $\text{g mol}^{-1}$ )	$M_{(\text{TEOS10})}$ ( $\text{g mol}^{-1}$ )	$X_{(\text{TEOS10})}$ ( $\text{mol mol}^{-1}$ )	$W_{(\text{TEOS10})}$ ( $\text{g g}^{-1}$ )
<b>Na<sup>+</sup></b>	+1	22.989 8	0.418 099 6	22.989 8	0.418 792 9	0.418 212 1	22.989 769 28(2)	0.418 807 1	0.306 595 8
<b>Mg<sup>2+</sup></b>	+2	24.305	0.047 552 0	24.305	0.047 163 7	0.047 558 3	24.305 0(6)	0.047 167 8	0.036 505 5
<b>Ca<sup>2+</sup></b>	+2	40.08	0.009 173 1	40.08	0.009 181 2	0.009 172 6	40.078(4)	0.009 182 3	0.011 718 6
<b>K<sup>+</sup></b>	+1	39.102	0.009 114 9	39.102	0.009 114 5	0.009 112 6	39.098 3(1)	0.009 115 9	0.011 349 5
Sr <sup>2+</sup>	+2	87.62	0.000 081 0	87.62	0.000 081 0	0.000 080 0	87.62(1)	0.000 081 0	0.000 226 0
<b>Cl<sup>-</sup></b>	-1	35.453	0.487 495 1	35.453	0.487 437 8	0.487 541 5	35.453(2)	0.487 483 9	0.550 339 6
<b>SO<sub>4</sub><sup>2-</sup></b>	-2	96.057 6	0.025 216 2	96.057 6	0.025 213 9	0.025 217 1	96.062 6(50)	0.025 215 2	0.077 131 9
<b>HCO<sub>3</sub><sup>-</sup></b>	-1	61.017 2	0.002 084 2	61.017 2	0.001 661 5	0.001 725 5	61.016 84(96)	0.001 534 0	0.002 980 5
<b>Br<sup>-</sup></b>	-1	79.904	0.000 753 3	79.904	0.000 751 1	0.000 755 2	79.904(1)	0.000 752 0	0.001 913 4
CO <sub>3</sub> <sup>2-</sup>	-2	(-)	(-)	60.009 2	0.000 173 2	0.000 200 0	60.008 9(10)	0.000 213 4	0.000 407 8
B(OH) <sub>4</sub> <sup>-</sup>	-1	(-)	(-)	78.839 6	0.000 074 5	0.000 075 0	78.840 4(70)	0.000 090 0	0.000 225 9
F <sup>-</sup>	-1	18.998 4	0.000 061 2	18.998 4	0.000 061 1	0.000 050 0	18.998 403 2(5)	0.000 061 0	0.000 036 9
OH <sup>-</sup>	-1	(-)	(-)	(-)	(-)	(-)	17.007 33(7)	0.000 007 1	0.000 003 8
B(OH) <sub>3</sub> <sup>aq.</sup>	0	61.832 2	0.000 369 4	61.832 2	0.000 293 6	0.000 300 1	61.833 0(70)	0.000 280 7	0.000 552 7
CO <sub>2</sub> <sup>aq.</sup>	0	(-)	(-)	(-)	(-)	(-)	44.009 5(9)	0.000 008 6	0.000 012 1
<b>Mean/Sum</b>	<b>0.0</b>	31.416	1.000 000 0	31.406	1.000 000 0	(31.412)	<b>31.404 ± 0.001</b>	1.000 000 0	1.000 000 0
<b>Mean2/S2</b>	<b>+42 10<sup>-5</sup></b>	31.401	0.999 488 4	31.385	0.999 316 5	(31.389)	31.381	0.999 258 2	0.998 534 8
<b>Mean1/S1</b>	<b>-25 10<sup>-3</sup></b>	31.147	0.978 362 9	31.144	0.978 608 3	(31.146)	31.144	0.978 674 0	0.970 572 8

- The Mean molar mass for M83 (31.412  $\text{g mol}^{-1}$ ) is computed with the molar mass  $M_{(M82)}$ , but is indicated in the column for the mole fraction  $X_{(M83)}$  (with a sum of 1.000 000 0).
- The eight major species (in **blue** and **red**) are for molar concentrations above 0.000 500 (or  $> 0.05\%$ ), leading to the **Mean2** values. The four main species (in **blue**) are for molar concentrations above 0.020 (or  $> 20\%$ ) leading to the **Mean1** values. The sum of  $X$  is normalized to 1.000 000 0 to compute the mean values **Mean2/S2** and **Mean1/S1** for  $M$  with the **blue+red** species or the **blue** species only.
- The mean electric charge is computed as  $\bar{Z} = \sum_j Z_j X_{j(\text{TEOS10})}$ .  $\bar{Z}$  is **0.0** if all the cations and anions are considered, whereas  $\bar{Z}$  is small but positive (**+0.000 42**) if (only) the eight major species (in **blue** and **red**) are retained (with a sum then normalized to 1.000 000 0).

Table 22: The “relative” molar entropies ( $S_{xxx}$ , in  $J K^{-1} mol^{-1}$ ) are given at  $25^\circ C$  and  $0.1 MPa$ , with mean molar values computed with the same molar fractions of Feistel and TEOS10 (2010, Table D.3, p.144) listed in the previous Table 21. The entropy of liquid water (first line) is the absolute (Third-law) definition. All other entropies are for aqueous species (cations, anions, and aqueous form of  $B(OH)_3$  and  $CO_2$ ) and are computed with respect to the standard hypothesis that the entropy of  $H^+$  is zero (this explaining the term ‘relative’).

- The molar entropies of aqueous ions ( $1 cal = 4.184 J$ ) computed in Latimer and Buffington (1926, “LB26” in Table 2, p.353) have been improved in Latimer et al. (1934, “LSH34” in Table III, p.84) and in Latimer et al. (1938, “LPS38” in Table II, p.1831) with improved accuracy and with additional uncertainty intervals.
- The molar entropy retained in Millero and Leung (1976, “ML76” in Table 32, p.1071) and Millero (1983, “M83” in Table X, p.35) are mainly from Lewis and Randall (1961, Table 12.3, p.137 for liquid water and Table 25-7, p.400-401 for ions, with  $1 cal = 4.184 J$ ).
- Other more recent molar entropy listed in the review of Wolery and Jové-Colón (2017, Tables 4, 5 and 8 p.29-32 and p.36-37) are from: Robie et al. (1978, “R78” for USG-1452), Wagman et al. (1982, “W82” for NBS-82) and Grenthe et al. (1992, “G92” for NEA-TDB).
- As usual for these datasets, the numbers in parentheses refer to the uncertainty in the corresponding last digits, with for instance 69.95(8) meaning  $69.95 \pm 0.08$  and  $-138.0(42)$  meaning  $-138.0 \pm 4.2$ .

$(H_2O)_{liq.}$	70.3	70.7		70.00	69.95(8)	69.91	69.95(3)
Solute	$S_{LB26}$	$S_{LSH34}$	$S_{LPS38}$	$S_{ML76}$ $S_{M83}$	$S_{R78}$ (USG-1452)	$S_{W82}$ (NBS-82)	$S_{G92}$ (NEA-TDB)
$H^+$	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$Na^+$	62.8	61.5(40)	58.6(17)	60.2	58.41(20)	59.0	58.45(15)
$Mg^{2+}$	-79.5	-148	-132.2(120)	-118	-138.0(42)	-138.1	-137(4)
$Ca^{2+}$	-37.7	-47.7	-47.7(13)	-55.2	-53.10(2)	-53.1	-56.2(10)
$K^+$	92	103(2)	101.3(8)	102.5	101.04(25)	102.5	101.2(2)
$Sr^{2+}$	(-)	(-)	-30.5(63)	-39.3	-33.00(85)	-32.6	-31.5(20)
$Cl^-$	64.9	56.5(4)	56.5(4)	55.2	56.73(16)	56.5	56.6(2)
$SO_4^{2-}$	37.7	14.6(20)	18.4(42)	17.2	20.00(85)	20.1	18.5(4)
$HCO_3^-$	(-)	(-)	92.9(33)	95.0	91.20(85)	91.2	98.4(5)
$Br^-$	85.8	81.2(17)	82.4(8)	80.8	82.84(20)	82.4	82.55(20)
$CO_3^{2-}$	-58.6	-53.1(20)	-54.4(42)	-51.3	-56.90(85)	-56.9	-50(1)
$B(OH)_4^-$	(-)	(-)	(-)	(~100)	(-)	102.5	(102.5)
$F^-$	-21	-20.9	-9.6(84)	-9.6	-13.18(54)	-13.8	-13.8(8)
$OH^-$	-8.4	-10.5	-10.4(3)	(-10.5)	-10.71(20)	-10.75	-10.9(2)
$B(OH)_3^{aq.}$	(-)	(-)	(-)	(~50)	(-)	162.3	162.4(6)
$CO_2^{aq.}$	(-)	(-)	(-)	(-)	(-)	117.6	119.36(60)
Mean	55.79	47.33 $\pm$ 2	47.00 $\pm$ 1.6	47.63	46.75 $\pm$ 0.4	46.93	<b>46.74 <math>\pm</math> 0.4</b>
Mean2	55.82	47.36	47.04	47.66	46.78	46.93	46.73
Mean1	53.90	45.64	45.21	45.87	45.01	45.14	44.97

- The entropy of  $(-10.5) J K^{-1} mol^{-1}$  for  $OH^-$  in the column of Millero and Leung (1976) and Millero (1983) is from Lewis and Randall (1961). The value  $(\sim +100) J K^{-1} mol^{-1}$  for  $B(OH)_4^-$  and  $(\sim +50) J K^{-1} mol^{-1}$  for  $B(OH)_3/aq.$  was estimated by Millero and Leung (1976) and Millero (1983) “by comparison with solutes of similar size and charge.” A few other values for  $B(OH)_4^-$  are indicated in the review of Wolery and Jové-Colón (2017):  $100.483 J K^{-1} mol^{-1}$  in Rossini et al. (1952, NBS-500),  $102.508 J K^{-1} mol^{-1}$  in Wagman et al. (1968, NBS-270-3) and  $102.5 J K^{-1} mol^{-1}$  in Wagman et al. (1982, NBS). No value is given in Grenthe et al. (1992, NEA-TDB, “G92”), where I have just recalled (into parentheses) the more recent value given in “W82” (NBS, Wagman et al., 1982).

- The meaning for blue/red colors are the same as in the Table 21.

Table 23: Values of the molar specific heat at constant pressure  $\overline{C}_p$  at 25°C for several of the major sea-salt cations and anions from: Lewis and Randall (1961, “LR61” see the Table 25-7, p.400-401, shown in the previous Fig. 25); and Wagman et al. (1982, “NBS82” see the Tables p.2-47, 2-50, 2-57, 2-260, 2-299, 2-328). Conversions from old calorie units of “LR61” are made with 1 cal = 4.184 J. The molar concentrations ( $X$ ) recalled in the previous Table 21 are from Feistel and TEOS10 (2010, Table D.3, p.144) and rounded values of Millero et al. (2008, Table 3, p.60). The rescaled values ( $\overline{X}$ ) in the last column lead to a sum of 1 for the 4 major cations and anions ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ).

	$\text{Na}^+$	$\text{Mg}^{2+}$	$\text{Ca}^{2+}$	$\text{K}^+$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{HCO}_3^-$	$\text{Br}^-$	(units)
LR61	7.9	4	−9	2.3	−30	−66	(−)	−31	(cal K <sup>−1</sup> mol <sup>−1</sup> )
LR61	33.1	16.7	−37.7	9.6	−126	−276	(−)	−130	(J K <sup>−1</sup> mol <sup>−1</sup> )
NBS82	46.4	(−)	(−)	21.8	−136.4	−293	(−)	−141.8	(J K <sup>−1</sup> mol <sup>−1</sup> )
$X$	0.418 81	0.047 17	0.009 18	0.009 12	0.487 48	0.025 22	0.001 53	0.000 75	(mol mol <sup>−1</sup> )
$\overline{X}$	0.427 93	0.048 20			0.498 10	0.025 77			(mol mol <sup>−1</sup> )

## 11 Basic Physical and Thermodynamic Constants

• The basic physical constants shown in Table 24 are from the old 2013-CODATA-set (Cohen, 1976; Chase, 1998, NIST-JANAF-4) and from the more recent 2017-CODATA-set (Newell et al., 2018).

For the more recent one, the best relative error ( $10^{-8}$ ) is the same for  $h$  and  $N_A$ . A larger relative error ( $5.5 \times 10^{-8}$ ) for  $K_{\text{ST}}$ , and even much larger relative errors ( $4 \times 10^{-7}$ ) for  $C_R$ ,  $c_2$  and  $R_*$ , are due to the larger relative error ( $3.6 \times 10^{-7}$ ) for  $k_B$ . The largest relative error ( $1.6 \times 10^{-6}$ ) is for  $\sigma$ , due to the impact of  $(k_B)^4$ , and thus about 4 times the relative error for  $k_B$ .

The consequence for moist air is a limitation to about 7 significant digits for all quantities that depend on the gas constant ( $R_*$ ), for the impact of the vibrations of the molecules ( $c_2$ ) and for the Sackur-Tetrode constant ( $K_{\text{ST}}$ ) to compute the translational part of the entropy of all gases. As for the radiative quantities, which depend on the Stefan-Boltzmann constant, they are limited to about 7 to 6 significant digits.

• However, in May 2019 and in addition to the speed of light in vacuum which was already set to an exact value

- $c = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$ ,

four other SI base units specified in the International System of Quantities were redefined as exact numerical values, when expressed in SI units:

- the Planck constant  $h = 6.626\,070\,15 \times 10^{-34} \text{ J s}$ ,
- the elementary electric charge  $e = 1.602\,176\,634 \times 10^{-19} \text{ C}$ ,
- the Boltzmann constant  $k_B = 1.380\,649 \times 10^{-23} \text{ J K}^{-1}$ ,
- and the Avogadro constant  $N_A = 6.022\,140\,76 \times 10^{23} \text{ mol}^{-1}$ ,

leading to the exact derived quantities:

- $R_* = 8.314\,462\,62 \text{ J K}^{-1} \text{ mol}^{-1}$  (the gas constant),
- $K_{\text{ST}} = 18.222\,850\,85$  (the Sackur-Tetrode entropy constant),
- $\sigma = 5.670\,374\,42 \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$ ,
- $c_2 = 1.438\,776\,88 \text{ cm K}$ ,
- $C_R = 40.275\,324\,09 \times 10^{-47} \text{ J s}^2 \text{ K}^2$ .

See the documentations:

- [https://en.wikipedia.org/wiki/2019\\_redefinition\\_of\\_the\\_SI\\_base\\_units](https://en.wikipedia.org/wiki/2019_redefinition_of_the_SI_base_units)
- <https://www.bipm.org/en/publications/si-brochure/>

Table 24: *The basic physical constants ( $c$ ,  $h$ ,  $k_B$  and  $N_A$ ) for the CODATA-1973 (Cohen, 1976) used in NIST-JANAF-4 (Chase, 1998), then for the more recent CODATA-2017 (Mohr et al., 2018; Newell et al., 2018) and CODATA-2018 (Tiesinga et al., 2019) datasets. The derived quantities are: the gas constant  $R_* = k N_A$ , the Stefan-Boltzmann constant  $\sigma = (2 \pi^5 k_B^4)/(15 h^3 c^2)$ , the second radiation constant  $c_2 = hc/k_B$ , the Sackur-Tetrode constant  $K_{ST} = 1.5 \ln(2\pi) + 2.5 \ln(k_B) - 3 \ln(h) - 1.5 \ln(N_A)$  and the constant for rotational temperature  $C_R = h^2/(8 \pi^2 k_B)$ . Values in parentheses indicate the accuracy (for the corresponding last digits, like  $C_R = 40.276\,2 \pm 0.001\,7$  for CODATA-1973).*

		CODATA-1973 NIST-JANAF-4 (1998)	CODATA-2017 CODATA-2018
Speed of light in vacuum	$c$	$2.997\,924\,58(1.2) \times 10^8 \text{ m s}^{-1}$	$2.997\,924\,58(0) \times 10^8 \text{ m s}^{-1}$
Planck constant	$h$	$6.626\,176(36) \times 10^{-34} \text{ J s}$	$6.626\,070\,150(69) \times 10^{-34} \text{ J s}$
Boltzmann constant	$k_B$	$1.380\,662(44) \times 10^{-23} \text{ J K}^{-1}$	$1.380\,649\,03(51) \times 10^{-23} \text{ J K}^{-1}$
Avogadro constant	$N_A$	$6.022\,045(31) \times 10^{23} \text{ mol}^{-1}$	$6.022\,140\,758(62) \times 10^{23} \text{ mol}^{-1}$
Gas constant	$R_*$	$8.314\,41(30) \text{ J K}^{-1} \text{ mol}^{-1}$	$8.314\,463(3) \text{ J K}^{-1} \text{ mol}^{-1}$
Stefan-Boltzmann constant	$\sigma$	$5.670\,32(81) \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$	$5.670\,375(9) \times 10^{-8} \text{ W m}^{-2} \text{ K}^{-4}$
Second radiation constant	$c_2$	$1.438\,786(45) \text{ cm K}$	$1.438\,776\,85(53) \text{ cm K}$
Sackur-Tetrode constant	$K_{ST}$	$18.222\,85(10)$	$18.222\,851(1)$
Rotational temp. constant	$C_R$	$40.276\,2(17) \times 10^{-47} \text{ J s}^2 \text{ K}^2$	$40.275\,323(16) \times 10^{-47} \text{ J s}^2 \text{ K}^2$

- The constants in the ARPEGE-IFS models are from the CODATA-86 version (Cohen and Taylor, 1986):  $c = 2.997\,924\,58 \times 10^8 \text{ m s}^{-1}$ ,  $h = 6.626\,075\,5(40) \times 10^{-34} \text{ J s}$ ,  $k_B = 1.380\,658(12) \times 10^{-23} \text{ J K}^{-1}$ ,  $N_A = 6.022\,136\,7(36) \times 10^{23} \text{ mol}^{-1}$  and  $R_* = 8.314\,510(70) \text{ J K}^{-1} \text{ mol}^{-1}$ .
- In the TEOS-10 software and manual (Feistel and TEOS10, 2010) only appear:  
 $N_A = 6.022\,141\,79(30) \times 10^{23} \text{ mol}^{-1}$  and  $R_* = 8.314\,472(15) \text{ J K}^{-1} \text{ mol}^{-1}$ .

Table 25: *The molar masses (in  $\text{g mol}^{-1}$ ) for the moist-air components  $N_2$ ,  $O_2$ ,  $Ar$ ,  $CO_2$  and  $H_2O$ .*

	$N_2$	$O_2$	$Ar$	$CO_2$	$H_2O$
IUPAC-1993 (Mills et al., 1993)	28.013 48(14)	31.998 80(60)	39.948(1)	44.009 8(7)	18.015 28(17)
NIST-JANAF-4 (Chase, 1998)	28.013 40(—)	31.998 80(—)	39.948(—)	44.009 8(—)	18.015 28(—)
TEOS10 (Feistel and TEOS10, 2010)	28.013 40(30)	31.998 80(40)	39.948(1)	44.009 5(9)	18.015 28(4)
IUPAC-2013 (Meija et al., 2016)	28.013 71(63)	31.998 80(54)	39.948(1)	44.009 4(13)	18.015 35(47)
IUPAC-2017 (Meija, 2017)	28.013 71(63)	31.998 80(54)	39.878(63)	44.009 4(13)	18.015 35(47)

- The only difference between IUPAC-2013 and IUPAC-2017 is the smaller value for Argon and with a much greater inaccuracy for the more recent dataset (in between  $39.792 \text{ g mol}^{-1}$  and  $39.963 \text{ g mol}^{-1}$ ).
- Molar masses used in the ARPEGE-IFS models are for  $H_2O$  ( $18.015\,3 \text{ g mol}^{-1}$ ) and dry air ( $28.964\,4 \text{ g mol}^{-1}$ ), from unknown sources.



Table 26: *The molar concentrations for the four main dry-air components  $N_2$ ,  $O_2$ , Ar and  $CO_2$ , from several books and papers.*

	$N_2$	$O_2$	Ar	$CO_2$	total
Benedict (1912, p.71+Table 72)	0.780 91	0.209 38	0.009 4	0.000 310	1.000 00
Krogh (1919, see p.3,19)	0.780 8	0.209 48	0.009 4	0.000 300	0.999 98
Paneth (1937, Table p.436)	0.780 9	0.209 5	0.009 3	0.000 300	1.000 0
Glueckauf (1951, Table V, p.6)	0.780 84	0.209 46	0.009 34	0.000 330	0.999 970
U.S. Standard Atmosphere (1976)	0.780 84	0.209 476	0.009 34	0.000 314	0.999 970
Waxman and Davis (1978)	0.781 2	0.209 2	0.009 3	0.000 320	1.000 02
Jones (1978, Table 1, p.421)	0.781 02	0.209 46	0.009 16	0.000 330	0.999 97
CIPM-81 (1981) Giacomo (1982)	0.781 01	0.209 39	0.009 17	0.000 400	0.999 97
Keeling (1988, Table 1, p.163)	0.780 67	0.209 46	0.009 34	0.000 339	0.999 809
Lemmon et al. (2000, Table 2)	0.781 0	0.209 5	0.009 2	0.000 300	1.000 0
Lemmon et al. (2000, Table 3)	0.781 2	0.209 6	0.009 2	—	1.000 0
Zdunkowski and Bott (2004)	0.780 9	0.209 5	0.009 3	0.000 300	1.000 0
Picard et al. (2008, Table 1, p.151)	0.780 848	0.209 390	0.009 332	0.000 400	0.999 970
Feistel et al. (2010a, Table A2)	(0.780 847 9)	0.209 390	0.009 332	0.000 400	(0.999 969 9)
Picard et al. (2008) rescaled	0.780 878	0.209 390	0.009 332	0.000 400	1.000 000

- Total sum different from unity are due to the concentrations in eight other gases (Ne, He,  $CH_4$ , Kr,  $H_2$ ,  $N_2O$ , CO and Xe), which should be taken into account.
- The last line (“Picard et al. (2008) rescaled”) corresponds to the CIPM-2007 values (Picard et al., 2008), but with a rescaled values for  $N_2$  leading to a total sum of 1.
- The value 0.780 847 9 for  $N_2$  given in Table A2 of Feistel et al. (2010a) should be 0.780 850 9 (this has been validated by Rainer Feistel in May, 2021, personal communication), with a new total of 0.999 972 9 for  $N_2$ ,  $O_2$  Ar and  $CO_2$  and with 0.000 027 1 coming from the eight other gases.

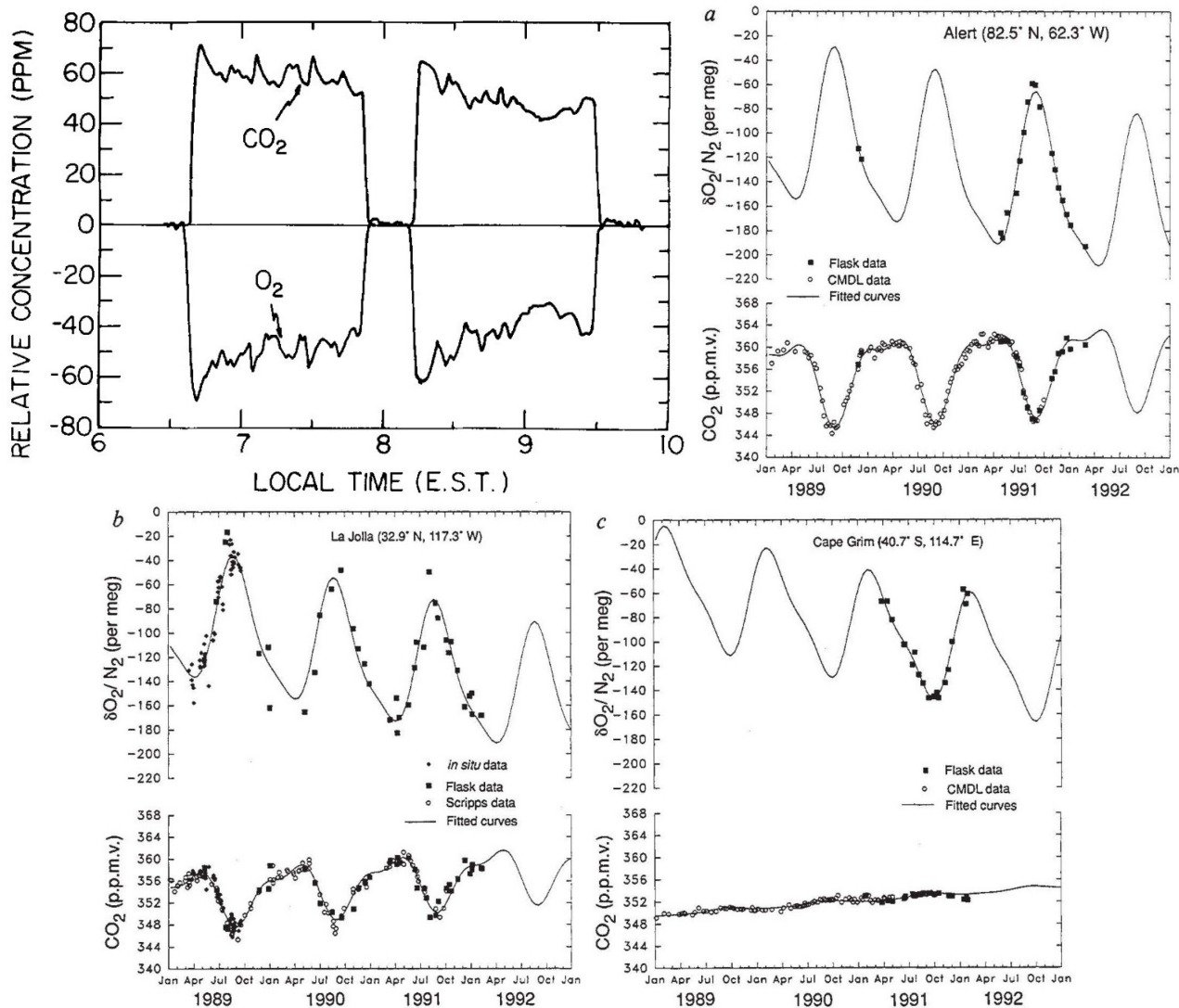


Figure 27: Example of changes in concentrations of O<sub>2</sub> and CO<sub>2</sub> (in “p.p.m.v.”, or the normalized ratio “O<sub>2</sub>/N<sub>2</sub>” (in “per meg”). Top-left: the Fig.2 of Keeling (1988) for selected time intervals on 26 October 1986 at Harvard University in Cambridge, Massachusetts. Top-right and bottom: the Figs. 1 of Keeling and Shertz (1992) and Figs.10.1 of Keeling and Severinghaus (2000) at Albert, Ellesmere Island at 82.5° N in (a), La Jolla, California at 32.9° N in (b) and Cape Grim, Tasmania at 40.7° S in (c).

The molar masses for N<sub>2</sub>, O<sub>2</sub>, Ar, CO<sub>2</sub> and H<sub>2</sub>O are shown in Table 25, where the difference between minimum and maximum values of the intervals provided in IUPAC-2013 and IUPAC-2017 have been translated into an average value equal to half of the sum of minimum and maximum values, with uncertainties equal to  $\pm 1/\exp(1) \approx \pm 0.368$  of the difference between maximum and minimum values.

The relative errors are about  $2 \times 10^{-5}$  for all gases in IUPAC-2013, but with a much larger one  $2 \times 10^{-3}$  for Argon in IUPAC-2017 (value to be confirmed or to be improved).

The consequence for moist air is a limitation to about 6 to 5 significant digits for all quantities that depend on the molar masses.

The atmospheric observed (molar) concentrations of N<sub>2</sub>, O<sub>2</sub>, Ar and CO<sub>2</sub> are shown in Table 26. These four gases represent 99.997 % of the whole dry air. The other gases (Ne, He, CH<sub>4</sub>, Kr, H<sub>2</sub>, N<sub>2</sub>O,

CO and Xe) represent less than 0.000 030 or 30 ppmv, which is about 7 % of the concentration in CO<sub>2</sub> (420 ppmv in 2021).

It is quite impressive to note that the concentrations shown in Table 26 have changed little in almost a century, between 1912 and 2008! However, there is still some uncertainty about these concentrations, due to the fact that concentration in CO<sub>2</sub> may vary in time and space, this in partial or complete proportion to the concentration in O<sub>2</sub>. These concentrations of dry-air components are therefore only indicative and it is not possible to give results with a precision better than about 0.000 05 mol mol<sup>-1</sup>, thus limiting all further calculations based on thermodynamic values for dry air (except by knowing the precise concentrations of O<sub>2</sub> and CO<sub>2</sub> for given time and location in space).

It is explained in Jones (1978) that Glueckauf (1951), in discussing the variation of the abundance of oxygen in the atmosphere, stated that “*all major variations of the O<sub>2</sub> content must result from the combustion of fuel, from the respiratory exchange of organisms, or from the assimilation of CO<sub>2</sub> in plants. The first process does not result in more than local changes of O<sub>2</sub> content, while the latter two processes, though locally altering the CO<sub>2</sub>/O<sub>2</sub> ratio, leave their sum unchanged. The assumed constancy of the sum of the O<sub>2</sub> and CO<sub>2</sub> abundance simplifies the adjustment of dry-air mass to account for departures from the CO<sub>2</sub> reference level and simplifies the estimation of the uncertainty in air density due to an uncertainty in CO<sub>2</sub> abundance. The constancy of the sum is expressed by the equation:*”

$$x_{\text{O}_2} + x_{\text{CO}_2} \approx 0.209\,390 + 0.000\,400 = 0.209\,790 \text{ mol mol}^{-1}. \quad (170)$$

Keeling (1988) similarly shows that the fluctuations in oxygen are strongly anti-correlated with changes in carbon dioxide, due to photosynthesis, respiration, and the burning of fuels (see the top-left part of Figs. 27). However, Keeling and Shertz (1992) and Keeling and Severinghaus (2000) show clear departure from the relation (170) due to imbalanced sources and sinks of O<sub>2</sub> and CO<sub>2</sub>, with in particular exchanges of O<sub>2</sub> between the atmosphere and the oceans (see the other parts (a,b,c) of Figs. 27).

It is finally assumed in Picard et al. (2008) that the mole fraction of carbon dioxide,  $x_{\text{CO}_2}$ , determines the mole fraction of atmospheric oxygen,  $x_{\text{O}_2}$ , from the relation (170), which expresses that processes of respiration, photosynthesis, combustion, etc are the only processes of importance. Therefore, this relationship (170) has been considered as a first-order approximation in this note, and in particular in the last line “Picard et al. (2008) rescaled” of the Table 26 (where the concentration of N<sub>2</sub> has been tuned).

Picard et al. (2008) evaluated a standard uncertainty of  $60 \times 10^{-6} \text{ mol mol}^{-1}$  or 0.000 060 mol mol<sup>-1</sup> for the sum 0.209 790 mol mol<sup>-1</sup> in Eq. (170). This corresponds to a standard uncertainty of  $\pm 60$  ppmv for the concentration in CO<sub>2</sub>, which also corresponds to the observed geographic and time variations of the concentration in CO<sub>2</sub> (for instance, seasonal variations of  $\pm 10.52$  ppmv was observed by Cao et al. (2009, Table 3, p.12) for the concentration of mid-tropospheric CO<sub>2</sub> at 80°N-90°N latitudes).

Therefore, since the concentrations in the Table 26 are to be rescaled to get a sum of 1.000 000, the uncertainties on O<sub>2</sub> and CO<sub>2</sub> impact the concentrations of all species with an uncertainty of the order of  $\pm 30 \times 10^{-6} \text{ mol mol}^{-1}$ , including for N<sub>2</sub> for which the relative error is thus of about  $\pm 4 \times 10^{-5}$ .

As a consequence for dry air, and thus for moist air, there is a limitation to about 5 significant digits for all quantities that depend on the concentrations of N<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub>.

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Before these papers of Glueckauf (1951), Jones (1978), Keeling (1988), Keeling and Shertz (1992), Keeling and Severinghaus (2000) and Picard et al. (2008), Benedict (1912) provided an interesting “*historical account of the development of methods for determining Oxygen (content)*”, back to the 1770s and the observations of Scheele in Sweden, Priestley, Cavendish and Dalton in England, von Humboldt in Germany, Landriani and Volta in Italy, Lavoisier and Gay-Lussac in France, among may others. The conclusion of Benedict (1912) is that: “*the combustion of fuel and the vital processes of men and*

*animals result in a local increase in carbon dioxide and decrease in oxygen on the one hand, and vegetable growth results in a decrease in carbon dioxide and increase in oxygen on the other.*” “*For every 0.01 per cent increase in the atmospheric carbon dioxide, one may safely assume a corresponding decrease in the percentage of oxygen.*”

Carpenter (1937) found that “*the composition of the atmospheric air at Boston with respect to its carbon dioxide and oxygen content was practically constant for a period of time covering nearly three years*” (0.031 % and 20.939 %, respectively). However, Giacomo (1982, CIPM-81 (1981)) retained the hypotheses of Krogh (1904a,b) and Krogh (1919) cited by Paneth (1937) and Glueckauf (1951), corresponding to Eq. (170) and a constant sum of concentrations for  $O_2$  and  $CO_2$ .

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## 12 Validations and physical meaning of absolute entropies / FAQs

### 12.1 Validations and physical meaning of absolute entropies / Nernst (1918-1926)

The way the absolute definition of the entropy has been first 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:

$$\ln\left(\frac{p_s}{p_u}\right) = \ln(p_s) - \ln(p_u) = -\frac{\lambda_0}{RT} + \frac{5}{2} \ln(T) + \frac{3}{2} \ln(M) + i_0. \quad (171)$$

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

$$i_0 = \ln\left[\frac{(2\pi)^{3/2} k^{5/2}}{h^3 N^{3/2}}\right] \approx 18.22285, \quad (172)$$

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

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This equation (171) for  $\ln(p_s)$  was in particular considered by:

- Eqs. 69 and 103, p.102 and 136, by Nernst (1918);
- Eq. 4, p.361, by Nernst (1921, Nobel prize lecture);
- Eq. 476, p.222, by Planck (1921b);
- Eqs. 69 and 84, p.124 and 132, by 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  $i = i_0 + (3/2) \ln(M)$

*“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. 28 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 (172), with a difference of about +21.95. This difference is

Figure 28: Excerpts from Nernst (1926) to show a validation of the Sackur-Tetrode constant  $i_0$ .

CHAPTER XIII			
THEORETICAL CALCULATION OF CHEMICAL CONSTANTS			
$\log_e p = -\frac{\lambda_0}{RT} + 2.5 \log_e T + i, \quad . \quad . \quad (101) \quad (p.166)$			
$i = \log_e \frac{(2\pi)^{3/2} k^{3/2}}{N^{3/2} h^3} + 1.5 \log_e M = i_0 + 1.5 \log_e M, \quad (104) \quad (p.167)$			
$\log_e p = -\frac{\lambda_0}{RT} + 2.5 \log_e T - \frac{1}{R} \int_0^T \frac{E}{T^2} dT + i. \quad (121)$			
after introducing common logarithms (p.179)			
$\log_{10} p = -\frac{\lambda_0}{4.571T} + 2.5 \log_{10} T - \frac{1}{4.570} \int_0^T \frac{E}{T^2} dT + C \quad (122) \quad (p.179)$			
$i = 2.303C. \quad (123)$			
3. Experimental Test.	C	M	$C_0$
H <sub>2</sub> . . .	$-1.23 \pm 0.15$	2.016	$-1.69 \pm 0.15$
Ar . . .	$0.75 \pm 0.06$	39.88	$-1.65 \pm 0.06$
Hg . . .	$1.83 \pm 0.03$	200.6	$-1.62 \pm 0.03$
$C = C_0 + 1.5 \log_{10} M, \quad C_0 = -1.62 \pm 0.03, \quad (p.185)$			
$C = \frac{i}{2.303} = \log_{10} \frac{(2\pi m)^{3/2} k^{3/2}}{h^3}$			
$C = C_0 + 1.5 \log M = -1.608 + 1.5 \log M \quad (125) \quad (p.186)$			

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 (171), 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 (H<sub>2</sub>), 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 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.*

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## 12.2 Validations and physical meaning of absolute entropies / Chemical reactions

- I show/recall in the present section that the absolute definition of the moist-air and seawater entropies must have an impact on several atmospheric and oceanic thermodynamic conditions.

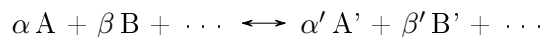
These impacts must occur via the chemical constants  $K_p$ , whose constant values  $K_p^{0??}$  (not depending on the temperature and pressure) depend on the absolute reference entropy of reactants and products.

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- The law of mass action gives the direct and reverse chemical rates

$$r = k [A]^\alpha [B]^\beta \dots \quad \text{and} \quad r' = k' [A']^{\alpha'} [B']^{\beta'} \dots$$

valid for the general reaction



with the equilibrium chemical constant  $K$  given by  $r = r'$ , and thus

$$K = \frac{k}{k'} = \frac{[A']^{\alpha'} [B']^{\beta'} \dots}{[A]^\alpha [B]^\beta \dots}, \quad (173)$$

where  $k$  and  $k'$  are the rate constants (previously called affinity constants).

Moreover a link at equilibrium between  $K$  and the Gibbs free enthalpy of reaction

$$\Delta_r G = \Delta_r H - T \Delta_r S_r = -R T \ln[ K(T) ],$$

leading to

$$K(T) = \exp\left(\frac{-\Delta_r G}{R T}\right) = \exp\left(\frac{\Delta_r S}{R}\right) \times \exp\left[\frac{-\Delta_r H}{R T}\right], \quad (174)$$

$$\text{and thus} \quad \ln[ K(T) ] = \frac{\Delta_r S}{R} - \frac{\Delta_r H}{R T}. \quad (175)$$

A way to predict the direction and extent of an equilibrium chemical reaction is to compute the “*reaction quotient*”  $Q_r$  defined by the right-hand-side of (173)

$$Q_r = \frac{[A']^{\alpha'} [B']^{\beta'} \dots}{[A]^\alpha [B]^\beta \dots}. \quad (176)$$

and only depending on the concentrations of reactants and product, and to compare the numerical value of  $Q_r$  with the constant of reaction  $K(T)$  given by (174), which depends on the temperature  $T$  and the entropy and enthalpy of reaction  $\Delta_r S$  and  $\Delta_r H$ , leading to the following rules due to Le Chatelier’s Principle:

- at equilibrium, the reaction quotient  $Q_r$  is equal to the equilibrium constant  $K(T)$ ;
- if  $Q_r > K$ , the formation of reactants (A and B) is favoured in order to tend towards equilibrium;
- when  $Q_r < K$ , the formation of products (A' and B') is favoured for the same purpose.

These equilibrium property and return-to-equilibrium rules demonstrate a clear physical impact of the absolute values of the entropies used to compute  $\Delta_r S$  in the formula (174) for  $K(T)$ , which impact the observable concentrations in reactants and products in (176). Any arbitrary changes in the value of  $\Delta_r S$  would corresponds to a change in these concentrations.

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• As a first example, it is valuable to study the possible impact of the absolute (third-law) values of the entropy on the ozone chemistry, which mainly controls the temperature profile in the stratosphere.

This ozone chemistry is initiated by the “*Chapman's cycle*” (Chapman, 1930; Dessler, 2000) via the set of three-body reactions:  $O + O \leftrightarrow O_2$ ,  $O + O_2 \leftrightarrow O_3$ ,  $O + O_3 \leftrightarrow 2 O_2$ .

There are so many other chemical reactions involved in the Ozone chemistry that it is not possible to recall all of them. However, it is sufficient to show at least one example of such an impact of the absolute (third-law) entropies to prove that the whole Ozone chemistry is controlled by such impact of the third law of thermodynamic.

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To do so, I will rely on the “*Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies*” published by DeMore et al. (1997), Sander et al. (2003) and the recent NASA-JPL publication 19-5 by Burkholder et al. (2020).

The aim of these NASA Panel is to be “*used primarily to model stratospheric and upper tropospheric processes, with particular emphasis on the ozone layer and its possible perturbation by anthropogenic and natural phenomena.*” In these NASA Panel are published: “*tables of Arrhenius A-factors and  $E_a/R$  for virtually every second-order reaction of stratospheric interest.*”

In particular, Burkholder et al. (2020, p.3-1) define the “*equilibrium constants*, as

$$K_{eq}(T) / cm^3 molecule^{-1} = A \exp\left(\frac{B}{T}\right), \quad (177)$$

$$\ln [K_{eq}(T) / cm^3 molecule^{-1}] = \ln(A) + \frac{B}{T}. \quad (178)$$

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 recalled in (175):

$$\ln [K_{eq}(T) / bar^{-1}] = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{R T}, \quad (179)$$

$$\ln [K_{eq}(T) / cm^3 molecule^{-1}] = \frac{\Delta_r S^\circ}{R} - \frac{\Delta_r H^\circ}{R T} + \ln(T) - 21.87 \times \ln(10), \quad (180)$$

where the superscript “ $\circ$ ” refers to a standard state of one bar.”

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Note that the relationship (180) including the  $\ln(T)$  term is known as the Eyring-Polanyi formulation based on statistical physics and including the impact of transition state theory, also known as activated-



complex theory, leading to the alternative but equivalent definition of  $A'$  and  $B'$  factors via

$$\ln[ K_{\text{eq}}(T) / \text{cm}^3 \text{ molecule}^{-1} ] = \ln(A') + \frac{B'}{T} \quad \text{and thus} \quad K_{\text{eq}}(T) = A' \exp\left(\frac{B'}{T}\right), \quad (181)$$

$$\text{with} \quad A' = \left( \frac{e R' T}{N_A} \right) \times \exp\left(\frac{\Delta_r S^\circ}{R}\right), \quad (182)$$

$$\text{and} \quad B' = - \left( \frac{\Delta_r H^\circ + R T}{R} \right) = - \frac{\Delta_r H^\circ}{R} - T, \quad (183)$$

where  $e = \exp(1) \approx 2.7183$ ,  $N_A \approx 6.02 \times 10^{23} \text{ molecules mol}^{-1}$  and  $R \approx 8.3145 \text{ J K}^{-1} \text{ kg}^{-1}$  are the basis of the natural logarithms, the Avogadro and gas constants, respectively.

The explanation for the other terms  $-21.87 \times \ln(10) \approx 50.36$  and  $R' \approx 83.145 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$  in (180) and (182) can be found by considering the molar equation of gases  $P V = n R T$  with  $n = 1$ , the volume  $V$  in  $\text{m}^3$ , the temperature  $T$  in Kelvin and the pressure  $P$  in Pascal.

Differently from these U.S.I units definitions, Burkholder et al. (2020, p.3-1) wrote (181) to (183) with  $1 \text{ m}^3 = 10^6 \text{ cm}^3$  for  $V$  and for a pressure of  $P = 1 \text{ bar} = 10^5 \text{ Pa}$ , and thus  $1 \text{ Pa} = 10^{-5} \text{ bar}$  leading to the above definition for  $R' = (10^6 \times 10^{-5}) R = 10 R \approx 83.145 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$  in the first term of  $A'$  (whereas  $R \approx 8.3145 \text{ J K}^{-1} \text{ kg}^{-1}$  must be used in all other terms of  $A'$  and  $B'$ ). Moreover, the term  $-21.87 \times \ln(10) \approx -50.36$  corresponds to the quantity  $\ln(R' / N_A) \approx \ln(1.3811 \times 10^{-22}) \approx -50.33$ , with the quantity  $e = \exp(1)$  in the first term of (182) balancing the last term  $-T$  in (183).

Burkholder et al. (2020, p.3-1) further explains that: “*When the entropy is known (or can be calculated from molecular properties) as a function of temperature, experimental values of  $K_{\text{eq}}(T)$  can be used to extract a value for  $\Delta_r H^\circ$ , and  $K_{\text{eq}}(T)$  can be calculated over a wide temperature range (Third law method).*”

The parameters  $A'$  and  $B'$  –corresponding to (182) and (183)– can then be determined from a linear fit via (181) of  $\ln(K_{\text{eq}})$  in terms of  $1/T$ . When only thermochemical values at 298 K were available, they were treated as temperature independent and used to calculate the equilibrium constants between 200 and 300 K:

$$B' \approx 600 \times \ln \left[ \frac{K_{\text{eq}}(200 \text{ K})}{K_{\text{eq}}(300 \text{ K})} \right] \quad \text{and} \quad \ln(A') \approx \ln(K_{\text{eq}}) - \frac{B'}{T}.$$

Otherwise, the relationships between the parameters  $A'$  and  $B'$  in (181) and the quantities  $\Delta_r S^\circ(298 \text{ K})$  and  $\Delta_r H^\circ(298 \text{ K})$  are given by (182) and (183)”

As a concrete examples of existing physical impacts of the absolute third-law values for entropies, I show in the Table 27 the values of the reaction constant  $A'$  computed from the relationship (182) for the reaction  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$  and from the entropy of reaction  $\Delta_r S^\circ = S^\circ(\text{N}_2\text{O}_3) - S^\circ(\text{NO}_2) - S^\circ(\text{NO})$ , which is computed with the absolute entropies  $S^\circ$  for the reactants and product at 298 K and 1 Bar in units of  $\text{J K}^{-1} \text{ kg}^{-1}$ .

The value  $A' \approx 3.3 \times 10^{-27} \text{ cm}^3 \text{ molecule}^{-1}$  recalled in the Table 27 and published in the Table 3-1 by Burkholder et al. (2020, p.3-1) for this reaction  $\text{NO} + \text{NO}_2 \rightleftharpoons \text{N}_2\text{O}_3$  is in agreement with the B-2020 ( $4.18 \times 10^{-27}$ ) and C-1998 ( $4.15 \times 10^{-27}$ ) values computed from the absolute entropies published by Burkholder et al. (2020, B-2020, Table 7-2, p.7-3) and Chase (1998, C-1998), respectively.

Similarly, I show in the Table 28 that the value  $A' \approx 1.24 \times 10^{-24} \text{ cm}^3 \text{ molecule}^{-1}$  published in the Table 3-1 by Burkholder et al. (2020, p.3-1) for the reaction  $\text{Cl} + \text{O}_2 \rightarrow \text{ClO}_2$  is of the same order of magnitude as those B-2020a ( $0.666 \times 10^{-24}$ ), B-2020b ( $1.455 \times 10^{-24}$ ) and C-1998 ( $0.592 \times 10^{-24}$ ) values computed from the absolute entropies published by Burkholder et al. (2020, B-2020a, Table 7-2, p.7-3 and 7-11), Burkholder et al. (2020, B-2020b, note 17, p.3-12 and Table 7-2, p.7-3 and 7-11) and Chase (1998,

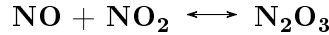
C-1998), respectively. The best agreement is obtained with the enhanced values for absolute entropy indicated in the note 17 (p.3-12) of Burkholder et al. (2020, B-2020b), with the value  $S^\circ(\text{ClOO}) \approx 66.02 \text{ cal K}^{-1} \text{ kg}^{-1} \approx 276.2 \text{ J K}^{-1} \text{ kg}^{-1}$  obtained by Müller and Willner (1993) using vibrational frequencies. Using, instead, the harmonic vibrational frequencies from Abbott and Schaefer III (2018) and isotope shifts (Abbott other communication, 2018) leads to  $S^\circ(\text{ClOO}) \approx 66.32 \text{ cal K}^{-1} \text{ kg}^{-1} \approx 277.5 \text{ J K}^{-1} \text{ kg}^{-1}$ . Accordingly, I have used for B-2020b the mean value  $276.8 \text{ J K}^{-1} \text{ kg}^{-1}$ .

As a consequence of the previous computations, we can say that the experimental values for the pre-exponential factor  $A'$  in the constants of many reactions involved in the  $\text{O}_3$ -chemistry are similar to those computed with (182) from the theoretical values of the third-law absolute entropies.

Therefore, the concentration of  $\text{O}_3$  in the stratosphere depends on the values of the theoretical values of the third-law absolute entropies, which means that, via the impact of radiative fluxes, the temperature in the stratosphere depends on the values of the theoretical values of the third-law absolute entropies.

Table 27: Values of  $A'$  (in  $\text{cm}^3 \text{ molecule}^{-1}$ ) computed from (182) and from values of absolute entropies  $S^\circ$  and (absolute) entropies of reaction  $\Delta_r S^\circ = S^\circ(\text{N}_2\text{O}_3) - S^\circ(\text{NO}_2) - S^\circ(\text{N}_2\text{O}_3)$  at 298 K and 1 Bar (in units of  $\text{J K}^{-1} \text{ kg}^{-1}$ ), for:

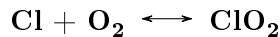
- the Tables 3-1 and 7-2 published in Burkholder et al. (2020, noted **B-2020**, p.3-3 and p.7-3);
- the NIST-JANAF4 dataset (Chase, 1998, noted **C-1998**)
- to be compared with the B-2020 (Tables 3-1) value  $A' \approx 3.3 \cdot 10^{-27} \text{ cm}^3 \text{ molecule}^{-1}$



	$S^\circ(\text{NO})$	$S^\circ(\text{NO}_2)$	$S^\circ(\text{N}_2\text{O}_3)$	$\Delta_r S^\circ$	$A'$
<b>B-2020</b>	216.76	240.17	314.74	-142.19	$4.18 \cdot 10^{-27}$
<b>C-1998</b>	210.76	240.04	308.54	-142.26	$4.15 \cdot 10^{-27}$

Table 28: Values of  $A'$  (in  $\text{cm}^3 \text{ molecule}^{-1}$ ) computed from (182) and from values of absolute entropies  $S^\circ$  and (absolute) entropies of reaction  $\Delta_r S^\circ = S^\circ(\text{Cl}) - S^\circ(\text{O}_2) - S^\circ(\text{ClO}_2)$  at 298 K and 1 Bar (in units of  $\text{J K}^{-1} \text{ kg}^{-1}$ ), for:

- the Tables 3-1 and 7-2 published in Burkholder et al. (2020, noted **B-2020a**, p.3-3, p.7-3 and p.7-11);
- the same Tables published in Burkholder et al. (2020, noted **B-2020b**, p.3-3, p.7-3 and p.7-11), but with a different value for  $S^\circ(\text{ClO}_2)$  described p.3-12;
- the NIST-JANAF4 dataset (Chase, 1998, noted **C-1998**)
- to be compared with the B-2020 (Tables 3-1) value:  $A' \approx 1.24 \cdot 10^{-24} \text{ cm}^3 \text{ molecule}^{-1}$



	$S^\circ(\text{Cl})$	$S^\circ(\text{O}_2)$	$S^\circ(\text{ClO}_2)$	$\Delta_r S^\circ$	$A'$
<b>B-2020a</b>	165.19	205.152	270.3	-100.04	$0.666 \cdot 10^{-24}$
<b>B-2020b</b>	165.19	205.15	276.8	-93.54	$1.455 \cdot 10^{-24}$
<b>C-1998</b>	165.19	205.15	269.32	-101.02	$0.592 \cdot 10^{-24}$

• In a way similar to the previous study of the stratospheric  $\text{O}_3$ -chemistry, it is possible to show that the composition of seawater in terms of its anions and cations must be influenced by the absolute (third-law) entropies via the chemical reaction constant  $K$ , or better its logarithm  $\ln(K)$ .

To do this, I will rely on the “*Handbook on carbon dioxide system in seawater*” written by the U.S. D.O.E. (Departement of Energy DOE, 1994, by Andrew G. Dickson & Catherine Goyet), where thermodynamics properties of several of the seawater chemical reactions are described. Of course, there are

so many other chemical reactions involved in the seawater that it is not possible to recall all of them. However, it is sufficient to show at least one example of such an impact of the absolute (third-law) entropies to prove that the whole seawater chemistry is controlled by such impact of the third law of thermodynamic.

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An important seawater chemical reaction is  $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  (ionization of the bicarbonate anion  $\text{HCO}_3^-$ ), which may be impacted by the corresponding chemical change in absolute entropy  $\Delta_r S^\circ = S^\circ(\text{CO}_3^{2-}) + S^\circ(\text{H}^+) - S^\circ(\text{HCO}_3^-) = S^\circ(\text{CO}_3^{2-}) - S^\circ(\text{HCO}_3^-)$  with the standard hypothesis that  $S^\circ(\text{H}^+) = 0 \text{ J K}^{-1} \text{ kg}^{-1}$ .

This chemical reaction  $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  is studied in the DOE (1994, Eq. 7.2.13, p.15) Handbook, with the resulting equilibrium constant of reaction:

$$\begin{aligned} \ln \left( \frac{K_2}{k^0} \right) = & - \frac{3351.6105}{T} - 9.226508 - 0.2005743 \ln(T) \\ & - \left( \frac{23.9722}{T} + 0.10690177 \right) \sqrt{S} + 0.1130822 S \\ & - 0.00846934 S \sqrt{S} + \ln(1 - 0.001005 S) , \end{aligned} \quad (184)$$

where  $k^0 = 1 \text{ mol} \cdot (\text{kg} \cdot \text{soln})^{-1}$  and  $S$  is the salinity. This relationship is almost the same as Eqs. 30 (p.254) derived by Roy et al. (1993):

$$\begin{aligned} \ln(K_2^*) = & - \frac{3351.6106}{T} - 9.226508 - 0.2005743 \ln(T) \\ & - \left( \frac{23.9722}{T} + 0.10690173 \right) \sqrt{S} + 0.1130822 S - 0.00846934 S \sqrt{S} , \end{aligned} \quad (185)$$

but without the last term of (184) due to the change of unit of  $K_2/k^0$  from  $K_2^*$ , and also with the last digits modified in two of the numerical constants. The temperature and salinity range of (185) was:  $0 < t < 45^\circ\text{C}$  and  $5 < S < 45 \text{ g kg}^{-1}$  (Roy et al., 1993, Table 1, p.250).

Note that this relationship (185) has been rewritten by Roy et al. (1993, Eqs. 31, 33 and 35, p.255) who: “*forced the values at  $S = 0$  to be equal to the values in pure water,  $\ln(K_2)$* ”

$$\ln(K_2^*) = \ln(K_2) + B \sqrt{S} + C S + D S \sqrt{S} + E S^2 , \quad (186)$$

where the values of the thermodynamic constants for the dissociation of carbonic acid in pure water are given by Millero (1979, Table 1, p.1652):

$$\boxed{\ln(K_2) = - \frac{11843.79}{T} + 207.6548 - 33.6485 \ln(T)} . \quad (187)$$

The full equations with the  $B$ ,  $C$ , etc. parameters are given by (Roy et al., 1993, Eqs. 35, p.255):”

$$\begin{aligned} \ln(K_2^*) = & \ln(K_2) + \left( -167.69908 + \frac{6551.35253}{T} + 25.928788 \ln(T) \right) \sqrt{S} \\ & + \left( 39.75854 - \frac{1566.1388}{T} - 6.171951 \ln(T) \right) S \\ & + \left( -2.892532 + \frac{116.270079}{T} + 0.45788501 \ln(T) \right) S \sqrt{S} - 0.00613142 S^2 . \end{aligned} \quad (188)$$

Note that the citation mentioned in the Table 1 of Millero (1979, p.1652) for the thermodynamic constants for the dissociation of carbonic acid in pure water was Harned and Scholes (1941), where  $\ln(K_2)$  was written differently (Eq. 9, p.1709) as:

$$\log_{10}(K_{2A}) = -\frac{2902.39}{T} + 6.4980 - 0.02379 T,$$

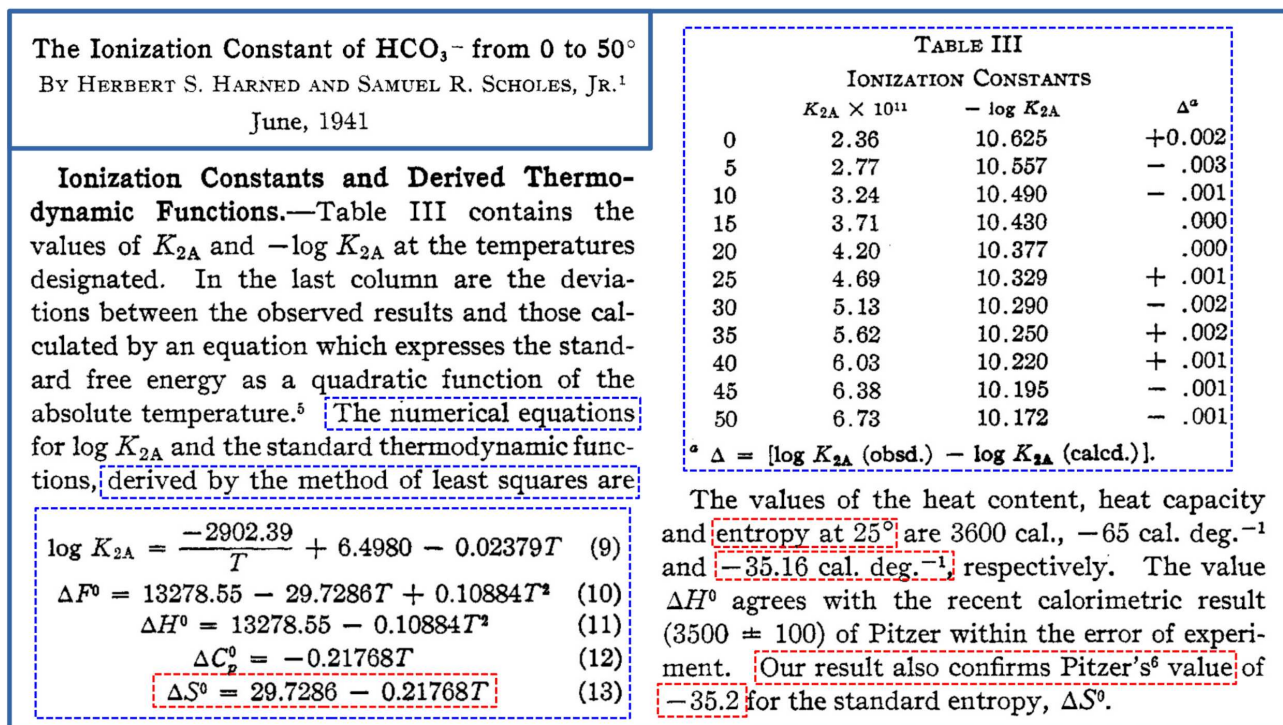
or equivalently  $\ln(10) \times \log_{10}(K_{2A}) = \boxed{\ln(K_{2A}) = -\frac{6683}{T} + 14.962 - 0.05478 T}, \quad (189)$

with the linear term  $T$  in (189) replaced by the  $\ln(T)$  function in the last term of (187), and with the three constants retuned.

It is easy to check that the two boxed relationships (189) and (187) for  $\ln(K_{2A})$  and  $\ln(K_2)$  give the same results for  $273.15 < T < 328.15$  K ( $0 < t = T - 273.15 < 50^\circ\text{C}$ ), with both  $\ln(K_{2A})$  and  $\ln(K_2)$  remaining close to  $-24$  units (between  $-24.5$  and  $-23.4$ ) and being very close to each others up to better than  $0.0005$  unit ( $0.002\%$ ) for  $13 < t < 50^\circ\text{C}$ , and to better than  $0.007$  unit ( $0.03\%$ ) for  $0 < t < 13^\circ\text{C}$ .

- It is therefore possible to rely on the study of Harned and Scholes (1941) to investigate the thermodynamic properties of the ionization of the bicarbonate reaction  $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ .

Figure 29: Some excerpts from the paper of Harned and Scholes (1941, Table-III, p.1708, and last section, p.1709) on the ionization constant for the reaction  $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  from  $0$  to  $50^\circ$  " where experimental value of the entropy of reaction ( $-35.16$  unit) is very close to the theoretical value ( $-35.2$  unit).



To do so, I recall in the Fig. 29 that Harned and Scholes (1941) not only computed the chemical constant  $K_{2A}$  with a method of least squares, but they also derived the adjustment formulas for the heat content ( $\Delta H^0$ ), heat capacity ( $\Delta C_p^0$ ) and entropy ( $\Delta S^0$ ) changes of reaction in Eqs. 11 to 13 (p.1709).

In particular, Harned and Scholes (1941, p.1709) assumed the hypothesis that the change in heat capacity can be written as the linear law  $\Delta C_p^0 = -2 D T$ , leading to the change in heat content computed with  $d/dT(\Delta H^0) = \Delta C_p^0$ , leading to  $\Delta H^0 = A - D T^2$ , with the change in entropy computed as the integral  $\Delta S^0 = \int C_p^0(T) d \ln(T) = C - 2 D T$ , where  $A$  and  $C$  and two constant of integration.

Accordingly, the Gibbs function can be written as  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = A - C T + D T^2$  corresponding to the relationship (10) studied by Harned and Scholes (1941), but noted  $\Delta F^\circ$ , which is also equal to  $-R T \ln(K_2)$  and thus with  $\ln(K_2) = -A/(R T) + C/R - (D/R) T$  corresponding to the relationship (9) studied by Harned and Scholes (1941).

The three constant  $A$ ,  $C$  and  $D$  were then determined from experimental data via the method of least squares, leading to the values in Eqs. 11 to 13 of Harned and Scholes (1941, p.1709) shown in the Fig. 29.

The important feature is that the constant  $C$ , which is determined by the adjustment of  $R \ln[K_2(T)] = \Delta_r S^\circ - \Delta_r H^\circ/T = C + (...)$  to observations made at different temperatures, must impact the chemical change in entropy  $\Delta S^0 = C - 2 D T$  via its constant term, which means that the third-law (absolute) values of the entropies must influence this term  $C$ .

- Harned and Scholes (1941, p.1709) explained that the observed value at 25°C

$$\Delta S^0 = -35.16 \text{ cal K}^{-1} \text{ kg}^{-1} \quad \text{or} \quad \Delta S^0 = -147.1 \pm 0.25 \text{ J K}^{-1} \text{ kg}^{-1}$$

was in full agreement with the value previously published by Pitzer (1937, see the line for Carbonic (2d) in the Table IV, p.2368):

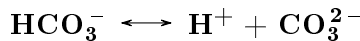
$$\Delta S^0 = -35.2 \pm 0.2 \text{ cal K}^{-1} \text{ kg}^{-1} \quad \text{or} \quad \Delta S^0 = -147.3 \pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1}.$$

I have computed the uncertainty  $\pm 0.25 \text{ J K}^{-1} \text{ kg}^{-1}$  for the experimental value of  $\Delta S^0$  thanks to the relationship  $\Delta G^0 = \Delta H^0 - T \Delta S^0 = -R T \ln(K)$ , with therefore a crude evaluations of  $\delta \Delta S^0 \approx R \delta \ln(K) \approx 8.314 \times 0.003 \approx 0.25 \text{ J K}^{-1} \text{ kg}^{-1}$ , with the value 0.003 being the largest value for  $\Delta$  in the Table III recalled in the Fig. 29. I have assumed that the uncertainty for the theoretical value of  $\Delta S^0$  may be of  $\pm 0.2 \text{ cal K}^{-1} \text{ kg}^{-1}$ , which corresponds to the uncertainty of next theoretical computations and to  $\pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1}$ .

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Table 29: *Values of absolute (third-law) entropies (in  $\text{J K}^{-1} \text{ kg}^{-1}$ ) for  $\text{HCO}_3^-$ ,  $\text{H}^+$  and  $\text{CO}_3^{2-}$  from:*

- *a recall of the line for Carbonic (2d) in the Table IV of Pitzer (1937, p.2368);*
- *the values of the book of Lewis and Randall (1961);*
- *the values of the USG-1452 (1978) Bulletin of Robie et al. (1978)*
- *the CODATA-1989 values from Cox et al. (1989);*
- *the NEA-TDB (1992-2020) values from Grenthe et al. (1992, 2020b).*



	$S^\circ(\text{HCO}_3^-)$	$S^\circ(\text{H}^+)$	$S^\circ(\text{CO}_3^{2-})$	$\Delta_r S^\circ$
Pitzer (1937)				$-147.3 \pm 1.7$
Lewis and Randall (1961)	95	(0)	-51.3	-146.3
USG-1452 (1978)	$91.20 \pm 0.85$	(0)	$-56.90 \pm 0.85$	$-148.1 \pm 1.7$
CODATA (1989)	$98.4 \pm 0.5$	(0)	$-50 \pm 1$	$-148.4 \pm 1.5$
NEA-TDB (1992-2020)	$98.4 \pm 0.5$	(0)	$-50. \pm 1$	$-148.4 \pm 1.5$

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- It is possible to compute more recent values for the theoretical value of  $\Delta S^0$ , given by the absolute (third-law) values of the entropies shown in the Table 29 for  $\text{HCO}_3^-$ ,  $\text{H}^+$  and  $\text{CO}_3^{2-}$ .

The Table 29 shows that the chemical change in absolute (third-law) entropy  $\Delta_r S^\circ$  due to the reaction

$\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  are similar in the new Thermochemical Tables than in the old theoretical value of Pitzer (1937). This means that the agreement between the experimental and theoretical (third-law) change in entropy mentioned by Harned and Scholes (1941) is still valid.

- As a consequence of the previous computations, we can say that the experimental and theoretical values for the constant of reaction are in agreement for at least one of the seawater chemical reaction ( $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$ ) and this constant of reaction  $K_2$  depends on the absolute (third-law) values of the entropies for  $\text{HCO}_3^-$ ,  $\text{H}^+$  and  $\text{CO}_3^{2-}$  via the relationships  $\Delta_r G^\circ = \Delta_r H^\circ - T \Delta_r S^\circ = -RT \ln(K_2)$  and  $\Delta_r S^\circ = S^\circ(\text{CO}_3^{2-}) + S^\circ(\text{H}^+) - S^\circ(\text{HCO}_3^-)$ .

Note that the conventional choice  $S^\circ(\text{H}^+) = 0$  has no impact on the entropy of reaction because any other arbitrary additional term  $S^\circ(\text{H}^+) = +\Lambda$  would imply a change  $-\Lambda$  for  $S^\circ(\text{HCO}_3^-)$  and a change  $-2\Lambda$  for  $S^\circ(\text{CO}_3^{2-})$  due to the electric charges of these ions, all these modifications leaving  $\Delta_r S^\circ$  unchanged due to the conservation of the electric charges and to  $-2\Lambda + \Lambda + \Lambda = 0$ .

Other chemical reactions involving the sea-salts ions must similarly depend on the changes in absolute (third-law) values for these ions. Some of these seawater reactions (Acid-Base equilibria, Carbonate system, ..) have been listed and considered by DOE (1994) and Frank (2016), among others:

- $\text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+ + \text{OH}^-$  ;  $\text{HSO}_4^- \leftrightarrow \text{H}^+ + \text{SO}_4^{2-}$  ;  $\text{HF} \leftrightarrow \text{H}^+ + \text{F}^-$  ;
- $\text{MgOH}^+ \leftrightarrow \text{OH}^- + \text{Mg}^{2+}$  ;  $\text{CO}_2(\text{g}) \leftrightarrow \text{CO}_2(\text{aq})$  ;  $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+ + \text{HCO}_3^-$  ;
- $\text{HCO}_3^- \leftrightarrow \text{H}^+ + \text{CO}_3^{2-}$  ;  $\text{Ca}^{++} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3(\text{s})$  ;  $\text{H}_2\text{CO}_3 \leftrightarrow \text{CO}_2 + \text{H}_2\text{O}(\text{l})$  ;
- $\text{H}_3\text{PO}_4 \leftrightarrow \text{H}^+ + \text{H}_2\text{PO}_4^-$  ;  $\text{H}_2\text{PO}_4^- \leftrightarrow \text{H}^+ + \text{HPO}_4^{2-}$  ;  $\text{HPO}_4^{2-} \leftrightarrow \text{H}^+ + \text{PO}_4^{3-}$  ;
- $\text{Si}(\text{OH})_4 \leftrightarrow \text{H}^+ + \text{SiO}(\text{OH})_3^-$  ;  $\text{B}(\text{OH})_3 + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{H}^+ + \text{B}(\text{OH})_4^-$  ;
- and so many other reactions involving the ions  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{K}^+$ ,  $\text{I}^-$ ,  $\text{F}^-$ ,  $\text{Br}^-$ , ...

Therefore, the concentrations of ions in the seawater depend on the values of the theoretical values of the third-law absolute entropies of the sea-salt ions and the liquid water.

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- As a general conclusion of this section, I have shown how the absolute (third-law) values of the entropies must influence the observed values of the concentrations of ozone in the atmosphere and sea salts in the oceans, which are observable quantity.

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### 12.3 Validations and physical meaning of absolute entropies / $\text{H}_2\text{O}$ at $25^\circ\text{C}$

In order to always maintain a critical mind and must be able to reproduce the results obtained by our elders, I have patiently undertaken for more than 10 years to recalculate the absolute entropies from theoretical and experimental data for the main gases making up the atmosphere ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ ,  $\text{CO}_2$ , dry air,  $\text{H}_2\text{O}$ ).

I recall in the Table 30 the values of the absolute entropies shown in the Table 1 that I have computed at  $T_0 = 0^\circ\text{C}$  and  $p_0 = 1000$  hPa in the Sections 3 and 4, where:

- 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 (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 the calorimetric method, by integrating the quantity  $C_p(T)/T$  from 0 K to the standard temperatures  $T_0$  ( $0^\circ\text{C}$  or  $25^\circ\text{C}$ ), 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  $\text{H}_2\text{O}$  only, due to the hydrogen bounds).

Table 30: *The same standard absolute entropies  $s_0(T_0, p_0)$  (in J/K/kg) at  $T_0 = 273.15$  K and  $p_0 = 1000$  hPa as in the Table 1 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.

- In addition to the low-temperatures validations of the Sackur-Tetrode third-law entropy constants  $C_0$  made close to 0 K by Nernst (1926, p.185-186) for  $H_2$ , Ar and Hg and recalled in the previous Section 12.1, it is possible to show another modern validation of the same theoretical and calorimetric third law values computed at the ambient temperature 0°C and for the water-vapour and ice-Ih entropies.

These two applications allow the computation of the saturation pressures, like  $p_s$  given by (171), from the third-law absolute entropies, like  $i_0$  given by (172), and if the latent heats, like  $\lambda_0$ , are known.

- To do so, I have first computed (see the Section 4.6) the third-law statistical-quantum value

$$\eta_{v/3rd}^{\text{stat.}}(T_0, p_0) \approx 10318 \pm 0.63 \text{ J K}^{-1} \text{ kg}^{-1}$$

via the relationship  $\eta = k \ln(W)$  represented by the blue arrow and path up to the blue disk in the Fig. 30(b) and with  $W$  corresponding to the translational, rotational and vibrational degrees of freedom of the 3D molecule  $H_2O$ .

I have also computed computed (see the Section 3.5) in a completely independent way the absolute calorimetric entropy

$$\eta_{i/3rd}^{\text{calor.}}(T_0) \approx 2295 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$$

for  $H_2O$  ice-Ih at 0°C via the relationship  $\eta_0 + \int_0^T c_p(T') d\ln(T')$  represented by the red arrow and path up to the red disk in the Fig. 30(b), with the values of  $c_p(T)$  plotted in the Fig. 30(a) and where  $\eta_0 \approx 189 \text{ J K}^{-1} \text{ kg}^{-1}$  is the Pauling-Nagle residual entropy at 0°K.

It is then possible to compute the calorimetric water-vapour entropy

$$\eta_{v/3rd}^{\text{calor.}}(T_0, p_0) \approx 10320 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$$

at  $T_0 = 273.15$  K and  $p_0 = 10^5$  Pa from the relationship

$$\eta_{v/3rd}^{\text{calor.}}(T_0, p_0) = \eta_{i/3rd}^{\text{calor.}}[T_0, p_{\text{sat}}(T_0)] + \frac{L_s(T_0)}{T_0} - R_v \ln \left[ \frac{p_0}{p_{\text{sat}}(T_0)} \right], \quad (190)$$

where  $L_s(T_0) \approx 2834.5 \pm 0.5 \text{ kJ kg}^{-1}$  is the latent heat of sublimation,  $R_v \approx 461.52 \text{ J K}^{-1} \text{ kg}^{-1}$  the gas constant for  $\text{H}_2\text{O}$  and  $p_{\text{sat}}(T_0) \approx 611.15 \pm 0.10 \text{ Pa}$  the water-vapour saturation pressure over ice-Ih at  $0^\circ\text{C}$ .

- Clearly, the absolute third-law calorimetric value ( $10320 \pm 13$ ) and the statistical-quantum entropies value ( $10318 \pm 13$ ) are in close agreement up to 0.02 %. This is another validation of the third law of thermodynamics.

- Conversely, one can use (190) to calculate either the latent heat of sublimation  $L_s(T_0)$  or the saturation pressure  $p_{\text{sat}}(T_0)$  variable from the other variable and from the “difference in third-law entropies”

$$\delta\eta(T_0, p_0) = \eta_{v/3\text{rd}}^{\text{stat.}}(T_0, p_0) - \eta_{i/3\text{rd}}^{\text{calor.}}[T_0, p_{\text{sat}}(T_0)] \approx 8023 \pm 2.5 \text{ J K}^{-1} \text{ kg}^{-1}$$

(i.e. the green arrow in the Fig. 30(b) in between the red and blue disks), by using the relationships

$$L_s(\delta\eta, p_{\text{sat}}, T_0, p_0) = T_0 \left\{ \delta\eta(T_0, p_0) + R_v \ln \left[ \frac{p_0}{p_{\text{sat}}(T_0)} \right] \right\} \quad (191)$$

$$\text{or } p_{\text{sat}}(\delta\eta, L_s, T_0, p_0) = p_0 \exp \left[ \frac{\delta\eta(T_0, p_0)}{R_v} - \frac{L_s(T_0)}{R_v T_0} \right] \quad (192)$$

to arrive at

$$L_s(T_0) \approx 2834.0 \pm 0.7 \text{ kJ kg}^{-1} \quad \text{or} \quad p_{\text{sat}}(T_0) \approx 609 \pm 6 \text{ Pa},$$

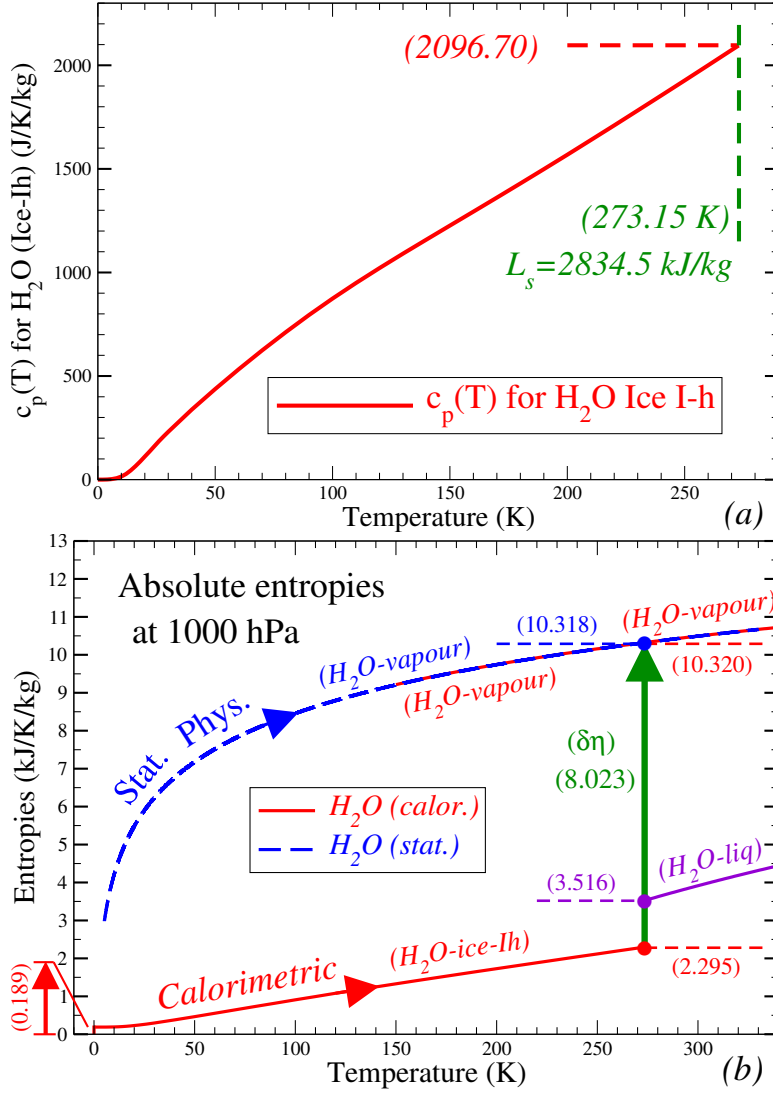
which are indeed in agreement with the experimental values with a good accuracy.

- 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.

- 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  $L_s(T_0)$  and  $p_{\text{sat}}(T_0)$ , which are generally considered to be independent experimental constants.



Figure 30: **(a)**: The specific heat at constant pressure  $c_p(T)$  for  $H_2O$  (Ice-Ih) for absolute temperatures  $T$  from 0 K to  $T_0 = 273.15$  K. **(b)**: The absolute entropies for  $H_2O$  (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 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 absolute entropies at  $T_0 = 273.15$  K.



## 12.4 Validations and physical meaning of absolute entropies / Absolute-Relative?

It is often considered by several referees of my papers that the concept of “absolute entropy” could be accompanied by the concept of “relative entropy” for which one could arbitrarily modify the reference values, as done in TEOS10-SIA and other studied of the moist-air atmosphere entropy for defining the equivalent values  $s_e(\theta_e)$  or the liquid-water value  $s_l(\theta_l)$  with a cancellation of the moist-air absolute-entropy increment  $\Delta s = (s_{vr} - s_{dr}) \times (q_v + q_l + q_i)$ , or as done in TEOS10-GSW for defining the sea-salts oceanic entropy with a cancellation of the absolute-entropy increment  $\Delta \eta = (\eta_{s0} - \eta_{w0}) \times (S_A - S_{S0})/1000$ .

It was indeed tempting to imagine that this “relative entropy”  $S_{rel}$  could correspond to a sort of “available part of the entropy”  $S_{rel} = S - S_{ref}$ , with  $S$  the non-interesting absolute entropy (that would not need to be computed) and  $S_{ref}$  the unavailable part of the absolute entropy, just as the available energy is defined in general thermodynamics by a difference  $A = U - U_{ref}$  with respect to a certain dead-state reference energy.

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In fact, the concept of “*relative entropy*” cannot be appealed to name the present standard value of atmospheric (liquid-water or equivalent) nor seawater (TEOS10) entropy, because the concept of “*relative entropy*” was already named by Shannon’s and is also known as the Kullback’s function, which is related but is different from the (information) entropy.

I explain or recall in the following that, 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) 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  $U$  into available  $A$  and unavailable  $U_0 + T (S - S_0)$  parts,
  - 5) in the suggested decomposition  $S_{abs.} = (S_{abs.} - S_{rel.}) + S_{rel.}$  the term  $(S_{abs.} - S_{rel.})$  can be computed.
- 

I have already explained in the Section 3 of the paper Marquet and Dauhut (2018, published in the JAS) that the concept of “*relative entropy*” cannot be considered as an alternative or counterpart to the term “*absolute entropy*” simply because the relative entropy is not an entropy and that the relative entropy is called “*Available energy*” or “*Exergy*” in general thermodynamics, atmospheric and oceanographic sciences.

In fact, the “relative entropy” or “Kullback-Leibler divergence” or “relative entropy” 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)

I may however provide additional information and recall in the Fig. 31 several sentences and equations in papers and books published since 1948 and precisely dealing with the concept of “relative entropy” that is different from the “entropy” and corresponds to the “exergy” concept.

It turns out that I have passed my PhD in 1994 on the subject of the exergy of the atmosphere. This is why I have been able to provide in the Section 3 of Marquet and Dauhut (2018) answers to Olivier Pauluis, who suggested the definition of a “relative entropy” for the “equivalent” moist-air entropy  $S_m(\theta_e)$  avoiding the use of the “absolute entropy” version  $S(\theta_s)$  I defined in 2011.

It was explained in Marquet and Dauhut (2018, p.3737-3738) that:

*“The concept of “relative entropy” is actually quite old. The term was coined in the famous papers of Shannon (1948) and Shannon and Weaver (1949), where the information entropy of a system with a set of probability  $(p_1, \dots, p_n)$  is computed by  $-\sum_j p_j \log(p_j)$ . This result was linked to the results of statistical mechanics and the famous Boltzmann’s “H theorem.” The “relative entropy” of a source was then defined as “the ratio of the actual to the maximum entropy of the source”, and the “conditional*

Figure 31: Excerpts from several papers and books dealing with the concept of “Relative entropy” or related quantities: Kullback-Leibler mean information, relative information, Contrast, ...

<p><b>The Bell System Technical Journal</b> Vol. XXVII July, 1948 No. 3</p> <p><b>A Mathematical Theory of Communication</b> By C. E. SHANNON</p> <p>We shall call <math>H = - \sum p_i \log p_i</math> the <u>entropy</u> of the set of probabilities (p.393)</p> <p>The ratio of the entropy of a source to the maximum value it could have while still restricted to the same symbols will be called its <u>relative entropy</u>. This is the maximum compression possible when we encode into the same alphabet. One minus the <u>relative entropy</u> is the <u>redundancy</u>. (p.398)</p>	<p><b>THE MATHEMATICAL THEORY OF COMMUNICATION</b> CLAUDE E. SHANNON and WARREN WEAVER (1949)</p> <p><math>H = - \sum p_i \log p_i</math> (p.14)</p> <p>(p.21) <math>H(x)</math> is the entropy or information of the source</p> <p>(p.20) Entropies calculated in this way, when there are two sets of symbols to consider, are called <u>relative entropies</u>. The particular one just described is the entropy of the message relative to the signal, and Shannon has named this also the <u>equivocation</u>.</p>
<p><b>ON INFORMATION AND SUFFICIENCY</b> (1951) By S. KULLBACK AND R. A. LEIBLER</p> <p>We shall denote by <math>I(1:2)</math> the mean information</p> <p><math>I(1:2) = \int f_1(x) \log \frac{f_1(x)}{f_2(x)} d\lambda(x)</math>. (p.80)</p> <p>We denote by <math>J(1, 2)</math> the “divergence” (p.81)</p> <p><math>J(1, 2) = J_{12}(X) = \int (f_1(x) - f_2(x)) \log \frac{f_1(x)}{f_2(x)} d\lambda(x)</math>.</p>	<p><b>Elements of Information Theory</b> THOMAS M. COVER and JOY A. THOMAS (1991)</p> <p>Mutual information turns out to be a special case of a more general quantity called <u>relative entropy</u> <math>D(p  q)</math> which is a measure of the “distance” between two probability mass functions <math>p</math> and <math>q</math>. It is defined as</p> <p><math>D(p  q) = \sum_x p(x) \log \frac{p(x)}{q(x)}</math> (1.6) (p.8)</p>
<p><b>ENERGY, ENTROPY AND EXERGY IN THE ATMOSPHERE</b> Sten Karlsson Göteborg 1990</p> <p>information-theoretical entropy <math>S_1^{(o)} = \sum p_j^{(o)} 2 \log \frac{1}{p_j^{(o)}}</math> (3)</p> <p><math>\mathbb{K}[\mathcal{P}^{(o)}, \mathcal{P}] = \sum_i p_j 2 \log \frac{p_j}{p_j^{(o)}}</math> (4) <u>relative information</u></p> <p>We get the exergy</p> <p><math>B = k_B T_o \mathbb{K}[\mathcal{P}_o, \mathcal{P}] = \mathcal{E} + p_o V - T_o S - \sum \gamma_{\#io} N_i</math> (13)</p> <p><math>B = \mathcal{E} - \mathcal{E}_o + p_o(V - V_o) - T_o(S - S_o) - \sum \gamma_{\#io}(N_i - N_{io})</math> (16)</p>	<p><b>Measuring Dynamical Prediction Utility Using Relative Entropy</b> RICHARD KLEEMAN (2002)</p> <p>Cover and Thomas 1991) provides a very natural measure of precisely this known as <u>relative entropy</u> <math>R</math>. This gives the information loss sustained by assuming climatology when the prediction distribution is available. If a discrete set of states are being predicted this is given by</p> <p><math>R = \sum_i p_i \ln \left( \frac{p_i}{q_i} \right)</math> (3) (p.2058)</p>

entropy” was defined by an equivalent of  $\sum_j p_j \log(p_j/q_j)$ , where  $(q_1, \dots, q_n)$  is the set of probability for a special configuration of the system. This concept of “relative entropy” was further explored in Kullback and Leibler (1951) and Kullback (1959), leading to the names “Kullback information,” “Kullback-Leibler distance,” “relative information,” “mean information” and “Contrast” functions, all defined by  $K = \sum_j p_j \log(p_j/q_j)$  where the  $p_j$ ’s represent a real state and the  $q_j$ ’s a reference state of the system.

Applications of this relative entropy or Kullback-Leibler distance to dynamical systems, quantum theory, statistical mechanics, general relativity, black holes, and cosmology can be found in Hiai and Petz (1991), Qian (2001), Vedral (2002), Shell (2008), Casini (2008), Akerblom and Cornelissen (2012), Villani (2012), Czinner and Mena (2016), and Longo and Xu (2017).

As for the interpretation suggested by Olivier Pauluis, it is possible to find explicit applications of the relative entropy function or Kullback-Leibler distance to atmospheric studies: Kleeman (2002), Majda et al. (2002), Tippett et al. (2004), Haven et al. (2005), Abramov et al. (2005), Shukla et al. (2006), Xu (2007), Ivanov and Chu (2007), DelSole and Tippett (2007), Majda and Gershgorin (2010), Bocquet et al. (2010), Weijs et al. (2010), Krakauer et al. (2013), Arnold et al. (2013), Zupanski (2013), Dirmeyer et al. (2014), and Nelson et al. (2016), among others. These papers and books deal with studies of dynamical prediction, the Lorenz attractor, data assimilation, seasonal forecasts, climate and oceanic models, weather predictions models, climate change, stochastic parameterizations, evaporative sources in the moist atmosphere, forecast skill scores, and predictability.

It is explained in Cover and Thomas (1991) that the relative entropy  $K$  of Kullback and Leibler is a measure of the “distance” between the two sets of probability  $(p_1, \dots, p_n)$  and  $(q_1, \dots, q_n)$  and that  $K$  is a non-symmetric measure of how much  $p_j$  deviates from  $q_j$ .

As for the thermodynamic vision, the relative entropy must be interpreted as the “free energy” associated with a minimum value and fluctuation density at equilibrium (Qian 2001; Casini 2008). The free energy corresponds to  $F = E - T S$ , where  $E$  is the internal energy,  $T$  the equilibrium temperature, and  $S$  the entropy. Therefore, the relative entropy does not correspond to an entropy  $S$ , which is only one part of  $E - T S$ .

This statement can be clearly understood by considering the applications to atmospheric processes of the Kullback information, relative information, “cross entropy,” or contrast functions by Jaynes (1957, 1968, 1978), Procaccia and D. Levine (1976), Eriksson and Lindgren (1987), Eriksson et al. (1987), Rosenkrantz (1989), Karlsson (1990), Marquet (1991, 1993, 1994), and Honerkamp (1998). The aim was to compute the same relative entropy or “directed divergence” defined by  $K = \sum_i p_j \log(p_j/q_j)$ , where  $p_j$  represents the real state and  $q_j$  represents a reference state of the atmosphere.

It has been shown (see in particular Karlsson, 1990) that  $K$  corresponds to the exergy functions written in terms of local basic atmospheric variables, leading to the “available energy” function

$$a_e = k_B T_0 K ,$$

$$a_e = (e - e_0) + p_0 (\alpha - \alpha_0) - T_0 (s - s_0) - \sum_j \mu_{j0} (x_j - x_{j0}) ,$$

where the subscript 0 denotes a reference state and  $k_B$  is the Boltzmann-Planck constant. The differences in specific, extensive values for the internal energy  $e$ , (...) volume  $\alpha = 1/\rho$ , entropy  $s$ , and contents of matter  $x_j$  are multiplicative factors of the intensive reference values (pressure  $p_0$ , temperature  $T_0$ , and Gibbs functions  $\mu_{0j} = h_{0j} - T_0 s_{0j}$ ).

This review proves that  $S_m(\theta_e)$  cannot be called the relative entropy.”

- These sentences recalled from the Section 3 of Marquet and Dauhut (2018, p.3737-3738) and concerning the moist-air entropy are also valid for the seawater entropy, and they similarly explain that it is not possible to suggest that the seawater entropy computed by TEOS10-GSW could be some kind of “relative entropy” defined as a counterpart of the seawater “absolute entropy.”

- Moreover, following the suggestion of defining some kind of “relative entropy” for the absolute seawater entropy noted  $\eta_{abs.}$ , in the decomposition  $\eta_{abs.} = \eta_{rel.} + (\eta_{abs.} - \eta_{rel.})$  the first term  $\eta_{rel.}$  would be the TEOS10-GSW value, where the reference values are set to zero at 0.01°C, whereas the term  $(\eta_{abs.} - \eta_{rel.})$  would not be “determinable” due to unknown values for  $\eta_{abs.}$ , and this term could be discarded in oceanic studies.

However, this term  $(\eta_{abs.} - \eta_{rel.})$  precisely corresponds to the absolute-entropy increment term

$$\Delta\eta_s = (\eta_{s0} - \eta_{w0}) \times \frac{(S_A - S_{S0})}{1000} \approx (-1880 \pm 17) \times \frac{(S_A - S_{S0})}{1000} \text{ J/K/kg} \quad (193)$$

that I derived in my 2025 paper. Therefore, the term  $(\eta_{s0} - \eta_{rel.})$  is not only “determinable” but has been determined from the Third law of thermodynamics.

- 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 (193) 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, ...

## 12.5 Validations and physical meaning of absolute entropies / 1956 ICPS conf. ?

A “*justification*” given in many IAPWS (pre-TEOS10) atmospheric and seawater thermodynamic documents for cancelling the internal energies and entropies at the triple point (273.16 K or 0.01°C) is that:

*“Since the 5th International Conference on the Properties of Steam in London in 1956, the specific internal energy and the specific entropy of the saturated liquid at the triple point have been set equal to zero.”*

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• This sentence was indeed written in the proceeding of the sixth Conference in New York City (Haywood, 1965, Note p.98), and was then recalled, again and again, in all the IAPWS (International Association for the Properties of Water and Steam) documents for pure water:

- IAPWS-95 / Wagner and Pruss (2002, p.429) / Eq. 6.7 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-97 / Erlangen (1997, p.7) / Eq. 8 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-97 / Wagner et al. (2000, p.154) / Eq. 16 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-R-95 / Doorwerth (2009, p.4) / Eq. 7 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-IF97 / Wagner and Kretzschmar (2008, International Steam Tables, 2nd Ed., p.13) / Eq. 2.4 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-R7-97 / Lucerne (2012, p.7) / Eq. 8 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-95-Revised / IAPWS (2018, p.4) / Eq. 7 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only;
  - IAPWS-IF97-Third / Kretzschmar and Wagner (2019, International Steam Tables, 3rd Ed., p.13) / Eq. 2.4 with  $u'_t = 0$ ,  $s'_t = 0$  for pure liquid water only.
- 

• Similarly, but without explicitly citing the resolution adopted at the 5th International Conference on the Properties of Steam in London in 1956, Feistel (2008, about Eqs. 6.16, p.1654) explained that:

*“In this implementation, the improved coefficients  $n_0^1$  and  $n_0^2$  of the IAPWS-95 (IAPWS, 2018) formulation adjusted to the reference point conditions of vanishing entropy and internal energy of the liquid phase at this triple point take the values, rounded to double precision  $n_0^1 \approx -8.320\,446\,483\,749\,69$  and  $n_0^2 \approx 6.683\,210\,527\,593\,23$ ”* (see in IAPWS, 2018, the Table 1, p.9).

• The same 1956 hypothesis is retained in the Appendix F of the TEOS10 documentation (McDougall et al., 2010, “Coefficients of the IAPWS-95 Helmholtz function of fluid water, with extension down to 50 K”), where it was explained that:

*“The IAPWS-95 reference state conditions define the internal energy and the entropy of liquid water to be zero at the triple point. A highly accurate numerical implementation of these conditions gave the following values rounded to 16 digits for the adjustable coefficients  $n_0^1 \approx -8.320\,446\,483\,749\,693$  and  $n_0^2 \approx 6.683\,210\,527\,593\,226$ . These are the values used in TEOS-10 (IAPWS-R-95 / Doorwerth, 2009; Feistel et al., 2008).”*

• The same 1956 hypothesis is also retained in the Appendix G of the TEOS10 documentation (McDougall et al., 2010, “Coefficients of the pure liquid water Gibbs function of IAPWS-09”), where:

*“Two of these 41 parameters ( $g_{00}$  and  $g_{10}$ ) are arbitrary and are computed from the reference-state conditions of vanishing specific entropy,  $\eta(T_t, p_t) = 0$ , and specific internal energy,  $u(T_t, p_t) = 0$ , of liquid  $H_2O$  at the triple point.”*

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- Still without an explicit citation to the 5th 1956 Conference, the same hypothesis was retained in the TEOS10 documentation (McDougall et al., 2010, Section 2.6 about “*Gibbs Function of Seawater*”), where about Eqs. 2.6.2, 2.6.3 and 2.6.4 it was explained that:

*“The Gibbs function (2.6.1) contains four arbitrary constants that cannot be determined by any set of thermodynamic measurements. These arbitrary constants mean that the Gibbs function (2.6.1) is unknown and unknowable up to the arbitrary function of temperature  $T$  and Absolute Salinity  $S_A$  (where  $T = \bar{T}_0 + t$  is the absolute temperature,  $t$  the Celsius temperature, and  $\bar{T}_0$  the Celsius zero point, 273.15 K):*

$$[a_1 + a_2 T] + [a_3 + a_4 T] S_A$$

*(see for example Fofonoff, 1962; Feistel and Hagen, 1995). The first two coefficients  $a_1$  and  $a_2$  are arbitrary constants of the pure water Gibbs function (...) while the second two coefficients  $a_3$  and  $a_4$  are arbitrary coefficients of the saline part of the Gibbs function (...). Following generally accepted convention, the first two coefficients are chosen to make the entropy and internal energy of liquid water zero at the triple point (...)  $\eta^W(t_t, p_t) = 0$  and  $u^W(t_t, p_t) = 0$ , respectively (...) as described in IAPWS-95 (Wagner and Pruss, 2002) and in more detail in Feistel (2008) for the IAPWS-95 Helmholtz function description of pure water substance.”*

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- It was therefore important to check in what these arguments discussed during this London (1956) conference was relevant, and to determine whether the words of Rainer Feistel (+ IAPWS + TEOS10) were correct, or not?

In particular, if these arguments discussed during this London (1956) conference were true and could be generalized to all substances (like the oceanic sea salts), they could amount to violate the third law of thermodynamics?

The difficulty was that, in a first step between 2014 (my first contacts with Rainer Feistel) and 2024 (my retirement), I did not find a copy of the proceeding of that London (1956) conference...

Fortunately, thanks to Rainer Feistel demand, Dr. Allan Harvey (U.S. National Delegate to IAPWS) sent me in December 2024 the copy of some pages of this old 1956 proceedings.

Therefore, I am now able to show and recall in the Figs. 32 the verbatim of several sentences written in this proceedings of the 1956 conference.

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- The first resolution proposed by the Professor Schmidt (accepted page 3/34, see the Figs. 32) was to change and define the new reference state at which the internal energy and the entropy cancel out to be the pure liquid water at the triple point of water (0.01°C), instead of the previous common habit to use the zero of the Celsius temperature (0.00°C).

This first resolution clearly corresponds to the choice retained by Rainer Feistel, IAPWS and TEOS10.

However, this first resolution was a mere convention valid for a system with only one component (the liquid and steam of water  $H_2O$ ), and this convention cannot be used without proof for the more general case of a mixture with the dry air (namely the moist-air atmosphere) nor the seawater (pure water including sea salts).

Figure 32: Excerpts showing the two resolutions adopted at the 5th International Conference on the Properties of Steam (5th-ICPS et al., July 1956), with the two propositions of Schmidt (1956, p.1/30-1/32 and 3/34) and Weir (1956, p.3/35-3/37)

<p>MINUTES OF THE FIFTH INTERNATIONAL CONFERENCE ON THE PROPERTIES OF STEAM JULY 10-12, 1956 LONDON, ENGLAND</p>	<p><b>Professor KEENAN:</b> (continued) 1/31 the numbers which will go into the table, but it will make a difference to the wording of the convention. <u>I think that it might be a good idea at this point to shift our base from zero of the enthalpy to zero of the energy.</u></p>
<p><b>Proposal for Use as the Reference State</b> 1/30 <u>Discussion</u> <b>Mr. LE FEVRE:</b> I should like to say a word about <b>Professor Schmidt's</b> proposal that the triple point might play a special role in the future as a <u>zero point for enthalpy and entropy.</u></p>	<p><b>Resolution: Definition of the Reference State</b> 3/34 <u>The draft resolution was carried unanimously.</u> <b>Mr. LE FEVRE:</b> I have spare copies if anyone wants them. I had the honour of presiding over this Sub-Committee and we rapidly agreed to recommend this meeting to consider this resolution:</p>
<p>1/31 <b>Professor KEENAN:</b> These suggestions are very interesting and timely. I should like to suggest that perhaps it will not matter very much if we do shift this base, even to the engineer, because there is such a small difference between zero celsius and the triple point. On the other hand, <u>I would suggest that as a matter of form, Dr. Schmidt's proposal might be slightly amended so that energy is taken rather than enthalpy, as well as making entropy zero at the triple point for the liquid phase.</u> It makes no difference as regards</p>	<ol style="list-style-type: none"><li>1. The reference state (which was sometimes previously at a non-stable point) should be changed to a stable point. <u>(i.e. a change from 0°C to 0.01°C)</u></li><li>2. <u>The new reference state for water shall be that of the liquid phase at the triple point of pure water.</u></li><li>3. <u>At this new reference state the entropy and the internal energy shall each conventionally be made exactly zero.</u></li></ol>
<p>MINUTES OF THE FIFTH INTERNATIONAL CONFERENCE ON THE PROPERTIES OF STEAM JULY 10-12, 1956 LONDON, ENGLAND</p>	<p>3/36 <b>Professor SCHMIDT:</b> The absolute values of enthalpy and entropy are not as well known as the different points which are involved here.</p>
<p>3/35 <b>Dr. C. D. WEIR (United Kingdom):</b> Could I raise one point? I suppose that Mr. Le Fevre might agree that <u>in theory the best datum is the completely stable state at absolute zero?</u> For certain purposes it is sometimes <u>desirable to have absolute free energy, and I suggest that in any printed steam table which is produced in the future should include values of the absolute entropy and the absolute free energy at the triple point so that we might get an absolute value from the steam tables by adding those quantities.</u></p>	<p>3/36 <b>Dr. WEIR:</b> I do not want to be misunderstood. All I want to get at is that for certain calculations of chemical thermodynamics <u>we want absolute values, of the free energy in particular. I do not suggest that those must be highly accurate values, but values are wanted.</u> Since steam table data are often used for other purposes than for calculating the efficiencies of turbines, <u>it would be a help if some figures could be included, (which need not necessarily be internationally agreed figures), which would facilitate expressing the entropy and enthalpy values in the table in absolute terms.</u> I do not suggest that there should be anything in the nature of a fundamental definition or internationally agreed values attached to these figures, but merely that they <u>should be given.</u></p>
<p>3/36 <b>Mr. LE FEVRE:</b> I agree about the desirability for certain more fundamental purposes of referring to absolute zero - but I do not think we can do it in practicable tables. <u>The suggestion for putting something in the beginning of tables to say what the rise is from the absolute zero is good.</u></p>	<p>3/37 <b>MR. LE FEVRE:</b> That will form admirably the subject of another resolution. I would, I think, support it. 3/37 <b>The CHAIRMAN:</b> It impresses the Chair as being a point of admonition to anybody who develops steam tables and prints them that they <u>should put those figures down. Those in favour of adopting the draft resolution on the reference points?</u> <u>The resolution was carried unanimously.</u></p>

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The other very interesting thing is the second resolution (accepted page 3/37, see the Figs. 32) suggested by Dr. C. D. Weir:

- “(...) in theory the best datum is the completely stable state at absolute zero” (namely the third law of thermodynamics);
- “(...) for certain calculations of chemical thermodynamics we want absolute values, of the free energy in particular” (therefore for  $F = U - T S$  including the absolute entropy  $S$ );
- “(...) any printed steam table which is produced in the future should include values of the absolute entropy and the absolute free energy at the triple point, so that we might get an absolute value from the steam table by adding those quantities.”

What a pity that this second resolution is never mentioned in the documents written by Rainer Feistel, IAPWS and TEOS10.

I think that my absolute definitions for the specific moist-air and seawater entropies are fully in line with this second resolution suggested by Dr. C. D. Weir (accepted p.3/37) during the 5th International Conference on the Properties of Steam in London in 1956, with the use if needed of the absolute values for the water-vapour perfect gas, the pure-liquid water and the sea salts.

---

Differently, 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 IAPWS and TEOS10 definitions 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...

Similarly, most of atmospheric community consider that the moist-air entropy might be computed by cancelling either the couple of dry-air and liquid-water reference entropies at 0°C to define the “*equivalent*” values  $s_e(\theta_e)$ , or the couple of dry-air and water-vapour reference entropies at 0°C to define the “*liquid-water*” values  $s_l(\theta_l)$ .

Clearly, all these moist-air and seawater definitions of the “*conventional*” values of entropies retained in most of atmospheric and oceanographic studies disagree with the third law of thermodynamics, with obvious physical impacts in the differential of moist-air and seawater entropies due to the leading-order linear terms (plus non-linear terms):

$$\text{for the moist air: } ds = (s_{v0} - s_{d0}) \times dq_t + (\dots), \quad (194)$$

$$\text{for the seawater: } d\eta_s = (\eta_{s0} - \eta_{w0}) \times \frac{dS_A}{1000} + (\dots). \quad (195)$$

These two differential relationships mean that the second laws of thermodynamics ( $ds/dt$  and  $d\eta_s/dt$ ) depends on the absolute or conventional definition of the reference entropies as soon as the total-water ( $q_t$ ) and sea-salts ( $S_A$ ) contents are not uniform (in time and space). The same is true for the turbulent fluxes of entropies  $\overline{w' s'}$  and  $\overline{w' \eta'_s}$  depending on  $\overline{w' q'_t}$  and  $\overline{w' S'_A}$  and on the values of the reference entropies  $s_{v0}$ ,  $s_{d0}$ ,  $\eta_{s0}$  and  $\eta_{w0}$  that the third law of thermodynamics explains how they must be computed, without arbitrariness.

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## 12.6 Validations and physical meaning of absolute entropies / Infinity at 0 K?

Olivier Pauluis’ criticisms (received during personal email contacts from about 2014 to 2025) can be summarised as follows:



We know that the reference values for energy and entropy have no measurable physical impact, and it is therefore meaningless to calculate (or even study) the properties of absolute entropy (derived from the third law of thermodynamics, for instance), with therefore the possibility to arbitrarily cancel out or set the reference entropy values to any values, and with anyhow infinite values for the entropy of perfect gases when the temperature tends towards absolute zero.

---

First, without proof of it, Pauluis et al. (2010) wrote in the Appendix A (p.3091) and about the relationships derived for the specific entropies for dry air, water vapour and liquid water:

*“The definitions of the specific entropies [(A2a)-(A2c)] include several integration constants: the reference temperature  $T_0$ , reference partial pressure for dry air  $p_0$ , and water vapor  $e_0$ , and the reference entropies for dry air  $s_{d,0}$ , water vapor  $s_{v,0}$ , and condensed water  $s_{l,0}$ . (...) A common practice is to choose some typical atmospheric values for  $T_0$  and partial pressures  $p_{d,0}$  and  $e_0$ , and to set the reference value for the specific entropies of dry air and of either liquid water or water vapor to 0” (namely at  $T_0 = 0^\circ\text{C}$ ).*

---

As a kind of justification for using such arbitrary “typical atmospheric values” Pauluis et al. (2010, p.3091) explained in the same Appendix-A that:

*“It should be noted that the entropy used in atmospheric sciences corresponds to the thermodynamic entropy in classical physics. It is a state variable that can be used in Clausius formulation of the second law. It does not, however, correspond to the absolute entropy based on Nernst’s theorem, which states that the entropy of a system should go to zero as the absolute temperature goes to zero. The expression for the entropy of an ideal gas in classical physics  $S = C_p \ln(T) - r \ln(p) + S_0$  is fundamentally incompatible with Nernst theorem as it is singular as  $T \rightarrow 0$ . This results from the fact that the classic concept of an ideal gas neglects quantum effects that are important at low energy and temperature. Nernst’s theorem is tied to the fact that, in quantum physics, there is a finite energy difference between individual quantum states. At very low temperature, thermal fluctuations are too weak to induce any state transition. It is not clear whether Nernst’s theorem should apply to systems in which energy levels form a continuum as is the case for an ideal gas in classical physics.”*

---

As a matter of fact, the true seminal “Heat Theorem” of Nernst (1906, 1907, 1910) did not imply that entropy itself is zero at absolute zero of temperatures.

Indeed, for Nernst it was only a matter of noticing that in numerous cases, and then of conjecturing by stating a general theorem, that the derivatives of the chemical change in energy  $dU/dT$  and of the associated change in the Helmholtz free energy  $dA/dT$  both tend towards 0 at absolute zero of temperatures, or in other terms that:

$$\lim_{T \rightarrow 0} \frac{dA}{dT} = 0 \quad \text{and} \quad \lim_{T \rightarrow 0} \frac{dU}{dT} = 0 \quad \text{for} \quad T = 0 \text{ K} ,$$

with therefore a similar property for the change in entropy  $S = (U - A)/T$  derived from the Helmholtz function  $A = U - T S$ :

$$\lim_{T \rightarrow 0} \frac{dS}{dT} = 0 \quad \text{for} \quad T = 0 \text{ K} .$$


---

However, the notations used by Nernst may have created confusion, because it is important to understand that the quantities considered by Nernst was in fact the change in energy  $\Delta U$  and the change in Helmholtz function  $\Delta A = \Delta U - T \Delta S$ , and not the Helmholtz function  $A$ , energy  $E$  nor entropy  $S = (U - A)/T$  quantities themselves. Therefore, Pauluis et al. (2010, p.3091) were wrong to associate the true Nernst's "*Heat Theorem*" with the entropy  $S$ , instead of the change in entropy  $\Delta S$ .

---

It was then Max Planck (1911, 1914, 1917, ...) who gradually invented the "*third law of thermodynamic*" by considering that:

*"the entropy (itself) of the more stable solid states (i.e. not for liquid nor gases; and excluding the possible residual entropy at 0 K) of all pure substance (i.e. not mixture) tends close to 0 K toward a universal value independent of the substance and the internal state of it (such as the magnetic field), a universal value which can be set to zero without loss of generality."*

This clearly explains why Olivier Pauluis was wrong when he tried to imagine that the third law could be applied to gases close to 0 K. The perfect gas relationship  $s = c_p \ln(T) - R \ln(p) + cste$  is only valid for ambient temperatures. Nor Nernst nor Planck have imagined that this relationship could be valid up to 0 K!

I can also remember the important old remarks written by Richardson (1922, p.159-160) that should be read by everyone, namely:

*"To find the true difference of (moist air) entropy we must trace in imagination some process of adding water-substance reversibly, and the question then arise: what energy and entropy are to be ascribed to unit mass of the incoming substance? (...) As there is an arbitrary constant of integration in the entropy, we must ask what would be the effect of an increase in this constant for the incoming water. Approximations are not here permissible, for the constant might be made indefinitely large."*

Richardson (1922, p.160) also clearly knew the solution of these problems (namely the need of absolute, third-law definitions for the entropies derived by Nernst, 1906, and generalized by Planck, 1911):

*"(...) the most natural way of reckoning the entropy of the water-substance would be to take it as zero at the absolute zero of temperature. It was formerly supposed that the presence of  $T$  in the denominator of the integral which gives the entropy would make the integral have an infinity where  $T = 0$  (i.e. due to the usual term  $c_p \ln(T)$  for the perfect gases, but under the assumption that  $c_p$  is a constant); but the measurements of Nernst, Lindemann, Koref and others have shown that the specific heats tend to zero at  $T = 0$  in such a way that the entropy remains finite there"* (namely for the solid species, and not the perfect nor real gases).

Therefore, I think that most has been said since these remarks by Richardson (1922, p.159-160).

---

## 12.7 Validations and physical meaning of absolute entropies / Entropy-meter?

It is often put forward (in particular by Rainer Feistel and Trevor McDougall) that the absolute entropy cannot have a physical meaning because there is not "*Entropy thermometer*" and thus no way to directly measure the moist-air or seawater entropy, and thus no way to determine which of the "*conventional*" or "*absolute*" version of the moist-air and seawater entropies are valid?

---

What a strange way of thinking!

First, I have recalled in the section 12.1 that the theoretical third-law constants  $C_0$  and  $i_0$  has been validated experimentally before the years 1920: this is a kind of "*(absolute) Entropy thermometer*."

I also show in the Section 12.3 that the absolute statistical (theoretical) and calorimetric (experimental) values of the entropy of water ( $\text{H}_2\text{O}$ ) correspond via the third-law absolute term  $\delta\eta$  to a strong constraint on the experimental values of the saturation vapour-ice pressure  $p_{\text{sat}}(T_0)$  and latent heat of sublimation  $L_s(T_0)$ .

These are kinds of “*(absolute) Entropy thermometer*” when the aim is to compute, via the Equations (191) or (192) in the Section 12.3, either  $p_{\text{sat}}(T_0)$  from  $\delta\eta$  and  $L_s(T_0)$ , or  $L_s(T_0)$  from  $\delta\eta$  and  $p_{\text{sat}}(T_0)$ .

---

Moreover and anyhow, the same is true for the quantity called potential vorticity in atmospheric science and defined by Ertel (1942a,b,c) as:

$$PV = \frac{\vec{\zeta}_a \cdot \vec{\nabla}(\psi)}{\rho}.$$

This quantity can be computed from the knowledge of the density ( $\rho$ ), the absolute vorticity ( $\vec{\zeta}_a$ ) and the gradient of any quantity  $\psi$ . However, even if there is no “*PV thermometer*” whatever the variable quantity  $\psi$  may be, this does not prevent us to daily and operationally study the PV variable as a numerical output of all NWP models!

---

More precisely, in the original German papers by Ertel (1942a,b,c), all translated in English and available in Schubert et al. (2004), Ertel explicitly suggested the three possibilities of:

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

Other moist-air variables  $\psi$  have been suggested and studied, such as:

- the virtual potential temperature ( $\psi = \theta_v$ ); or
- the equivalent potential temperature ( $\psi = \theta_e$ ); or
- the pseudo-adiabatic potential temperature ( $\psi = \theta'_w$ ); or
- the moist-air entropy potential temperature ( $\psi = \theta_s$ ).

Accordingly, I have studied and compared in Marquet (2014) the four moist-air entropy variables:

- $PV$  based on the “*dry-air*” version  $\psi = c_{pd} \ln(\theta)$ ;
- $PV_v$  based on the “*virtual*” version  $\psi = c_{pd} \ln(\theta_v)$ ;
- $PV_e$  based on the “*equivalent*” version  $\psi = c_{pd} \ln(\theta_e)$ ;
- $PV_s$  based on the “*absolute*” version  $\psi = c_{pd} \ln(\theta_s)$ .

It turns out that the differences may be large, for instance in frontal regions, in the moister regions in the lower-part of the atmosphere, and in particular for revealing the slantwise convection regions.

This means that not only the  $PV$  variables has been used to study the dynamics of atmospheric motions since the seminal paper by Hoskins et al. (1985), but also to study several features of the moist-air convection, even if there is no “*PV thermometer*” in the atmosphere!

---

Therefore, even if there is no “*absolute entropy thermometer*” this does not mean that the absolute third-law entropy cannot be defined, computed and studies in the moist-air atmosphere (like the  $PV$ ), and in the seawater oceans as well (like any complex quantity that may be computed from other oceanic variables).

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## 12.8 Validations and physical meaning of absolute entropies / Second law?

- I have often tried to explain that the second law of thermodynamics seems to be impacted by the use of reference values for entropies that are different from those –absolute– recommended by the third law.

There is however a real rejection of this idea with the guide, at worst and without proof, that it should not be possible (?), or at best and in a more erudite manner, that these absolute values of the reference entropies do not impact the so-called positive production term ( $\sigma \geq 0$ ) and that, therefore, there is effectively no impact of the third on the second principle.

- In order to respond precisely and with reason to my detractors, I believe I have reread almost all the articles and books dealing with the subject of the entropy equation for a fluid (such as the moist-air atmosphere or the sea-salts ocean), to check where these absolute reference entropy values can act.

---

• I can first recall that the general entropy equations was first derived in Jaumann (1911, Eqs. 278-281, Section p.509-528), Lohr (1917, Eq. 6, p.341) and Jaumann (1918, Eqs. 165, p.522), and then in Onsager (1931, p.407) and von Meixner (1939, Eqs. 2.21-2.23, p.715). These general entropy equations were written for a finite mass (or volume) entropy  $S$ , or the entropy density  $s = S/\rho$ , or the entropy per gram, of an homogeneous substance or isotropic media, leading to a formulation that can be (re)written as:

$$\frac{dS}{dt} = -\vec{\nabla} \cdot \vec{J}_S + \sigma = -\vec{\nabla} \cdot \vec{J}_S + \overbrace{\sum_k X_k Y_k}^{\sigma}, \quad (196)$$

where  $\vec{J}_S$  is the entropy boundary flux (toward or from the environment) and  $\sigma = \sum_k X_k Y_k$  is the (internal) positive “*entropy production*” term or “*dissipation function*.”

The positive entropy-production term is written as  $\sigma = \sum_k X_k Y_k$  and is therefore a sum of products of “flows”  $X_k$  (of matter, heat or electricity) by the associated “generalized forces”  $Y_k$  (gradients of the chemical potential  $\mu$ , absolute temperature  $T$  or electrical potential  $U$ , respectively).

The positive entropy-production term is written as  $\sigma = \sum_k X_k Y_k$  and is therefore a sum of products of “flows”  $X_k$  (of matter, heat or electricity) by the associated “generalized forces”  $Y_k$  (gradients of the chemical potential  $\mu$ , absolute temperature  $T$  or electrical potential  $U$ , respectively).

It is possible to simply illustrate the separation into a flux  $\vec{J}_S$  and a positive production term  $\sigma$  for the particular case of thermal conduction (Fourier’s law) with a flux of energy (expressed in term of temperature)  $\vec{F}_T$  and a heating rate  $\dot{Q}|_T = -(\vec{\nabla} \cdot \vec{F}_T)$ . The second law of thermodynamics suggests that

$$\left. \frac{dS}{dt} \right|_{cond.} = \frac{\dot{Q}|_T}{T} = \frac{-(\vec{\nabla} \cdot \vec{F}_T)}{T} = -\vec{\nabla} \cdot \left( \frac{\vec{F}_T}{T} \right) + \vec{F}_T \cdot \vec{\nabla} \left( \frac{1}{T} \right), \quad (197)$$

where the last two terms are another way of writing  $-(\vec{\nabla} \cdot \vec{F}_T)/T$ .

The term  $\vec{F}_T/T$  can then be considered as a contribution to  $\vec{J}_S$ , while  $\vec{F}_T \cdot \vec{\nabla} (1/T) = -\vec{F}_T \cdot \vec{\nabla} (T)/T^2$  may be considered as a contribution to  $\sigma$ , since it is positive for the usual case of energy fluxes that operate in counter-gradients with temperature, via the Fourier’s law with  $\vec{F}_T = -a \vec{\nabla} T$  and  $a > 0$  leading to  $\vec{F}_T \cdot \vec{\nabla} (1/T) = +a [\vec{\nabla} (T)]^2/T^2 \geq 0$  (precisely like in Bertrand, 1887, see above).

However, it must be taken into account that, for the atmosphere, conduction processes and the Fourier’s law are negligible except for the first few millimetres or centimetres above the ground (see the Figs. 33).

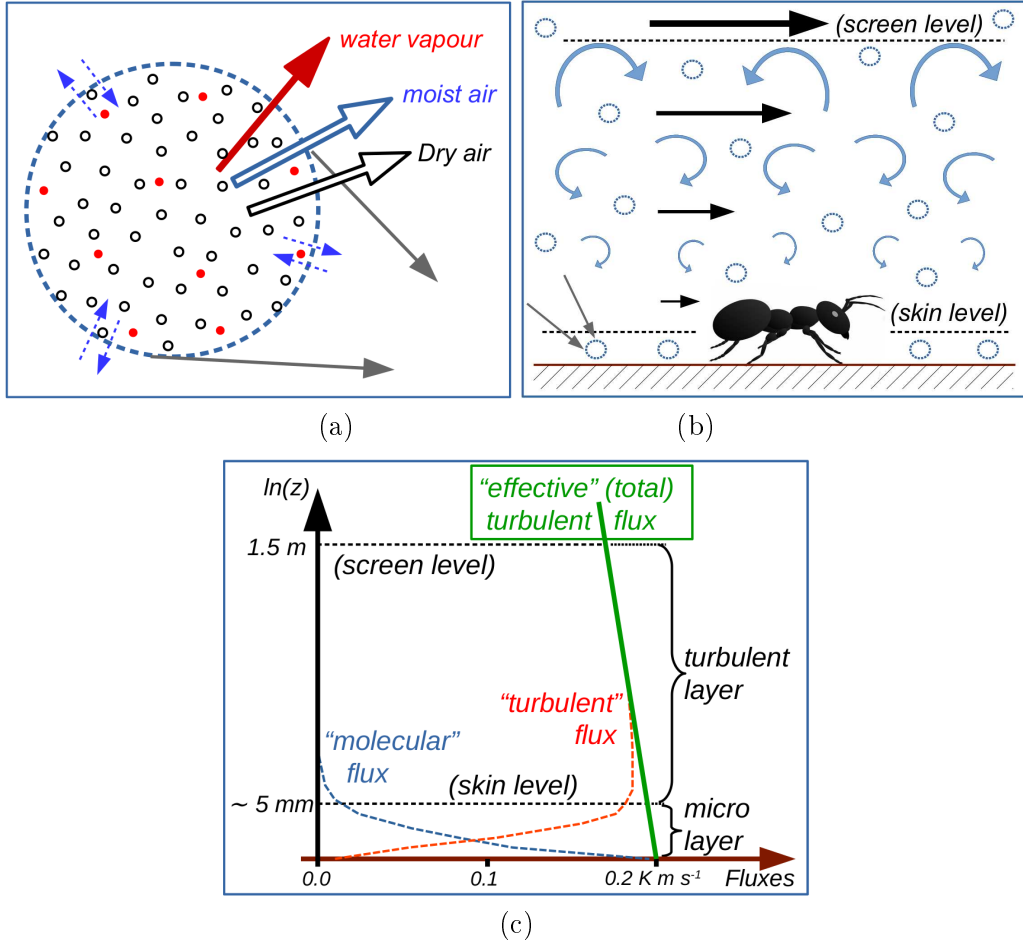


Figure 33: (a): an open parcel of moist air with barycentric and specific mean velocities for molecules of dry-air in black (mainly  $N_2$  and  $O_2$ ) and molecules of water vapour in red ( $H_2O$ ). (b): the “constant flux” surface layer with parcels of moist air located either in the micro layer (below the skin level) or in the turbulent layer (between the skin and screen levels). (c): the vertical transport  $w'\theta'$  in the “constant flux” surface layer adapted from the Fig. 7.1 of Stull (1988).

- Let us briefly give additional informations about these papers of Jaumann (1911), Lohr (1917), Jaumann (1918), Onsager (1931) and von Meixner (1939), where the entropy equations were first defined.

First, Jaumann (1911, Eq. 241, p.511) explicitly wrote the entropy of an ideal gas as  $s = c_v \ln(T) - R \ln(\rho)$ , without any additional integration constant ( $S_0$ ).

However, Jaumann (1911, p.514) also explicitly referred to the previous works of Massieu, Gibbs, Helmholtz, Voigt and Planck. And in particular Jaumann (1911, Eqs. 247, p.512) considered the Gibbs’s writing of thermodynamic functions for heterogeneous substances as the sum of the partial values for each of the components, with  $S = \sum_x S_x$  for the entropy,  $U = \sum_x U_x$  for the internal energy, and  $P = \sum_x P_x$  for the pressure (see the Fig. 34 with Eq. 277 for the pressure and Eq. 278 for the entropy, both extracted from the paper of Gibbs, 1875-1878).

Similarly, Lohr (1917, Eq. 183, p.373) considered the case of a mixture of ideal gases and wrote the corresponding entropy as

$$S = \sum_x \rho_x [c_x \ln(T) - R \ln(\rho_x) + (R + c_x + N_x - C_x)] , \quad (198)$$

where in the last parenthesis ( $R + c_x + N_x - C_x$ ) several constants of integrations or reference values appeared.

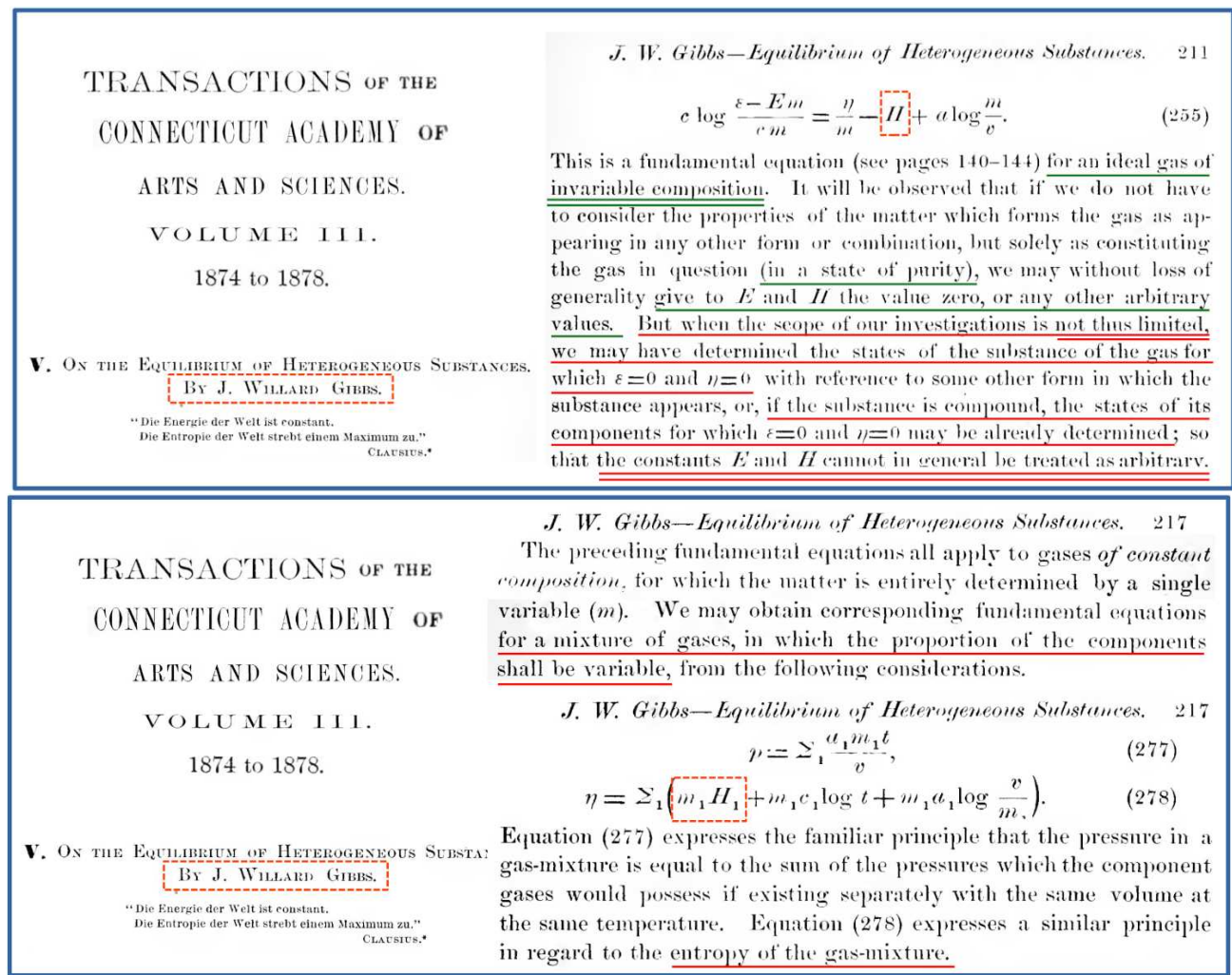


Figure 34: Excerpts from the fundamental papers of Gibbs (1875-1878), where the entropy (noted “ $\eta$ ” by Gibbs) of a given gas (top) and for a mixture of gases (bottom) are defined, together with the need to determine the constant of integration (where “...  $H$  cannot in general be treated as arbitrary”), noted  $\sum_1 m_1 H_1$  by Gibbs in (278) and corresponding to  $\sum_k q_k s_{k0}$  with modern notations.

- Eckart (1940a, p.267, with the entropy noted “ $\eta$ ”) was the first to write the entropy equations valid for continuous and heterogeneous systems (like the moist-air atmosphere made of a mixing of ideal gases) for the specific entropy ( $s$ ) expressed per unit mass of a gas, leading to

$$\rho \frac{ds}{dt} = \rho \frac{\partial s}{\partial t} + \rho \vec{v} \cdot \vec{\nabla} s = \frac{\partial \rho s}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v}) = - \vec{\nabla} \cdot \vec{J}_s + \sigma, \quad (199)$$

where the continuity equation  $d\rho/dt + \rho \vec{\nabla} \cdot \vec{v} = 0$  was used to derived the second part of (199), expressed as a sum of the convergence of a non-convective entropy flux ( $\vec{J}_s$ ) plus a local (specific) entropy production  $\sigma \geq 0$ , whereas the term  $\rho s \vec{v}$  was the convective entropy flux.

Such local equations like (199) explicitly refer to Gibbs (1906)'s collected scientific papers (namely Gibbs, 1906), and in particular to the paper about the “*Equilibrium of heterogeneous substances*” (therefore Gibbs, 1875-1878) for defining the second law and to derive the entropy equation for “*a simple viscous fluid*.” Note that Eckart (1940a, p.268-269) recalled that the entropy (he noted  $\eta$ ) was expressed “*per gram of the substance*” (i.e., ex. of moist-atmosphere or sea-salts seawater)

Other studies of entropy equations like (199) were by: Eckart (1940b), von Meixner (1941), von Meixner (1942), von Meixner (1943a), von Meixner (1943b).

In his second paper, Eckart (1940b, p.271-273) explicitly considered the case of the entropy equation for “*Fluid Mixtures*” before to make (p.273) an “*Elimination of the Entropy from the Equations*” by “*replacing it by the temperature*” expressed “*following Gibbs by  $\theta = \partial \epsilon / \partial \eta$* ” or equivalently by  $T = \partial u / \partial s$  by using the modern notations for the absolute temperature ( $T$ ), the internal energy ( $u$ ) and the entropy ( $s$ ). Finally Eckart (1940b, p.273-275) considered the case of “*Mixtures of Ideal Gases*.”

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• Then von Meixner (1941, Eqs. 13 and 14, p.340) studied in the section entitled “*The continuity equations for thermal diffusion*” the case of a mixture of two gases noted “1” and “2” with the internal energy ( $U$ ) and the entropy ( $S$ ) defined according to Gibbs as the following weighted sums:

$$U = \frac{\rho_1}{\rho} u_1 + \frac{\rho_2}{\rho} u_2, \quad \text{and} \quad S = \frac{\rho_1}{\rho} s_1 + \frac{\rho_2}{\rho} s_2. \quad (200)$$

Accordingly, von Meixner (1941, Eq. 17, p.341) computed from (200) the derivative of the entropy as

$$\frac{dS}{dt} = \left( \frac{\rho_1}{\rho} \right) \frac{ds_1}{dt} + \left( \frac{\rho_2}{\rho} \right) \frac{ds_2}{dt} + s_1 \frac{d}{dt} \left( \frac{\rho_1}{\rho} \right) + s_2 \frac{d}{dt} \left( \frac{\rho_2}{\rho} \right). \quad (201)$$

This entropy equation is similar to (199), but written by von Meixner (1941, Eq. 22, p.341) as

$$\rho \frac{dS}{dt} + \vec{\nabla} \cdot \vec{S}' = \vartheta. \quad (202)$$

Clearly, for von Meixner (1941) the entropy ( $S$ ) did not need to be determined by somehow integrating the entropy equation (202), but is predetermined and can be computed according to Gibbs' equations as the weighted sum (200) of the partial entropies of the gases composing the mixture ( $S_1, S_2, \dots$ ).

von Meixner (1941, Eqs. 21, 23 and 24, p.341-342) gave explicit values for the Entropy flow vector (“*Entropiestömung*”)

$$\vec{S}' = \frac{\vec{W}}{T} + \Phi_1 \vec{D}_1 + \Phi_2 \vec{D}_2, \quad (203)$$

which therefore depends on the heat flow  $\vec{W}$ , the barycentric diffusion fluxes  $\vec{D}_i = \rho_i (\vec{v}_i - \vec{v})$  for  $i = (1, 2)$ , and the Massieu's potential

$$\Phi_i = -\frac{\mu_i}{T} - \frac{R}{M_i} = -\frac{h_i}{T} + s_i - \frac{R}{M_i} \quad (i = 1, 2), \quad (204)$$

where  $\mu_i = h_i - T s_i$  ( $i = 1, 2$ ) are the Gibbs' chemical potentials.

Note that these diffusion fluxes  $\vec{D}_i$  ( $i = 1, 2$ ) were associated (von Meixner, 1941, Eq. 10, p.339) with the following definitions for the continuity equations

$$\frac{d\rho}{dt} + \rho \vec{\nabla} \cdot \vec{v} = 0, \quad (205)$$

$$\frac{d}{dt} \left( \frac{\rho_i}{\rho} \right) + \frac{1}{\rho} \vec{\nabla} \cdot \vec{D}_i = 0 \quad (i = 1, 2). \quad (206)$$

von Meixner (1941, Eq. 24, p.342) also gave explicit values for the entropy generation (“*Entropieerzeugung*”) positive term:

$$\vartheta = \vec{W} \cdot \vec{\nabla} \left( \frac{1}{T} \right) + \vec{D}_1 \cdot \vec{\nabla}(\Phi_1) + \vec{D}_2 \cdot \vec{\nabla}(\Phi_2) + \vec{D}_1 \cdot \frac{\vec{K}_1}{T} + \vec{D}_1 \cdot \frac{\vec{K}_2}{T} + [\dots], \quad (207)$$

where  $\vec{K}_1$  and  $\vec{K}_2$  are the external forces (per gram) acting on the two types of molecules and where the last term  $[\dots]$  represent the impact of strain-pressure dynamical forces.

Finally, the entropy equation is also written in von Meixner (1941, Eqs. 25 and 26, p.342) like in the second part of (199), in terms of the total entropy flow (“*gesamte Entropieströmung*”):

$$\vec{S} = \vec{S}' + \rho S \vec{v}, \quad (208)$$

thus including the flux of entropy ( $\rho S \vec{v}$ ) due to “*convection*” (in fact advection), and leading to:

$$\frac{\partial(\rho S)}{\partial t} = -\vec{\nabla} \cdot \vec{S} + \vartheta. \quad (209)$$

However, von Meixner (1941) did not studied, nor even considered the impact of the reference values of entropies on the different terms of the entropy equation.

In fact, von Meixner (1941) did not compute explicitly  $S_1$  nor  $S_2$  in terms of the temperature ( $T$ ), the partial pressures  $p_1$  and  $p_2$  and the two needed constant reference values  $s_{01}$  and  $s_{02}$ , and thus without the need to manage the resulting “reference entropy varying term”

$$S_0 = \frac{\rho_1 s_{01} + \rho_2 s_{02}}{\rho}. \quad (210)$$

The study of this reference term  $S_0$  forming a variable part of  $S$  (if  $\rho_1$  and  $\rho_2$  are not two constant terms) would have shown that the r-h-s of (202) and  $\vartheta$  given by (207) does not depend on  $s_{01}$  and  $s_{02}$ , because the impacts are via the two terms  $\vec{\nabla}(\Phi_1)$  and  $\vec{\nabla}(\Phi_2)$  given by (204), and thus with both  $\vec{\nabla}(s_{01}) = 0$  and  $\vec{\nabla}(s_{02}) = 0$ . This means that the impacts of  $S_0$  on the l-h-s of (202) must be 0, with a balance of the existing individual impacts of  $S_0$  on both the derivative ( $dS/dt$ ) and the divergence of flux ( $\vec{\nabla} \cdot \vec{S}'$ ) terms.

Differently, both the l-h-s and r-h-s of the relationship (209) do depend on  $S_0$  and the reference entropies  $s_{01}$  and  $s_{02}$  (via the two terms  $\partial(\rho S)/\partial t$  in the l-h-s and  $\vec{\nabla} \cdot \vec{S}$  in the r-h-s). This show that depending on the choice of this or that definition for computing the entropy equation, it may be needed to manage the study of the impact of the reference entropies  $s_{01}$  and  $s_{02}$  via the variable part  $S_0$  given by (210) of  $S$  given by (200).

Note that the whole formalism described here for a mixture of two gases by von Meixner (1941) is a precursor of the barycentric continuous-systems formalism next adopted by the Belgian school, but popularised and still available in the books by de Groot and Mazur (1962), Glansdorff and Prigogine (1971a,b), Dufour and van Mieghem (1975) and de Groot and Mazur (1986).

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- The same kind of results are published in von Meixner (1942), with a similar application to the case of a two components (1,2) fluid and with the same barycentric formulation, entropy flux and entropy production term.

von Meixner (1943a), generalized the previous results to the case of a mixture with an arbitrary number  $n = (1, 2, \dots, n)$  of components, and with the internal energy explicitly written (top of p.256) as the weighted sum  $U = \sum_{i=1}^n c_i (C_v T + u_{i0})$ , and thus with the constant reference values  $u_{i0}$  generating



the variable weighted sum  $U_0 = \sum_{i=1}^n c_i u_{i0}$  (with corresponding impacts on the entropy equation that was not studied by von Meixner, 1943a). The similar weighted sum for the entropy  $S = \sum_{i=1}^n c_i (\dots + s_{i0})$  was not written, and thus with the impact on the entropy equation of the reference values of entropies ( $s_{i0}$ ) that was not studied by von Meixner (1943a).

von Meixner (1943b) studied the properties of a mixture of  $n = (1, 2, \dots, n)$  components, with explicit formulations for the free energy ( $F$ ) and the entropy ( $S$ ) in Eqs. 17 and 19, p.250:

$$F = \sum_{i=1}^n c_i \{ f_i(T) + R T [\ln(\rho c_i) - 1] \} , \quad (211)$$

$$S = - \frac{\partial F}{\partial T} = - \sum_{i=1}^n c_i \left\{ \frac{\partial f_i}{\partial T} + R [\ln(\rho c_i) - 1] \right\} . \quad (212)$$

The partial continuity equations (206) was generalized by von Meixner (1943b, Eq. 25, p.252) into

$$\frac{d}{dt} \left( \frac{\rho_i}{\rho} \right) + \frac{1}{\rho} \vec{\nabla} \cdot \vec{D}_i = \frac{1}{\rho} \Gamma_i \quad (i = 1, 2) , \quad (213)$$

by including the production rate  $\Gamma_i$  of each species  $i$  by chemical transformations, dissociations, excitations (and changes of phases), but leading to the same total continuity equation (205).

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• Prigogine (1947, his PhD report, in French), Prigogine (1949, in *Physica*, in French) and Prigogine (1967, by Wiley & Sons, in English, first published in 1955) computed the entropy budget for continuous systems (Chapter IX in the French PhD) by explicitly assuming the Gibbs local equation (Eq. 9.4, p.95, written in terms of the local internal energy  $e = u$  and the local density  $v = 1/\rho$ ) written as

$$T \frac{ds}{dt} = \frac{du}{dt} + p \frac{d}{dt} \left( \frac{1}{\rho} \right) - \sum_{\gamma} \mu_{\gamma} \frac{dq_{\gamma}}{dt} , \quad (214)$$

for  $\gamma = (1, \dots, c)$  constituents in the system.

Previously, Prigogine (1947, Eq. 4, p.2) split the total change in entropy

$$dS = d_e S + d_i S \quad (215)$$

into the sum of “*external*” changes ( $d_e S$ , due to boundary fluxes of heat and matter) and “*internal*” changes ( $d_i S$ , due to chemical reactions or phase changes if metastable or irreversible).

Prigogine (1947, Eq. 1.6 and 4.1, p.14 and 44) similarly split the rate of increase of mass ( $dm/dt$ ) and of the heat received by the system ( $dQ$ ), according to:

$$\frac{dm}{dt} = \frac{d_e m}{dt} + \frac{d_i m}{dt} , \quad \text{and} \quad dQ = d_e Q + d_i Q . \quad (216)$$

The same relationships as (216) are written for the rate of change of the enthalpy ( $dh/dt$ ), of the entropy ( $ds/dt$ ) and of other thermodynamic quantities.

Moreover, the heat  $dQ$  received by an open system surrounded by several phases, with only some of them (the “*feeding*” phases) exchanging matter and heat with the system, is split by Prigogine (1947, Eq. 4.21, p.48) into the sum

$$dQ = d_n Q + d_a Q , \quad (217)$$

where  $d_n Q$  is the heat received from the “*feeding* (*nourricières*)” sources and  $d_a Q$  from the “*other* (*autres*)” sources.

Then Prigogine (1947, Eq. 9.9, p.96) arrived, like in von Meixner (1941, 1942, 1943a), to a budget equation for a multi-components system like (199), written as an equivalent of

$$\rho \frac{ds}{dt} = \frac{\partial \rho s}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v}) = -\vec{\nabla} \cdot \vec{J}_S + \sigma. \quad (218)$$

$$\frac{\partial \rho s}{\partial t} = -\vec{\nabla} \cdot (\rho s \vec{v} + \vec{J}_S) + \sigma = -\vec{\nabla} \cdot \vec{\Phi} + \sigma, \quad (219)$$

and therefore with the total flux of entropy  $\vec{\Phi} = \rho s \vec{v} + \vec{J}_S$  made of the “*convective*” part  $(\rho s \vec{v})$  plus the “*diffusive*” part  $(\vec{J}_S)$ .

However, Prigogine (1947) used several peculiar notations to express both  $\vec{\Phi}$  and  $\sigma$  in terms of the thermodynamic variables.

First, like von Meixner (1941, 1943a,b) made before him, Prigogine (1947, Eqs. 7.15 to 7.17, p.79) defined the barycentric mean density  $(\rho)$ , the barycentric mean velocity vector  $(\vec{\omega})$  and the diffusion vector  $(\vec{\Delta}_\gamma)$  in terms of the following weighted sums of the individual densities  $\rho_\gamma$  and wind velocity vectors  $\vec{\omega}_\gamma$  for all the  $\gamma = (1, \dots, c)$  constituents:

$$(\text{Eq. 7.16}) \dots \rho = \sum_{\gamma} \rho_{\gamma}, \quad (220)$$

$$(\text{Eq. 7.15}) \dots \vec{\omega} = \frac{1}{\rho} \sum_{\gamma} \rho_{\gamma} \vec{\omega}_{\gamma}, \quad (221)$$

$$(\text{Eq. 7.17}) \dots \vec{\Delta}_\gamma = \vec{\omega}_\gamma - \vec{\omega}. \quad (222)$$

These notations will be replaced in many next studies by  $\vec{v}$  (instead of  $\vec{\omega}$ ) for the barycentric velocity and  $\vec{D}_k$  of  $\vec{J}_k$  (instead of  $\rho_\gamma \vec{\Delta}_\gamma$ ) for the diffusion flux.

Using these definitions and notations (221)-(222), Prigogine (1947, Eqs. 9.10, p.96) computed the entropy equation and arrived at the “entropy flux” written as

$$(\text{Eq. 9.10}) \dots \vec{\Phi}(S) = \rho s \vec{v} + \frac{\vec{W}}{T} - \sum_{\gamma} \mu_{\gamma} \frac{(\rho_{\gamma} \vec{\Delta}_{\gamma})}{T} = \rho s \vec{v} + \frac{\vec{W}}{T} - \sum_{\gamma} \left( \frac{h_{\gamma}}{T} - s_{\gamma} \right) (\rho_{\gamma} \vec{\Delta}_{\gamma}), \quad (223)$$

thus including the impact of the heat flux  $(\vec{W})$  and of the diffusion of gases via  $\rho_{\gamma} \vec{\Delta}_{\gamma}$  and with the chemical potential  $\mu_{\gamma} = h_{\gamma} - T s_{\gamma}$ . The corresponding “entropy source” (Eq. 9.13, p.97) was written as

$$(\text{Eq. 9.13}) \dots \sigma(S) = -\vec{W} \cdot \frac{\vec{\nabla}(T)}{T^2} - \sum_{\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma}) \cdot \vec{\nabla} \left( \frac{\mu_{\gamma}}{T} \right) + \frac{A \dot{v}}{T} + (\dots), \quad (224)$$

where  $A$  is the affinity associated with the chemical rate of reaction  $\dot{v} = d\xi/dt$  (creation rate of the species), and where the terms  $(\dots)$  depends on the impacts of pure “dynamical” terms (pressure, etc).

Prigogine (1947, p.97) explained that “*the entropy production  $\sigma(S)$  results from three factors: 1) the non-uniformity of the intensive variables (like  $T, \rho, \dots$ ); 2) the impact of chemical reactions (via  $A$  and  $\dot{v}$ ); 3) the degradation of more “noble” energy into the (dead state, degraded) internal energy (mechanical dissipation, etc).*”

It is possible to derive an alternative formulation of (224) by introducing the definition  $\mu_{\gamma} = h_{\gamma} - T s_{\gamma}$  for the chemical potentials, leading to:

$$\sigma(S) = - \left[ \vec{W} - \sum_{\gamma} h_{\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma}) \right] \cdot \frac{\vec{\nabla}(T)}{T^2} - \sum_{\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma}) \cdot \left[ \frac{1}{T} \vec{\nabla}(h_{\gamma}) - \vec{\nabla}(s_{\gamma}) \right] + \frac{A \dot{v}}{T} + (\dots), \quad (225)$$

This is the reason why other formulations were derived by Prigogine (1947, Eqs. 9.11, 9.12 and 9.15, p.97-98) for the flux of entropy and the entropy production term, with the introduction (p.97) of the new (reduced) heat flux

$$\text{(Eq. 9.11) ... } \vec{\mathcal{W}} = \vec{W} - \sum_{\gamma} h_{\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma}) , \quad (226)$$

leading (p.97) to the “*very simple formulation*” for the entropy flux

$$\text{(Eq. 9.12) ... } \vec{\Phi}(S) = \frac{\vec{\mathcal{W}}}{T} + \rho s \vec{v} - \sum_{\gamma} \rho_{\gamma} s_{\gamma} (\vec{\omega}_{\gamma} - \vec{\omega}) = \frac{\vec{\mathcal{W}}}{T} + \sum_{\gamma} \rho_{\gamma} s_{\gamma} \vec{\omega}_{\gamma} , \quad (227)$$

(where the diffusion fluxes  $\vec{\Delta}_{\gamma}$  are thus replaced by the velocities  $\vec{\omega}_{\gamma}$  due to Eqs. 7.17 and 7.15) and leading (p.98) to the associated entropy production term:

$$\text{(Eq. 9.15) ... } \sigma(S) = - \vec{\mathcal{W}} \cdot \frac{\vec{\nabla}(T)}{T^2} - \sum_{\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma}) \cdot \left[ \frac{h_{\gamma}}{T^2} \vec{\nabla}(T) + \vec{\nabla}\left(\frac{\mu_{\gamma}}{T}\right) \right] + \frac{A \dot{v}}{T} + (\dots) ; \quad (228)$$

or equivalently, by using  $\mu_{\gamma} = h_{\gamma} - T s_{\gamma}$ , to the other way to write (228):

$$\sigma(S) = - \vec{\mathcal{W}} \cdot \frac{\vec{\nabla}(T)}{T^2} - \sum_{\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma}) \cdot \left[ \frac{\vec{\nabla}(h_{\gamma}) - T \vec{\nabla}(s_{\gamma})}{T} \right] + \frac{A \dot{v}}{T} + (\dots) . \quad (229)$$

- Prigogine (1947) did not studied, nor even considered, the impact of the reference values of entropies on the different terms of the entropy equation (entropy flux and entropy production).

The apparent advantage of the formula recalled in (228) is that both  $\vec{\nabla}(h_{\gamma})$  and  $\vec{\nabla}(s_{\gamma})$  are independent of the reference (constant) values for the enthalpies ( $h_{0\gamma}$ ) and the entropies ( $s_{0\gamma}$ ) because the gradients of these constant quantities cancel out within the squared brackets.

However, both the reduced heat flux  $\vec{\mathcal{W}}$  in Eq. 9.11 recalled in (226) and the associated entropy flux  $\vec{\Phi}(S)$  in Eq. 9.12 recalled in (227) depend on the reference enthalpies and entropies. Indeed the two weighted sums  $\sum_{\gamma} h_{0\gamma} (\rho_{\gamma} \vec{\Delta}_{\gamma})$  and  $\sum_{\gamma} \rho_{\gamma} s_{0\gamma} \vec{\omega}_{\gamma}$  do not cancel out for a variable composition mixture and if the reference terms  $(h_{0\gamma})'$ s and the  $(s_{0\gamma})'$ s are not the same for all components of the mixture.

Therefore, via this term  $\vec{\mathcal{W}}$  the entropy production terms in  $\sigma(S)$  given by (228) and (229) depends on the reference values  $(h_{0\gamma})$  of the enthalpies!

Moreover, both the left-hand-side  $\partial(\rho s)/\partial t$  of (219) and the right-hand-side divergence term  $-\vec{\nabla} \cdot \vec{\Phi}$  of (219) given by (223) or (227) depend on the reference values  $(s_{0\gamma})$  of the entropies!

- In its founding English book, de Groot (1951) expressed the entropy equation for continuous, multi-components systems (Chapter VII, Eqs. 21-26, p.98) like (199) and written as

$$\rho \frac{ds}{dt} = - \vec{\nabla} \cdot \vec{J}_s + \sigma , \quad (230)$$

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

$$\frac{\partial(\rho s)}{\partial t} = - \vec{\nabla} \cdot (\vec{J}_s + \rho s \vec{v}) + \sigma . \quad (231)$$

In particular, the “entropy flow” due to the Fourier’s law and the (molecular) diffusion processes is

$$\vec{J}_s = \frac{1}{T} \left( \vec{J}_q - \sum_k \mu_k \vec{J}_k \right) \quad (232)$$

(here  $\vec{J}_q$  is the heat flow previously noted  $\vec{W}$  or  $\vec{F}_T$ , with the diabating heating rate  $\dot{q} = -\vec{\nabla} \cdot \vec{J}_q$ , and  $\vec{J}_k$  is the same diffusion flux noted  $\vec{D}_j$  or  $\rho_\gamma \vec{\Delta}_\gamma$  in previous studies). The associated “entropy production” term (Eq. 26, p.98) is

$$\sigma = -\vec{J}_q \cdot \frac{\vec{\nabla}(T)}{T^2} - \sum_k \vec{J}_k \cdot \vec{\nabla} \left( \frac{\mu_k}{T} \right) + (\dots) . \quad (233)$$

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• In the other studies by von Haase (1951a), von Haase (1951b), von Haase (1953) ... up to von Haase (1990, Eqs. 1-6.8 a,d 1-6.9 p.16), all state functions are expressed as the weighted sums  $Z = \sum_k n_k Z_k$  and  $\bar{Z} = \sum_k x_k Z_k$  (thus for the internal energy, enthalpy and entropy).

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• Mazur (1952, in French) derived the local (specific) entropy equation (4.4, p.189) which can be written as

$$\rho \frac{ds}{dt} = -\vec{\nabla} \cdot \vec{S} + \sigma \quad (234)$$

with the same entropy flux

$$\vec{S} = \frac{1}{T} \left( \vec{W} - \sum_\gamma \rho_\gamma \vec{\Delta}_\gamma \mu_\gamma \right) \quad (235)$$

and entropy source

$$\sigma = -\vec{W} \cdot \frac{\vec{\nabla}(T)}{T^2} + \sum_\gamma (\rho_\gamma \vec{\Delta}_\gamma) \cdot \vec{\nabla} \left( \frac{\mu_\gamma}{T} \right) + (\dots) \quad (236)$$

as in Prigogine (1947), but with a positive sign for the second term of  $\sigma$  depending on the Gibbs potential  $\mu_\gamma$ .

The status of “*Minimum of entropy production*” is defined by Mazur (1952, Eqs. 4.8) as

$$\rho ds/dt = 0 \quad \text{and thus} \quad -\vec{\nabla} \cdot \vec{S} + \sigma = 0 , \quad (237)$$

and thus with a clear impact of the reference values of entropies

$$s_\gamma(T, p) = s_\gamma(T_0, p_0) + (\dots) , \quad (238)$$

via the relationships

$$ds/dt = \sum_\gamma s_\gamma(T_0, p_0) d(\rho_\gamma/\rho)/dt + (\dots) \quad (239)$$

$$\text{and} \quad -\vec{\nabla} \cdot \vec{S} = -\sum_\gamma s_\gamma(T_0, p_0) \vec{\nabla} \cdot (\rho_\gamma \vec{\Delta}_\gamma) + (\dots) , \quad (240)$$

with therefore a clear impact of the reference values of the entropies on both sides of the entropy equation

$$\rho ds/dt = -\vec{\nabla} \cdot \vec{S} + \sigma . \quad (241)$$

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• Similarly, von Meixner and Reik (1959) relied on the (local, Gibbs, Eqs. 3.4 and 3.5) differential equations

$$ds = \frac{du}{T} + \frac{p}{T} d\left(\frac{1}{\rho}\right) - \sum_{i=1}^{n-1} \frac{\mu_i - \mu_n}{T} d\gamma_i , \quad (242)$$

$$\text{and } d(\rho s) = \frac{1}{T} d(\rho u) - \sum_{i=1}^n \frac{\mu_i}{T} d\rho_i , \quad (243)$$

where  $\gamma_i = \rho_i/\rho$  ( $i = 1, 2, \dots, n-1$ ) are the concentrations,  $\rho_i$  ( $i = 1, 2, \dots, n$ ) the densities and  $\mu_i$  ( $i = 1, 2, \dots, n$ ) the chemical potentials.

The (Gibbs) budget-entropy equations was then written by von Meixner and Reik (1959, Eq. 5.1) as

$$\frac{Ds}{Dt} = \frac{1}{T} \frac{Du}{Dt} + \frac{p}{T} \frac{D}{Dt} \left( \frac{1}{\rho} \right) - \sum_{i=1}^n \frac{\mu_i}{T} \frac{D\gamma_i}{Dt} , \quad (244)$$

which is then written in the usual form (Eqs. 5.4 to 5.7) like in (230), (232) and (233) of de Groot (1951), but written as:

$$\rho \frac{Ds}{Dt} = \vec{\nabla} \cdot \vec{J}_s + \sigma_s , \quad (245)$$

$$\vec{J}_s = \frac{1}{T} \left( \vec{J}_u - \sum_{i=1}^n \mu_i \vec{J}_i \right) , \quad (246)$$

$$\text{and } \sigma_s = \vec{J}_u \cdot \vec{\nabla} \left( \frac{1}{T} \right) - \sum_{i=1}^n \vec{J}_i \cdot \vec{\nabla} \left( \frac{\mu_i}{T} \right) - \sum_{i=1}^n \Gamma_i \frac{\mu_i}{T} + (\dots) , \quad (247)$$

where the budget operator (Eq. 4.8) is  $D/Dt = \partial/\partial t + \vec{v} \cdot \vec{\nabla}(\dots)$ .

Therefore, the budget-entropy equation in the form (245), with (246) and (247), can be understood as a balance equation for entropy with the “total entropy flux density” vector

$$\vec{\Phi}_s = \vec{J}_s + \rho s \vec{v} , \quad (248)$$

thus including the convective entropy transport, and with the entropy production density  $\sigma_s$ , leading (Eq. 5.8 and 5.9) to the alternative writings:

$$\frac{\partial}{\partial t}(\rho s) = - \vec{\nabla} \cdot \vec{\Phi}_s + \sigma_s , \quad (249)$$

$$\text{or equivalently } \frac{\partial}{\partial t}(\rho s) = \frac{1}{T} \frac{\partial}{\partial t}(\rho u) - \sum_{i=1}^n \frac{\mu_i}{T} \frac{\partial \rho_i}{\partial t} . \quad (250)$$

---

• The next important steps are the German-language papers of Herbert (1973a,b, 1975), along with those written later in English (Herbert, 1980, 1983).

In particular (for the first time it seems) Herbert (1975, Eq. I-6, p.7) started from the local (microscopic) equations of any specific quantity  $\varphi$ , like the entropy equation for  $\varphi = s$ , to build the associated turbulent entropy equation.

More precisely, Fritz Herbert (1975) started from the local entropy equation

$$\frac{\partial(\rho s)}{\partial t} + \vec{\nabla} \cdot (\rho s \vec{v} + \vec{J}_s) = \sigma_s \quad (251)$$

to derive the turbulent entropy equation

$$\frac{\partial(\bar{\rho} \hat{s})}{\partial t} + \vec{\nabla} \cdot (\bar{\rho} \hat{s} \vec{v} + \overline{\rho s'' \vec{v}''} + \vec{J}_s) = \bar{\sigma}_s, \quad (252)$$

where  $\overline{\rho s'' \vec{v}''}$  is the turbulent flux of entropy and where the mean entropy flux  $\vec{J}_s$  and entropy production term  $\bar{\sigma}_s$  are averaged version of Eqs. 5.5 and 5.7 by von Meixner and Reik (1959, p.423) recalled in (246) and (247).

Note that the turbulent entropy-flux term  $\overline{\rho s'' \vec{v}''}$  does not appear in most of modern papers and books dealing with the moist-air entropy equations.

Like others before him, and in particular von Meixner (1941, see his Eq. 14, p.340 recalled in (200)), Herbert (1975, Eq. I-8, p.7) wrote the specific value for any extensive property ( $\hat{\phi}$ ) as

$$\hat{\phi}(\hat{T}, \hat{p}, \hat{m}_k) = \sum_k \hat{\phi}_k \hat{m}_k, \quad (253)$$

in terms of the mean temperature ( $\hat{T}$ ), pressure ( $\hat{p}$ ) and concentrations ( $\hat{m}_k, k = 0, 1, 2, 3$  for dry air, water vapour, liquid water and ice, respectively).

Accordingly, the specific entropy ( $\hat{s}$ ) and the specific chemical potential ( $\hat{\mu} = \hat{h} - \hat{T}$ , see Herbert, 1975, before Eq. III-3, p.17) must be written like the specific enthalpy, which is explicitly given (Herbert, 1975, Eq. I-12, p.8) by

$$\hat{h}(\hat{T}, \hat{m}_k) = \sum_k \hat{h}_k \hat{m}_k, \quad \text{with} \quad \hat{h}_k = \hat{h}_k(\hat{T}) = \left( \int_{\hat{T}_0}^{\hat{T}} \hat{c}_{pk} d\hat{T} \right) + \hat{h}_k(\hat{T}_0), \quad (254)$$

with as such  $\hat{h}_k(\hat{T})$  only depending on the temperature  $\hat{T}$  and with all the reference values  $\hat{h}_k(\hat{T}_0)$  left undetermined.

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- I know since 1989 the paper of Hauf and Höller (1987) thanks to Jean-François Geleyn.

The fundamental Herbert's equation (253) valid for the specific values of any state functions like the internal energy ( $u$ ), enthalpy ( $h$ ), entropy ( $s$ ) and chemical potential ( $\mu = h - T s$ ), is similarly written in Hauf and Höller (1987, Eq. 2.11, p.2890) as  $\boxed{\psi = \psi_n m^n}$  with the implicit Einstein's notation for the sum over the  $n$  (and also for  $n = 0, 1, 2, 3$  for dry air, water vapour, liquid water and ice, respectively).

Accordingly, the specific value of the moist-air entropy is written by Hauf and Höller (1987, Eq. 3.1, p.2890) as  $\boxed{s = s_n m^n}$  (following unpublished lectures notes of Hinkelmann and the papers of Herbert, 1973a,b, 1975).

Then Hauf and Höller (1987, Eq. 3.9, p.2891) explicitly computed the specific moist-air entropy by computing this sum  $s = s_n m^n$  with all the partial entropies ( $s_n$ ) written in terms of the temperature ( $T$ ), partial pressures ( $p_0$  and  $p_1$ ) and the reference values ( $s_{0n}$ ), leading to:

$$s = s_n m^n = c_p \ln\left(\frac{T}{T_0}\right) - R_d \ln\left(\frac{p_d}{p_0}\right) - R_v \ln\left(\frac{p_v}{p_0}\right) + s(0), \quad (255)$$

where the moist-value for the specific heat is the mass-weighted average  $c_p = s_n m^n$ , and where I have replaced  $R_0$  and  $p_0$  for the dry air by  $R_d$  and  $p_d$ , and similarly  $R_1$  and  $p_1$  for the water vapour by  $R_v$  and  $p_v$ .

The last term of (255) is  $s(0) = s_{0n} m^n$  and: “*is the entropy reference value which is a mass-weighted average of the partial zero-entropies  $s_{0n}$  and thus is not a constant*” (Hauf and Höller, 1987, see p.2891, after Eq. 3.9).

Note that the reference values  $s_{0n}$  for the partial entropies at  $T_0 = 273.15$  K and  $p_0 = 1000$  hPa are set to their absolute (Third-law) values (Hauf and Höller, 1987, see p.2891, before Eq. 3.10):

- $s_{d0}(T_0, p_0) \approx 6\,775$  J K<sup>-1</sup> for the dry air,
- $s_{v0}(T_0, p_0) \approx 10\,320$  J K<sup>-1</sup> for the water vapour,
- $s_{l0}(T_0) \approx 3517$  J K<sup>-1</sup> for the liquid vapour, and
- $s_{i0}(T_0) \approx 2296$  J K<sup>-1</sup> for water-Ice-Ih.

Note that the chemical potentials ( $\mu_k$ ) and the affinities ( $a_{ij} = \mu_i - \mu_j$ ) are also fully computed by Hauf and Höller (1987, Eqs. 3.10 to 3.12, p.2891).

Hauf and Höller (1987, Eq. 3.13, p.2891) also considered the Gibbs differential equation written as

$$T ds = dh - \frac{1}{\rho} dp - \mu_n dm^n \quad (256)$$

written in terms of the temperature ( $T$ ), the enthalpy ( $h$ ), the pressure ( $p$ ), the density ( $\rho$ ), the chemical potentials ( $\mu_n$ ) and the concentrations ( $m_n$ ).

Note the important result that this Gibbs equation (256) derived by Hauf and Höller (1987) is valid for the specific entropy predefined as a weighted sum and computed with (255), just like for von Meixner (1941, see his Eqs. 14 and 22, p.340 and 341, both recalled in (200) and (202)) before him.

However, Hauf and Höller (1987) did not explicitly studied the impact of the reference enthalpies and/or entropies on the entropy equation.

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• In a more recent book, Zdunkowski and Bott (2004, dedicated to the memory of K. H. Hinkelmann) similarly considered that the specific values of any state functions like the internal energy ( $u$ ), the enthalpy ( $h$ ), the entropy ( $s$ ) and the chemical potential ( $\mu = h - T s$ ), can be written like in Hauf and Höller (1987, Eq. 2.11, p.2890) as  $\boxed{\psi = \psi_n m^n}$  (Zdunkowski and Bott, 2004, Eq. 1.16, p.9), with the same implicit Einstein’s notation for the sum over the  $n$  (and also for  $n = 0, 1, 2, 3$  for dry air, water vapour, liquid water and ice, respectively). Note that Zdunkowski and Bott (2004) also cited (and was inspired by) the previous approaches of Eckart (1940a) and Herbert (1973b).

Zdunkowski and Bott (2004, Eq. 4.16, p.50) started with the Gibbs entropy equation noted

$$T ds = dh - \frac{1}{\rho} dp - \mu_n dm^n, \quad (257)$$

namely the same differential equation as in the previous papers and books.

Zdunkowski and Bott (2004, Eqs. 4.20 to 4.22, p.51) derived the same kind of entropy equation as in Hauf and Höller (1987), for instance, namely:

$$\rho \frac{ds}{dt} = - \vec{\nabla} \cdot \vec{F}_s + Q_s, \quad (258)$$

where the (non-convective) entropy flux ( $\vec{F}_s$ ) and the entropy sources ( $Q_s$ ) were written as:

$$\vec{F}_s = \frac{\vec{J}_s^h}{T} + s_n \vec{J}^n, \quad (259)$$

$$Q_s = \vec{J}^h \cdot \vec{\nabla} \left( \frac{1}{T} \right) - \vec{J}^n \cdot \vec{\nabla} \left( \frac{\mu_n}{T} \right) + \mathbb{J} \cdot \vec{\nabla} \vec{v} - \frac{\mu_k I^k}{T} \geq 0. \quad (260)$$

Here, in (259) and (260):

- $\vec{J}_s^h/T$  is called the reduced sensible heat flux;
- where  $\vec{J}_s^h = \vec{J}^h - h_n \vec{J}^n$  is the sensible enthalpy flux;
- $\vec{J}^h$  is the heat flux vector (enthalpy flux);
- and  $-h_n \vec{J}^n$  is the diffusive enthalpy flux;
- $\vec{J}^n$  is the diffusion flux of the substance  $n$ ;
- $\mathbb{J}$  is the viscous stress tensor; and
- $I^k$  (for  $k = 1, 2, 3$  only) is the phase transition rate of substance  $k$  (describing the transition changes due to transition between the various phases of water vapor, liquid and ice).

In a next step, Zdunkowski and Bott (2004, section 7.3, p.101-109) then studied the “*Meteorological applications of the theory of irreversible fluxes.*”

Moreover, just like Hauf and Höller (1987, Eqs. 3.10 and 3.12, p.2891), Zdunkowski and Bott (2004, Eqs. 4.23) defined the chemical affinities as the difference of the chemical potentials

$$a_{21} = a_{lv} = R_v \ln \left( \frac{p_{sat/l}(T)}{p_v} \right) = \mu_l - \mu_v = -L_v(T) - T [s_l(T) - s_v(T, p_v)] , \quad (261)$$

$$a_{31} = a_{iv} = R_v \ln \left( \frac{p_{sat/f}(T)}{p_v} \right) = \mu_f - \mu_v = -L_s(T) - T [s_f(T) - s_v(T, p_v)] . \quad (262)$$

The entropy equation (258), with the entropy flux (259) and the entropy production (260), were obtained from the enthalpy equation previously written by Zdunkowski and Bott (2004, Eq. 3.36, p.31) as:

$$\frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} = -\frac{1}{\rho} \vec{\nabla} \cdot (\vec{J}^h + \vec{F}_r) + \frac{1}{\rho} \mathbb{J} \cdot \vec{\nabla} \vec{v}, \quad (263)$$

where  $\vec{F}_r$  is the radiative net heat flux. Note that the entropy flux (259) is derived and written without the impact of this radiation fluxes  $\vec{F}_r$  duly included in (263) (see the explanations below).

Note that it is easy to recover the entropy flux and production terms (259) and (260) corresponding to the (material, without the impact of radiation) entropy equation (258), simply by inserting the enthalpy equation (263) into the Gibbs equation (257) rewritten with  $\mu_k = h_k - T s_k$  as

$$T \frac{ds}{dt} = \left[ \frac{dh}{dt} - \frac{1}{\rho} \frac{dp}{dt} \right] - h_n \frac{dm^n}{dt} + T s_n \frac{dm^n}{dt}. \quad (264)$$

However, Zdunkowski and Bott (2004) did not studied the impact of the reference enthalpies and/or entropies on this entropy equation.

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• Gassmann and Herzog (2015) did not referred to the previous papers or books of Eckart (1940a,b), von Meixner (1941, 1942, 1943a,b), Prigogine (1947), van Mieghem (1947), Prigogine (1949), von Haase



(1951a,b, 1953), von Meixner and Reik (1959), Prigogine (1967), Herbert (1973a,b, 1975, 1980, 1983), von Haase (1990), Zdunkowski and Bott (2004), ...

Instead, Gassmann and Herzog (2015) only referred to (and relied on) the formalism of de Groot and Mazur (1984). Thanks to Jean-François Royer, I know since 1989 the famous synthesis book of de Groot and Mazur (1962) about “*Non-equilibrium thermodynamics*” summarized before in de Groot (1959) and republished in de Groot and Mazur (1984).

Gassmann and Herzog (2015, Eqs. 17 and 20, p.858) wrote a turbulent entropy equation in a form similar to (252) written by Fritz Herbert (1975), but written as an equivalent of

$$\begin{aligned} \text{like (Herbert, 1975): } \bar{\rho} \frac{\hat{d}\hat{s}}{dt} &= \frac{\partial(\bar{\rho} \hat{s})}{\partial t} + \vec{\nabla} \cdot (\bar{\rho} \hat{s} \vec{v}) + \vec{\nabla} \cdot (\bar{\rho} s'' \vec{v}'') , \\ \text{with: } \bar{\rho} \frac{\hat{d}\hat{s}}{dt} &= - \vec{\nabla} \cdot \bar{J}_s + \bar{\sigma}_s , \end{aligned} \quad (265)$$

The turbulent flux of entropy  $\bar{\rho} s'' \vec{v}''$  is therefore included in (265) in the  $\hat{d}/dt$  operator, with both  $\bar{J}_s$  and  $\bar{\sigma}_s$  explicitly written by Gassmann and Herzog (2015), like in de Groot and Mazur (1984), in terms of gradients of the absolute temperature  $T$  and of the chemical potentials (Gibbs functions)  $\mu_i = h_i - T s_i$  for dry air, water vapour, liquid water and ice. Note that (265) is indeed similar to the relationship (252) previously derived by Herbert (1975, Eq. I-5, p.7).

Moreover, Gassmann and Herzog (2015, bottom right of p.858) expressed the moist-air turbulent entropy equation in terms of a potential temperature they noted  $\hat{\theta}$  (thus like for the dry air), but with the assumption that the specific (moist-air) entropy may be represented as

$$\hat{s} = c_{pd} \ln(\hat{\theta}) + s_0 , \quad \text{and thus with } \hat{d}\hat{s} = c_{pd} \hat{d}\ln(\hat{\theta}) . \quad (266)$$

Note that this definition (266) precisely leads to the same moist-air entropy potential temperature “ $\theta_s$ ” I have defined in Marquet (2011a, Eq. 59, p.781). Even more precisely, the definition (266) of Gassmann and Herzog (2015) corresponds, from Marquet (2011a, about this Eq. 59, p.781) to

$$s_0 = s_{ref} = s_{d0}(T_0, p_0) - c_{pd} \ln(T_0) \approx 1138.56 \text{ J/K/kg}$$

with  $T_0 = 273.15 \text{ K}$  and  $p_0 = 1000 \text{ hPa}$  standard values.

Gassmann and Herzog (2015, top left of p.855) explained that:

*“In another group of articles, the potential temperature is traditionally considered as an appropriate substitute for entropy. Hauf and Höller (1987) first defined a moist entropy potential temperature in terms of the specific entropy for moist air. Marquet (2011a, 2015a) succeeded in deriving the most general expression of this entity”* (namely  $\theta_s$ , and only in the older 2011 paper about the moist-air entropy, since the 2015 paper was about the moist-air enthalpy instead).

*“He argues that this moist entropic potential temperature is the most suitable conserved quantity to be mixed by subgrid-scale turbulence schemes. As will be discussed in the present contribution, this usual subgrid-scale turbulent mixing concept does not allow for a distinction between entropy flux divergences and material entropy sources on the discrete level and does not necessarily guarantee total energy conservation.”*

I confess I did not understand these criticisms of Gassmann and Herzog (2015) against the variable  $\theta_s$ , because  $\theta_s$  being completely synonymous with the specific moist-air entropy via  $s = c_{pd} \ln(\theta_s) + s_0$ , the entropy equation  $ds/dt = (...)$  is thus automatically verified for  $(c_{pd}/\theta_s) d\theta_s/dt = (...)$ , and thus automatically verified for  $d\theta_s/dt = (\theta_s/c_{pd})(...)$  expressed in terms of  $\theta_s$ . This means that, if the concept of “*subgrid-scale turbulent*” would lead to any issue in the study of Gassmann and Herzog (2015), it is not due to the definition of  $\theta_s$ , but due to other part of the study and to possible difficulty to interpret or manage the entropy equation itself.

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- Other turbulent entropy equations similar to (252) are also studied in Gassmann (2018, Eqs. 15 and 20), with special values for  $\overline{J}_s$  and  $\overline{\sigma}_s$  expressed in terms of the dry-air value of the potential temperature  $\theta$ , and therefore without studying the impact of the reference entropies of the moist-air atmosphere.

The (Gibbs) entropy equation is not studied in Gassmann (2019), where only the potential vorticity  $PV(\theta)$  is studied, with  $\theta$  the dry-air value of potential temperature, and therefore without studying the impact of the reference entropies of the moist-air atmosphere like in Marquet (2014).

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- Landau and Lifshitz (1969, 1980, 1987) derived several entropy equations in the book about the “*Fluid Mechanics*.”

The first entropy equation was derived by Landau and Lifshitz (1987, Eq. 49,4, p.193) in the Chapter V about “*Thermal conduction in Fluids*” and the section §49 about “*The general equation of heat transfer*.” This Eq. 49.4 was derived for a given fluid with the viscosity tensor  $\sigma'_{ik}$  and the thermal conduction coefficient  $\kappa$ , leading to:

$$\rho T \left[ \frac{\partial s}{\partial t} + \vec{v} \cdot \vec{\nabla} s \right] = \sigma'_{ik} \frac{\partial v_i}{\partial x_k} + \vec{\nabla} \cdot (\kappa \vec{\nabla} T) . \quad (267)$$

This entropy equation was called by Landau and Lifshitz (1987, p.194) the “*general equation of heat transfer*.”

The second entropy equation derived by Landau and Lifshitz (1987, Eq. 58,6, p.229) in the Chapter VI about “*Diffusion*” and the section §58 about “*The equations of fluid dynamics for a mixture of fluids*” was written as:

$$\rho T \left[ \frac{\partial s}{\partial t} + \vec{v} \cdot \vec{\nabla} s \right] = \sigma'_{ik} \frac{\partial v_i}{\partial x_k} - \vec{\nabla} \cdot (\vec{q} - \mu \vec{i}) - \vec{i} \cdot \vec{\nabla} \mu , \quad (268)$$

where  $\vec{q}$  is the “*total energy flux in the fluid*” and  $\vec{i}$  represents the (diffusion) source of the continuity equation for one component of the mixture, with more precisely (Eq. 58,3, p.228):  $\rho dc/dt = -\vec{\nabla} \cdot \vec{i}$ .

This “*change in entropy*” equation (268) was considered by Landau and Lifshitz (1987, p.229) as a generalisation of (267) for a mixture of fluid, but it “*become determinate only when  $\vec{i}$  and  $\vec{q}$  are replaced by expressions in terms of the gradients of concentration and temperature*” like in §59 about “*Coefficients of mass transfer and thermal diffusion*” (p.230) where, for the case of small gradients of concentration and temperature:

$$\vec{i} = -\alpha \vec{\nabla}(\mu) - \beta \vec{\nabla}(T) , \quad \vec{q} = -\delta \vec{\nabla}(\mu) - \gamma \vec{\nabla}(T) + \mu \vec{i} .$$

Moreover, by the symmetry of the kinetic coefficients, we must have  $\delta = \beta T$  and thus

$$\vec{q} = (\mu + \beta T/\alpha) \vec{i} - \kappa \vec{\nabla}(T) ,$$

where  $\kappa = \gamma - \beta^2 T/\alpha$  the (generalized) thermal conduction coefficient.

Therefore Landau and Lifshitz (1969, 1980, 1987) did not studied the impact of the reference entropies in variable composition mixtures.

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- As a synthesis, in order to demonstrate that the second law of thermodynamics is impacted by the use of reference values for entropies that would be different from those –absolute– recommended by

the third law, we can start with the turbulent entropy equations written by Herbert (1975) recalled in (252) and Gassmann and Herzog (2015, Eq. 17, p.858) recalled in (265), rewritten as:

$$\bar{\rho} \frac{d\hat{s}}{dt} = \frac{\partial(\bar{\rho} \hat{s})}{\partial t} + \vec{\nabla} \cdot (\bar{\rho} \hat{s} \vec{v}) + \vec{\nabla} \cdot (\bar{\rho} s'' \vec{v}'') = -\vec{\nabla} \cdot \vec{J}_s + \bar{\sigma}_s, \quad (269)$$

where the entropy-flux and entropy-production terms can be, respectively, written as:

$$\vec{J}_s = \frac{\vec{J}_u}{\hat{T}} + \sum_{i=1}^n \hat{s}_i \vec{J}_i^*, \quad (270)$$

$$\text{and } \bar{\sigma}_s = \left( \vec{J}_u + \hat{T} \sum_{i=1}^n \hat{s}_i \vec{J}_i^* \right) \cdot \vec{\nabla} \left( \frac{1}{\hat{T}} \right) - \sum_{i=1}^n \frac{\vec{J}_i^* \cdot \vec{\nabla} \hat{\mu}_i}{\hat{T}} - \sum_{i=1}^n \frac{I_i \hat{A}_i}{\hat{T}} + \frac{\varepsilon_{sh}}{\hat{T}}. \quad (271)$$

These formulations for  $\vec{J}_s$  and  $\bar{\sigma}_s$  are the same as those derived by de Groot and Mazur (1984, 1986, Eqs. 26 and 28, p.26 and 27), although with different notations ( $\vec{J}'_q$ ,  $\vec{J}'_k$  and  $J_j$  instead of  $\vec{J}_u$ ,  $\vec{J}_i^*$  and  $I_i$ , in particular). Note that, due to a possible typo and a comparison with de Groot and Mazur (1984, 1986, Eq. 28, p.27), I have also changed the term  $I_i \hat{\mu}_i$  into  $I_i \hat{A}_i$  in (271), with the Affinity usually noted  $A_i$ , whereas  $\mu_i$  is the chemical potential or Gibbs function.

Gassmann and Herzog (2015, p.858) called (269) to (271): “*the second law in differential form* ( $\bar{\rho} d\hat{s}/dt = \dots$ ) *It contains the divergence of the non-convective entropy-flux terms* ( $\vec{J}_s$ ) *and the local internal entropy-production terms* ( $\bar{\sigma}_s$ ) ... *in which the ... source/production terms have to be non-negative.*”

Now that we have the equations (269) to (271) to describe the second law of thermodynamics by calculating the differential evolution of entropy, all that remains is to know the specific entropy  $s$  (and its Reynolds average  $\hat{s}$ ) to test the impact of the reference values on the second law.

To do so, we can rely on the moist-air specific entropy  $s = c_{pd} \ln(\theta_s) + s_0$  defined in Marquet (2011a, Eq. 59, p.781) and retained as such by Gassmann and Herzog (2015, bottom right of p.858), who wrote the definition recalled in (266):

$$\hat{s} = c_{pd} \ln(\hat{\theta}) + s_0, \quad \text{and thus with } d\hat{s} = c_{pd} d\ln(\hat{\theta}) = \left( \frac{c_{pd}}{\hat{\theta}} \right) d\hat{\theta},$$

because  $s_0 = s_{d0}(T_0, p_0) - c_{pd} \ln(T_0)$  is a (dry-air) true constant.

I have derived in Marquet (2011a, Eq. 47, p.773) the first-order approximation of the potential temperature  $\theta_s$ , with the Reynold average

$$\hat{\theta}_s \approx \hat{T} \left( \frac{p_0}{\hat{p}} \right)^\kappa \exp \left[ - \frac{\hat{L}_v \hat{q}_t + \hat{L}_s \hat{q}_i}{c_{pd} \hat{T}} \right] \exp(\Lambda_r \hat{q}_t)$$

where

$$\Lambda_r = \frac{s_{vr}(T_r, p_{vr}) - s_{dr}(T_r, p_r - p_{vr})}{c_{pd}} \approx 5.865 \pm 0.004$$

depends on the difference in the third-law absolute entropy for water vapour ( $s_{vr}$ ) and dry air ( $s_{dr}$ ).

Accordingly, the first-order approximation of the moist-air entropy is

$$\hat{s} \approx c_{pd} \ln(\hat{T}) - R_d \ln \left( \frac{\hat{p}}{p_0} \right) - \frac{\hat{L}_v \hat{q}_t + \hat{L}_s \hat{q}_i}{\hat{T}} + c_{pd} \Lambda_r \hat{q}_t + s_0,$$

where  $\hat{q}_t = \hat{q}_v + \hat{q}_l + \hat{q}_i$  is the total water content.

It is possible to show that the reference enthalpies constants ( $h_{i0}$ ) and entropy constants ( $s_{i0}$ ) have no impact on the entropy production term  $\overline{\sigma_s}$  given by (271), where the Gibbs functions (chemical potentials) depends on the enthalpies and entropies via:  $\hat{\mu}_i = \hat{h}_i - \hat{T} \hat{s}_i$ . Accordingly, the parts depending on  $\hat{s}_i$  and  $\hat{\mu}_i$  in (271) can be rewritten as

$$\begin{aligned} \hat{T} \left( \sum_{i=1}^n \hat{s}_i \vec{J}_i^* \right) \cdot \vec{\nabla} \left( \frac{1}{\hat{T}} \right) - \sum_{i=1}^n \frac{\vec{J}_i^* \cdot \vec{\nabla} \hat{\mu}_i}{\hat{T}} &= - \left( \sum_{i=1}^n \frac{\hat{s}_i \vec{J}_i^*}{\hat{T}} \right) \cdot \vec{\nabla}(\hat{T}) - \sum_{i=1}^n \frac{\vec{J}_i^* \cdot \vec{\nabla}(\hat{h}_i)}{\hat{T}} + \sum_{i=1}^n \frac{\vec{J}_i^* \cdot \vec{\nabla}(\hat{T} \hat{s}_i)}{\hat{T}} \\ &= - \frac{1}{\hat{T}} \sum_{i=1}^n \vec{J}_i^* \cdot \left[ \vec{\nabla}(\hat{h}_i) - \hat{T} \vec{\nabla}(\hat{s}_i) \right]. \end{aligned} \quad (272)$$

As a consequence, since the enthalpies and entropies depend on the reference enthalpies constants ( $h_{i0}$ ) and entropy constants ( $s_{i0}$ ) via  $\hat{h}_i = h_{i0} + (\dots)$  and  $\hat{s}_i = s_{i0} + (\dots)$ , all constants  $h_{i0}$  and  $s_{i0}$  have no impact in the gradients  $\vec{\nabla}(\hat{h}_i)$  and  $\vec{\nabla}(\hat{s}_i)$ , and thus have no impact in (272), and thus have no impact on the whole entropy production term  $\overline{\sigma_s}$  in (271).

Differently, the second-law derivative  $\bar{\rho} \hat{d}\hat{s}/dt$  depends on  $(c_{pd} \Lambda_r \bar{\rho}) \hat{d}\hat{q}_t/dt$ , with therefore a direct impact of the positive third-law value  $\Lambda_r$ . In particular, an arbitrary modification of  $s_{vr}$  and/or  $s_{dr}$  could change the sign or cancel out  $\Lambda_r$ , with therefore arbitrary positive, null or negative changes in the second-law derivative  $\bar{\rho} \hat{d}\hat{s}/dt$  for a given change in  $\hat{q}_t \dots$ . This cannot be true, otherwise the second law derivative  $\bar{\rho} \hat{d}\hat{s}/dt$  would be arbitrary, and thus meaningless!

Similarly, the turbulent flux  $\overline{\rho s'' \vec{v}''}$  depends on  $(c_{pd} \Lambda_r) \overline{\rho (\hat{q}_t)'' \vec{v}''}$ , which can be made negative, null or positive depending on arbitrary changes in  $s_{vr}$  and/or  $s_{dr}$ , and thus in  $\Lambda_r \dots$ . This cannot be true, otherwise the turbulent flux of entropy  $\overline{\rho s'' \vec{v}''}$  would be arbitrary, and thus meaningless!

Similarly, the impact of the reference entropies  $s_{ir}$  for all species ( $i = 1, \dots, n$ ) can be evaluated in the second term  $\sum_{i=1}^n \hat{s}_i \vec{J}_i^*$  of the entropy-flux  $\vec{J}_s$  given by (270). Clearly, even if these reference entropies  $s_{ir}$  are true constant terms, the weighted sum  $\sum_{i=1}^n \hat{s}_{ir} \vec{J}_i^*$  is a priori different from 0 in a mixture if the diffusion fluxes  $\vec{J}_i^*$  are different from zero. Moreover, this weighted sum might be made negative, null or positive depending on arbitrary changes in any (or all) of the reference entropies  $s_{ir} \dots$ . This cannot be true, otherwise the entropy-flux  $\vec{J}_s$  would be arbitrary, and thus meaningless!

The only way to avoid these impacts due to unrealistic arbitrary definitions of the reference entropy constants, with in particular possible changes of signs and thus violations of the second-law via the derivative  $\bar{\rho} \hat{d}\hat{s}/dt$ , is to rely on the absolute third-law definitions for these reference entropy constants.

• • Like the atmosphere, even if the seawater is a mixture of sea salts solved into a pure-liquid water solvent, the same general entropy equation

$$\bar{\rho} \frac{\hat{d}\hat{\eta}}{dt} = - \vec{\nabla} \cdot \vec{J}_\eta + \overline{\sigma_\eta} \quad (273)$$

must be valid for the seawater entropy  $\hat{\eta}$ , with however the entropy-flux  $\vec{J}_s$  and the entropy-production  $\overline{\sigma_s}$  terms, both valid for a mixture of gases and given by (270) and (271), to be modify in order to agree with the more complex non-linear electrolyte formulation for the seawater entropy.

I show in my 2025 paper submitted to the Comptes Rendus Géosciences that the reference entropies of pure liquid water ( $\eta_{w0}$ ) and sea salts ( $\eta_{s0}$ ) impact the seawater entropy via the first-order linear function of the salinity  $\hat{S}_A$  (in g/kg):

$$(\eta_{s0} - \eta_{w0}) \times \frac{\hat{S}_A}{1000} \approx (-1880 \pm 17) \times \frac{\hat{S}_A}{1000} \text{ J/K/kg}, \quad (274)$$

where the negative numerical value  $(\eta_{s0} - \eta_{w0}) \approx -1880 \pm 17$  J/K/kg is computed from the absolute reference entropies  $\eta_{s0} \approx 1633.3 \pm 15$  J/K/kg and  $\eta_{w0} \approx 3513.4 \pm 1.7$  J/K/kg. This seawater linear function of the salinity  $(\eta_{s0} - \eta_{w0}) \times (\hat{S}_A/1000)$  is the equivalent of the moist-air entropy term  $(c_{pd} \Lambda_r) \times \hat{q}_t = (s_{vr} - s_{dr}) \times \hat{q}_t$  where  $c_{pd} \Lambda_r = s_{vr} - s_{dr} \approx c_{pd} \times (+5.865 \pm 0.004)$  J/K/kg.

Therefore, the impact on the change in seawater entropy  $\hat{d}\hat{\eta}/dt$  recalled in (273) of the two reference entropies  $\eta_{s0}$  and  $\eta_{w0}$  is

$$\frac{(\eta_{s0} - \eta_{w0})}{1000} \times \frac{\hat{d}\hat{S}_A}{dt} \approx \frac{(-1880 \pm 17) \text{ J/K/kg}}{1000} \times \frac{\hat{d}\hat{S}_A}{dt}. \quad (275)$$

Therefore, just like the moist-air, the second law via the seawater entropy equation (273) and via (275) depends on the numerical values of  $\eta_{s0}$  and  $\eta_{w0}$ . Therefore, just like the moist-air, the quantity (275) might be made negative, null or positive depending on arbitrary changes in  $\eta_{s0}$  and/or  $\eta_{w0}$ ... This cannot be true, otherwise the seawater second law derivative  $\bar{p} \hat{d}\hat{\eta}/dt$  would be arbitrary, and thus meaningless! The only way to avoid such spurious impacts is to rely on the absolute third-law definitions for these seawater reference entropy constants  $\eta_{s0}$  and  $\eta_{w0}$ .

## 12.9 Validations and physical meaning of absolute entropies / Lewis number?

- I show in this section that the absolute version of the entropy of the atmosphere  $s = c_{pd} \ln(\theta_s) + Cste$  leads to an improvement in the calculation of turbulent exchange coefficients for moist boundary layers, with positive exchange coefficients  $K_s(\theta_s)$  and  $K_w(q_t)$  associated with the absolute-entropy potential temperature  $\theta_s \approx \theta_l \exp(\Lambda_r q_t)$  and the total water content  $q_t = q_v + q_l + q_i$ , where  $\Lambda_r \approx 5.87$ .

Conversely, the use of the actual Betts (1973) variables  $(\theta_l, q_t)$ , where  $\theta_l$  is contrary to the third law of thermodynamics  $\Lambda_r \approx 0$ , leads to inconsistencies and negative exchange coefficients  $K_h(\theta_l)$ .

In particular, the Lewis number  $Le_t = K_h/K_w$  (noted “ $s = h/k$ ” by Warren K. Lewis, 1922) is set to unity ( $Le_t \equiv 1$ ) in almost all present GCM and NWP models, namely with the use of the same value for the exchange coefficients  $K_h(\theta_l) = K_w(q_t)$  for the two Betts’ variables  $\theta_l$  and  $q_t$ .

Differently, I show that the standard Lewis number  $Le_t = K_h/K_w$  is ill-defined (negative values) for several LES for the BOMEX, RICO, ARM-Cu campaigns, whereas the absolute-entropy version  $Le_{ts} = K_s/K_w$  is well-defined with moderate values in stable layers ( $0 < Le_{ts} < 1$ ) and larger values in convective layers ( $1 < Le_{ts} < 4$ ).

The turbulent “*Eddy motion in the atmosphere*” were first expressed in Taylor (1915) like an equation for the propagation of heat

$$\frac{\partial \theta}{\partial t} = \frac{\kappa}{\rho c_p} \frac{\partial^2 \theta}{\partial z^2} = K \frac{\partial^2 \theta}{\partial z^2} \quad (276)$$

and “*since the air preserves the (dry-air) potential temperature*” noted  $\theta = T (p_0/p)^{(R_d/c_{pd})}$ , where  $p_0 = 1000$  hPa is the reference (standard) pressure,  $\rho$  the density,  $c_p$  the specific heat and  $\kappa$  the “eddy conductivity” of the atmosphere.

The use of the potential temperature  $\theta$  in Taylor (1915) can be understood because it is an invariant in adiabatic transformations of dry air and with “gentle turbulent motions”, namely with “neutral” conditions and no (or negligible) impact of surface fluxes or radiation. In particular, the conservation of  $\theta$  corresponds to the dry adiabatic gradient for the temperature  $T = \theta (p/p_0)^{(R_d/c_{pd})}$ , which effectively decreases in the planetary boundary layer as the pressure  $p$  decreases with altitude and with  $\theta$  constant.

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This equation of Taylor (1915) has then been generalized in three ways in the papers of Richardson (1919a,b) and the prophetic book of Richardson (1922):

- (1) for the atmosphere where  $\kappa$  and  $K = \kappa/(\rho c_p)$  are not constant;
- (2) not only for  $\theta$  but for all other variables  $X$ ;
- (3) in order to compute not only  $\partial X/\partial t$  but also the vertical flux of  $X$  (namely  $\overline{w'X'}$ ).

Indeed, Richardson (1919a) explains (page 9) about these variables  $X$ : “*The total water in a portion of air, or the total entropy in it, are not altered by gently mixing it; and the same is true if its horizontal momentum in a fixed azimuth*” (...) and then (p.10) about (Eq. 10) that: “*X must be unchanged by the simple transportation of air to a different level*” (...) and then (p.10) about (Eq. 11) that: “*The total Z in a definite portion of air must be unchanged by its removal to a different level.*”

Similarly, Richardson (1921) explains (page 1) that the variable  $X$  “*is either potential temperature, or else mass of water, or smoke per mass of atmosphere.*”

Moreover, Richardson (1922, p.68) clearly explained that  $X$  must be defined “*per unit mass of a definite portion of air,*” (namely for the specific value defined per unit mass of moist air in the atmosphere, or per unit mass of seawater for the oceans) “*mass-of-water-per-mass-of-atmosphere* (and thus for the total water content  $q_t$ ) *or else potential-temperature.*”

More precisely, Richardson (1922, p.160) explained that: “*the most natural way of reckoning the entropy of the water-substance would be to take it as zero at the absolute zero of temperature. (...) but the measurements of Nenst, Lindemann, Koref and others have shown that the specific heats tend to zero at  $T = 0$  in such a way that the entropy remains finite there.*” Here Richardson (1922) was expressly referring to the absolute versions of entropies as defined by the third law of thermodynamics by Planck (1911, 1914, 1917).

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Note that, even if Richardson (1922) could no relies on the first extended list of absolute values for entropies published in Lewis and Randall (1923), Richardson (1922) could have mentioned that the absolute entropy were already computed for mono-atomic and several poly-atomic bodies in several papers, and in particular in German by:

Sackur (1911); Tetrode (1912a,b); Sackur (1913a,b); Planck (1915a,b,c, 1916, 1921a);  
and even in English in the papers and book by:

Tetrode (1915); Sackur (1917); Lewis and Gibson (1917, 1920).

Differently, Richardson (1922, p.160) rather chose an expedient and a non-physical way to get around the problem, by saying: “*However the most natural reckoning may not be the most expeditious, in view of the existence of the Hertz and Neuhoff diagrams of adiabatics of moist air (...) we must recognise any energy which can be extracted from water substance by cooling it to the lowest temperature occurring in the atmosphere, say to 180 K, but that with regard to any energy or entropy remaining at that temperature we may either ignore it altogether or else give to it an arbitrary fixed value per mass of ice.*”

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The aim of the Chapter 8/2/6 in Richardson (1922, p.158-166) was to answer the question:

“*Shall we use Entropy-per-mass ( $s = \sigma$ ), or the Potential Temperature ( $\theta = \tau$ )?*”

Richardson (1922, p.158) explained that: “*In the classical thermodynamics entropy occupies a central position, whereas potential temperature is rarely mentioned. In meteorological theories these positions are almost reversed.*” Richardson (1922, p.162-164) also studied “*The behaviour of entropy-per-mass and of potential temperature in regard to turbulence.*”

As a conclusion, Richardson (1922, p.165) suggested in his “*Plan Adopted*” that:

- “ *It appears to be more convenient to use entropy-per-mass for treating the eddy diffusion in the upper air.* ”
- “ *On the contrary, for dealing with the thermal boundary condition at the earth’s surface, the procedure is simpler if we use instead the potential temperature at the local and instantaneous surface pressure* ”

However, it is possible to show that the non-linear part of the moist-air entropy is of very small impact in the turbulent fluxes and surface fluxes of entropy, and thus that it is likely possible to use both of them as synonymous quantities.

To show this, let us define the moist-air entropy as in Marquet (2011a) in terms of the potential temperature  $\theta_s$  according to

$$s = c_{pd} \ln(\theta_s) + Cste ,$$

with  $c_{pd}$  a constant and where  $\theta_s \approx \theta_l \exp(\Lambda_r q_t)$  both depends on the variable  $\theta_l$  of Betts (1973) and the total water content  $q_t = q_v + q_l + q_i$ , with the factor  $\Lambda_r \approx 5.87$  depending on the third-law absolute entropies for water vapour and dry air. Let us then introduce the Reynolds average value  $\overline{\theta_s}$  and the turbulent departure from this  $\theta'_s = \theta_s - \overline{\theta_s}$ , leading to

$$s = c_{pd} \ln\left(\frac{\overline{\theta_s} + \theta'_s}{\overline{\theta_s}}\right) + c_{pd} \ln(\overline{\theta_s}) + Cste ,$$

$$s = c_{pd} \ln(1 + x) + c_{pd} \ln(\overline{\theta_s}) + Cste ,$$

$$\text{where } x = \frac{\theta'_s}{\overline{\theta_s}} \quad \text{with } |x| \ll 1 \quad (\text{i.e. } x = 0.03 \text{ for } \theta'_s = 10 \text{ K and } \overline{\theta_s} \approx 330 \text{ K}) .$$

Therefore, due to the Taylor expansion  $\ln(1 + x) \approx x - x^2/2 + (\dots)$  for small  $|x| \ll 1$ , we find

$$s \approx c_{pd} \left[ \frac{\theta'_s}{\overline{\theta_s}} - \frac{(\theta'_s)^2}{2 (\overline{\theta_s})^2} \right] + c_{pd} \ln(\overline{\theta_s}) + Cste .$$

The Reynolds average of this entropy relationship can then be computed with  $\overline{\theta'_s} = 0$ , leading to:

$$\overline{s} \approx c_{pd} \left[ \overbrace{\ln(\overline{\theta_s}) - \frac{1}{2} \frac{(\overline{\theta'_s})^2}{(\overline{\theta_s})^2}}^{\approx 1.6 - 1.1 \cdot 10^{-4}} \right] + Cste .$$

The numerical values computed with  $\theta'_s = 5 \text{ K}$ ,  $(\overline{\theta'_s})^2 \approx 25 \text{ K}^2$  and  $\overline{\theta_s} \approx 330 \text{ K}$  shows that we can write  $\overline{s} \approx c_{pd} \ln(\overline{\theta_s}) + cste$  as a first order relationship, with a very good relative accuracy of  $10^{-4}$ .

The more important feature for turbulence processes is to evaluate the way the departures in entropy ( $s'$ ) can be written in terms of the departure in potential temperature ( $\theta'_s$ ), namely :

$$s' = s - \overline{s} \approx \left( \frac{c_{pd}}{\overline{\theta_s}} \right) \overbrace{\theta'_s}^{\approx 5 \text{ K}} - \left( \frac{c_{pd}}{\overline{\theta_s}} \right) \overbrace{\frac{(\theta'_s)^2 - (\overline{\theta'_s})^2}{2 \overline{\theta_s}}}^{< 0.05 \text{ K}} \approx \left( \frac{c_{pd}}{\overline{\theta_s}} \right) \theta'_s .$$

The numerical values are computed as before with  $\theta'_s = 5 \text{ K}$ ,  $(\theta'_s)^2 - (\overline{\theta'_s})^2 \approx 25 \text{ K}^2$  and  $\overline{\theta_s} \approx 330 \text{ K}$ , showing that we can write  $s' \approx (c_{pd}/\overline{\theta_s}) \theta'_s$  as a first order relationship, with a good relative accuracy of  $10^{-2}$  even for large departures in temperatures of  $\pm 5^\circ\text{C}$ .

A more direct way to compute the departure in entropy is to compute the differential of the exact formula  $s = c_{pd} \ln(\theta_s) + Cste$ , where  $c_{pd}$  is a true constant, leading to:

$$ds = \left( \frac{c_{pd}}{\theta_s} \right) d\theta_s ,$$

which is similar to the previous first-order approximation  $s' \approx (c_{pd}/\overline{\theta_s}) \theta'_s$ .

All these computations confirm that, up to some factors like  $c_{pd}$  and  $(c_{pd}/\overline{\theta_s})$ , it is possible to use either the moist-air entropy  $s$  or the entropy potential temperature  $\theta_s$  to describe the moist-air turbulence, for instance via the turbulent Reynolds averages and turbulent fluxes:

$$\overline{s} \approx c_{pd} \ln(\overline{\theta_s}) + cste \quad \text{and} \quad \overline{w' s'} \approx \left( \frac{c_{pd}}{\overline{\theta_s}} \right) \overline{w' \theta'_s}.$$

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As a summary, the variables  $X$  on which the moist-air turbulence acts were listed as followed for the first time by Richardson (1919a,b, 1921, 1922):

- (1) the total mass of water “ $q_t = q_v + q_l + q_i$ ” per unit mass of (moist) atmosphere;
- (2) the (specific) entropy “ $s$ ” per unit mass, or the associated potential temperature “ $\theta_s$ ”; and
- (3) the velocity components “ $(u, v)$ .”

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Richardson (1919a, Eqs. 7, 8, 11b and 15) explained that the turbulent equations for a variable  $X$  are:

$$\rho \overline{w' X'} = -c \frac{\partial X}{\partial z}; \quad \frac{\partial(\rho X)}{\partial t} = -\frac{\partial}{\partial z} (\rho \overline{w' X'}) = \frac{\partial}{\partial z} \left( c \frac{\partial X}{\partial z} \right) \quad \text{or} \quad \frac{\partial X}{\partial t} \approx \frac{\partial}{\partial p} \left( \xi \frac{\partial X}{\partial p} \right),$$

with the use of the hydrostatic balance  $dp = -\rho g dz$ . Note that Richardson (1922, p.67 and 69) called “ $c$ ” the “eddy-conductivity” and “ $\xi = \rho g^2 c$ ” the “turbulivity.”

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Almost all present GCM and NWP models use the Betts (1973) variables  $(\theta_l, q_t)$  as turbulent thermodynamic variables, with the exchange coefficients  $K_w(q_t)$  and  $K_h(\theta_l)$  defined from:

$$\overline{w' \theta'_l} \approx -K_w \frac{\partial \overline{\theta_l}}{\partial z} \quad \text{and} \quad \overline{w' q'_t} \approx -K_h \frac{\partial \overline{q_t}}{\partial z}.$$

These relationships show that there is no guarantee that the exchange coefficients  $K_w$  or  $K_h$  will be positive, since the vertical fluxes and vertical gradients can be positive, zero, or negative independently of each other. These exchange coefficients  $K_w$  and  $K_h$  can even become infinite for null vertical gradients of  $\overline{\theta_l}$  or  $\overline{q_t}$ .

The total-water specific content  $q_t = q_v + q_l + q_i$  is intended to be a “*conservative variable*” as already put forward by Richardson (1919a,b, 1921, 1922). Indeed, reversible changes of phases correspond for instance to  $dq_v = -dq_l$  for an evaporation of liquid water, with  $q_t$  remaining a constant.

The other liquid-water variable  $\theta_l$  has been derived by Betts (1973, Eq. 1, p.180) as a kind of “*equivalent version*” of the moist-air entropy, although with several approximations made to integrate the moist-air adiabatic (and closed) differential entropy equation.

Betts (1973, Eq. 1, p.180) first recalled the moist-air adiabatic (and closed) differential entropy equation integrated by (Saunders, 1957, Eq. 1, p.345) and corresponding to Marquet and Geleyn (2015, Eq. 7.4, p.257):

$$d \left( \frac{S}{q_d} \right) = d \left( \frac{S}{1 - q_t} \right) = d[(1 + r_t) S] = 0 = (c_{pd} + r_t c_l) \frac{dT}{T} + d \left[ \frac{L_v(T) r_{v/sat}}{T} \right] - R_d \frac{dp_d}{p_d},$$

where  $c_{pd}$  and  $c_l$  are the specific capacity for dry air and liquid water,  $L_v(T)$  is the latent heat of vaporisation,  $r_{v/sat}$  is the saturation mixing ratio,  $r_t$  is the total water mixing ratio,  $R_d$  is the dry-air



gas constant and  $p_d$  is the dry-air pressure. Here, the entropy  $S/q_d = S/(1 - q_t) = (1 + r_t) S$  is a quantity defined per unit mass of dry air and for a closed parcel, namely with constant values for both the dry-air content  $q_d$  and the total water content  $q_t = 1 - q_d = q_v + q_l$  (with  $q_i = 0$ ).

Betts (1973, Eq. 10, p.180) arrived at the alternative moist-air entropy for defining the liquid-water potential temperature variable  $\theta_l$  as:

$$0 = C_{pm} \frac{d\theta_l}{\theta_l} = C_{pm} \frac{dT}{T} - R_m \frac{dp}{p} - \left[ \frac{L_v(T)}{T} \right] dq_l ,$$

“with the constraint that the total water ( $r_t = r_{v/sat} + r_l$ ) is constant” (Eq. 3, p.180)

$$dr_t = 0 = dr_{v/sat} + dr_l$$

and where

$$C_{pm} = q_d c_{pd} + q_{v/sat} c_{pv} + q_l c_l \quad \text{and} \quad R_m = q_d R_d + q_{v/sat} R_v$$

are variable moist-air values for the specific heat capacity ( $C_{pm}$ ) and gas constant ( $R_m$ ) depending on the dry-air specific content  $q_d = 1 - q_t$ , the saturation water-vapour specific content  $q_{v/sat} = r_{v/sat}/(1 + r_t)$  and the liquid-water specific content  $q_l = r_l/(1 + r_t)$ , with  $p = p_d + e_{sat}$  the total pressure.

Then the following approximations was made by Betts (1973):

$$C_{pm}(q_{v/sat}, q_l, q_t) \approx c_{pd} \quad \text{and} \quad R_m(q_{v/sat}, q_l, q_t) \approx R_d \quad (277)$$

to arrive at:

$$c_{pd} \frac{d\theta_l}{\theta_l} \approx c_{pd} \frac{d\theta}{\theta} - \left[ \frac{L_v(T)}{T} \right] dq_l \quad \text{or equivalently} \quad d\ln(\theta_l) \approx d\ln(\theta) - \left[ \frac{L_v(T)}{c_{pd} T} \right] dq_l ,$$

where  $\theta = T (p_0/p)^{R_d/c_{pd}}$  is the well-known dry-air potential temperature.

It is then necessary to make the further approximation

$$d\ln(\theta_l) \approx d\ln(\theta) - d \left[ \frac{L_v(T) q_l}{c_{pd} T} \right] + \overbrace{q_l d \left[ \frac{L_v(T)}{c_{pd} T} \right]}^{(\text{to be neglected})} ,$$

i.e. by neglecting the last term, and thus the impact of the change with  $T$  of the quantity  $L_v(T)/T$  (namely with more rapid changes in  $q_l$ ), to arrive (Eq. 13, p.181) at the “liquid-water” potential temperature:

$$\theta_l \approx \theta \exp \left[ - \frac{L_v(T) q_l}{c_{pd} T} \right] \quad \text{where} \quad \theta = T \left( \frac{p_0}{p} \right)^{R_d/c_{pd}} .$$

Similarly, the “equivalent” potential temperature was defined (as a consequence of Eq. 11, p.181, without the saturation subscript) as:

$$\theta_e \approx \theta \exp \left[ \frac{L_v(T) q_v}{c_{pd} T} \right] \quad \text{or equivalently} \quad \theta_e = \theta_l \exp \left[ \frac{L_v(T) q_t}{c_{pd} T} \right] .$$

If Richardson (1919a,b, 1921, 1922) had rightly suggested the moist-air entropy (or the associated potential temperature variable  $\theta_s$ ) as a conservative variable by taking advantage of the particular properties of the general entropy thermodynamic state function, all the assumptions mentioned above made by Betts (1973) prevent his variables  $\theta_l$  and  $\theta_e$  from fully representing the entropy of moist air in general.

In particular, since the total water content  $q_t = r_t/(1 + r_t)$  is assumed to be a constant, the variables  $\theta_l$  and  $\theta_e$  can only be defined up to any arbitrary function of  $q_t$ . As an example, we can include any multiplicative factor of the kind  $\exp(\alpha q_t)$  in the definition of  $\theta_l$  or  $\theta_e$ , with  $\alpha$  a negative, null or positive term. By the way, we can interpret the difference between  $\theta_l$  and  $\theta_e$  as such a term with  $\alpha = L_v(T)/(c_{pd} T)$ , with the same additional assumption made by Betts (1973) that  $L_v(T)/T$  is nearly a constant independent of  $T$ .

Therefore, due to all the hypotheses made by Betts (1973), we cannot be sure that his variables  $\theta_l$  and/or  $\theta_e$  may represent the moist-air entropy in general, and in particular with possible missing arbitrary factor  $\exp(\alpha q_t)$  that can be included in the relationships defining  $\theta_l$  and  $\theta_e$ .

I have shown since Marquet (2011a) that the first-order approximation of the absolute (third-law) moist-air entropy ( $s$ ) and the associated potential temperature ( $\theta_s$ ):

- only partly depends on the variable  $\theta_l$  of Betts (1973);
- with the natural liquid-ice generalisation  $\theta_{li}$  of Tripoli and Cotton (1981);
- with the need to add the factor  $\exp(\Lambda_r q_t)$  with  $\Lambda_r \approx 5.865 \pm 0.004$  to take into account of the absolute third-law definitions of the dry-air and water-vapour reference entropies values at  $0^\circ\text{C}$ , computed from the standard values at  $25^\circ\text{C}$  available in all Thermodynamic Tables.

As a summary, I have shown that:

---

(1a) The first-order approximation  $\theta_{s1}$  of  $\theta_s$  (Marquet, 2011a, QJRMS) :

$$s \equiv c_{pd} \ln(\theta_s) + \text{Cste} \quad (278)$$

$$\text{where } \theta_s \approx \theta_{s1} = \underbrace{\theta \times \exp\left(-\frac{L_v q_l + L_s q_i}{c_{pd} T}\right)}_{\approx \theta_{li} \text{ of Tripoli and Cotton (1981)}} \times \underbrace{\exp[(5.865 \pm 0.004) q_t]}_{\text{absolute entropy factor}} \quad (279)$$

$$\text{and } \Lambda_r = \frac{s_{vr}(T_0, p_{v0}) - s_{dr}(T_0, p_{d0})}{c_{pd}} \approx 5.865 \pm 0.004$$

with  $T_0 = 273.15 \text{ K}$ ,  $p_0 = 1000 \text{ hPa} = p_{v0} + p_{d0}$ ,  $p_{v0} = p_{v/sat.}(T_0) \approx 6.1121 \text{ hPa}$ .

---

More precisely, I have computed the third-law term  $\Lambda_r$  starting from the standard quantum-statistical values  $s_{v0} \approx 10317.92 \pm 0.6 \text{ J K}^{-1} \text{ kg}^{-1}$  and  $s_{d0} \approx 6776.34 \pm 0.5 \text{ J K}^{-1} \text{ kg}^{-1}$  recalled in the Table 1 for the conditions  $T_0 = 0^\circ\text{C}$  and  $p_0 = 1000 \text{ hPa}$ . I have then computed the reference values  $s_{vr}$  and  $s_{dr}$  still at  $T_0 = 273.15 \text{ K}$ , but for the partial pressures  $p_{v0} = p_{v/sat.}(T_0) \approx 6.1121 \text{ hPa}$  and  $p_{d0} = p_0 - p_{v0} \approx 993.89 \text{ hPa}$ , according to:

$$s_{dr}(T_0, p_{d0}) = s_{d0}(T_0, p_0) - R_d \ln\left(\frac{993.89}{1000}\right) \approx 6778.1 \pm 0.6 \text{ J K}^{-1} \text{ kg}^{-1},$$

$$s_{vr}(T_0, p_{v0}) = s_{v0}(T_0, p_0) - R_v \ln\left(\frac{6.1121}{1000}\right) \approx 12670.9 \pm 1.7 \text{ J K}^{-1} \text{ kg}^{-1},$$

including the additional uncertainties on  $R_d \approx 287.05 \pm 0.05 \text{ J K}^{-1} \text{ kg}^{-1}$ ,  $R_v \approx 461.5 \pm 0.2 \text{ J K}^{-1} \text{ kg}^{-1}$  and  $c_{pd} \approx 1004.7 \pm 0.2 \text{ J K}^{-1} \text{ kg}^{-1}$ .

As a summary, I have shown that:

---

(1b) The second-order approximation  $\theta_{s2}$  of  $\theta_s$  (Marquet, 2015b, 2019b, 2022) writes:

$$\theta_s \approx \theta_{s2} = \theta \times \underbrace{\exp\left(-\frac{L_v q_l + L_s q_i}{c_{pd} T}\right)}_{\approx \theta_{li}} \times \underbrace{\exp[\Lambda_r q_t]}_{\text{(third-law)}} \times \underbrace{\exp\left[-\gamma q_t \ln\left(\frac{r_v}{r_*}\right) - \gamma (q_l + q_i)\right]}_{\text{(2nd-order terms)}}$$


---

with still the third-law factor  $\Lambda_r \approx 5.865 \pm 0.004$  like for  $\theta_{s1}$ , but with the additional 2nd-order terms in the third exponential, where  $\gamma \approx R_v/c_{pd} \approx 0.4594$  and where  $r_* \approx 12.4 \text{ g kg}^{-1}$  is a tuning parameter.

---

Therefore, it appears that it is needed to set  $\alpha = \Lambda_r \approx 6$  in the aforementioned factor  $\exp(\alpha q_t)$  in order to satisfy the third law of thermodynamics and the corresponding value  $\theta_s$ , whereas  $\alpha = 0$  generates the liquid-water value  $\theta_l$ , and  $\alpha = L_v(T)/(c_{pd} T) \approx 9$  generates the equivalent value  $\theta_e$ . We see that  $\theta_s$  must therefore be in about a 2/3 position between  $\theta_l$  and  $\theta_e$ , whatever  $q_t$  may be.

The next question therefore arises as to what is the impact on the moist-air turbulence of the use of this particular value  $\theta_s$  in accordance with the third law.

---

One way to answer this question is to study accurate Large Eddy Simulations (LES) to determine if what is known as the Lewis number  $Le_t = K_h/K_w$  (noted “ $s = h/k$ ” by Warren K. Lewis, 1922) can indeed be set to unity ( $Le_t \equiv 1$ ) like in almost all present GCM and NWP models?

These exchange coefficients  $K_w$  (for  $q_t$ ),  $K_s$  (for  $\theta_s$ ) and  $K_h$  (for  $\theta_l$ ) can be defined as:

---

(2) The K-gradient hypotheses according to Richardson (1919a,b, 1921, 1922) or Betts (1973)

$$\overline{w'q'_t} \approx -K_q \frac{\partial \overline{q_t}}{\partial z} \quad \text{and} \quad \overline{w'\theta'_s} \approx -K_s \frac{\partial \overline{\theta_s}}{\partial z} \quad \text{or} \quad \overline{w'\theta'_l} \approx -K_h \frac{\partial \overline{\theta_l}}{\partial z} .$$


---

For  $Le_t = K_h/K_w = 1$ , and thus  $K_h = K_w$ , it is possible to show that due to  $\theta_s \approx \theta_l \times \exp(\Lambda_r q_t)$  only depending on  $\theta_l$  and  $q_t$ , the absolute-entropy Lewis number is equal to unity ( $Le_{ts} = K_s/K_w = 1$ ), which means that the absolute (third-law) exchange coefficients is almost equal to others:  $K_s \approx K_h = K_w$ .

Differently, if  $Le_{ts1} = K_s/K_w \neq 1$ , the usual computations made in present GCM and NWP models should be modified according to:

---

(3) Impact of the Lewis function  $\text{Le}_{ts} = K_s/K_q \neq 1?$  on the usual turbulent fluxes for  $\theta_l$ :

$$\overline{w'\theta'_l} \approx -K_q \left[ \underbrace{(\text{Le}_{ts1})}_{\neq 1?} \times \frac{\partial \overline{\theta_l}}{\partial z} + \underbrace{5.865 \times (\text{Le}_{ts1} - 1) \times \overline{\theta_l} \times \frac{\partial \overline{q_t}}{\partial z}}_{\text{additional term if } Le_{ts1} \neq 1?} \right] \neq -K_h \frac{\partial \overline{\theta_l}}{\partial z} \quad (280)$$


---

This relationship (280) has been established as follows:

$$\begin{aligned}
\theta_{s1} &= \theta_l \exp(\Lambda_r q_t); \quad \ln(\theta_{s1}) = \ln(\theta_l) + \Lambda_r q_t; \quad \frac{\overline{w'\theta'_{s1}}}{\theta_{s1}} = \frac{\overline{w'\theta'_l}}{\theta_l} + \Lambda_r \frac{\overline{w'q'_t}}{q'_t}; \\
\frac{\overline{w'\theta'_l}}{\theta_{s1}} &= \frac{\theta_l}{\theta_{s1}} \frac{\overline{w'\theta'_{s1}}}{\theta_{s1}} - \Lambda_r \theta_l \frac{\overline{w'q'_t}}{q'_t} = -K_{s1} \frac{\theta_l}{\theta_{s1}} \frac{\partial \theta_{s1}}{\partial z} + K_q \Lambda_r \theta_l \frac{\partial q_t}{\partial z}; \\
\frac{\theta_l}{\theta_{s1}} \frac{\partial \theta_{s1}}{\partial z} &= \frac{\partial \theta_l}{\partial z} + \Lambda_r \theta_l \frac{\partial q_t}{\partial z}; \quad \frac{\overline{w'\theta'_l}}{\theta_{s1}} = -K_{s1} \frac{\partial \theta_l}{\partial z} - K_{s1} \Lambda_r \theta_l \frac{\partial q_t}{\partial z} + K_q \Lambda_r \theta_l \frac{\partial q_t}{\partial z}; \\
\frac{\overline{w'\theta'_l}}{\theta_{s1}} &= -K_{s1} \frac{\partial \theta_l}{\partial z} - \Lambda_r (K_{s1} - K_q) \theta_l \frac{\partial q_t}{\partial z} = -K_q \left[ \frac{K_{s1}}{K_q} \frac{\partial \theta_l}{\partial z} + \Lambda_r \left( \frac{K_{s1}}{K_q} - 1 \right) \theta_l \frac{\partial q_t}{\partial z} \right],
\end{aligned}$$

with the main Richardson's  $K$ -gradient hypotheses  $\overline{w'\theta'_{s1}} = -K_{s1} (\partial \theta_{s1} / \partial z)$  and  $\overline{w'q'_t} = -K_q (\partial q_t / \partial z)$  applied to the third-law absolute entropy variable  $\theta_{s1}$  and the total-water content  $q_t = q_v + q_l$ , and with at the end (280) obtained from the last line and with the Lewis number written as  $\text{Le}_{ts1} = K_{s1} / K_q$ .

It is possible to derive a second-order approximation of  $\overline{w'\theta'_{li}}$  corresponding to the use a turbulence based on the (third-law) absolute-entropy variable  $\overline{w'\theta'_{s1}}$ , namely with the hypothesis  $\theta_s \approx \theta_{s2}$  and the value of  $\theta_{s2}$  derived in Marquet (2015b, 2019b, 2022) and previously recalled:

$$\theta_{s2} = \theta_{li} \times \underbrace{\exp[\Lambda_r q_t]}_{\text{(third-law)}} \times \underbrace{\exp \left\{ -\gamma q_t \ln \left[ \frac{q_t - q_l - q_i}{(1 - q_t) r_*} \right] - \gamma (q_l + q_i) \right\}}_{\text{(2nd-order terms)}}, \quad (281)$$

where

$$\theta_{li} = \theta \exp \left( - \frac{L_v q_l + L_s q_i}{c_{pd} T} \right)$$

is the natural liquid-ice generalisation (with  $q_i \neq 0$ ) of the Betts (1973) liquid-water variable  $\theta_l$  (and thus with  $\theta_{li}$  almost like in Tripoli and Cotton, 1981). The same third-law factor  $\Lambda_r \approx 5.865 \pm 0.004$  is used in the first exponential, like for  $\theta_{s1}$ , but with additional 2nd-order terms in the second exponential where  $\gamma \approx R_v / c_{pd} \approx 0.4594$ , with  $r_v$  replaced by  $r_t - r_l - r_i = (q_t - q_l - q_i) / (1 - q_t)$  and with  $r_* \approx 12.4 \text{ g kg}^{-1}$  a constant tuning parameter.

Note that the first-order approximation (279) can be logically obtained from (281) with the assumptions  $\gamma = 0$ , with  $\theta_{li}$  replaced by  $\theta_l$ , and with  $q_i = 0$  in  $q_t = q_v + q_l$ .

The same kind of computations for the vertical gradients  $\partial \theta_{s1} / \partial z$  and turbulent vertical fluxes  $\overline{w'\theta'_{s1}}$  leading to the first-order relationship (280) can be undergone for  $\partial \theta_{s2} / \partial z$  and  $\overline{w'\theta'_{s2}}$ , to arrive at the second-order, more accurate relationship (282) based on the differential equation of (281):

$$\frac{d\theta_{s2}}{\theta_{s2}} = \frac{d\theta_{li}}{\theta_{li}} + \underbrace{\left[ \Lambda_r - \gamma \ln \left( \frac{r_v}{r_*} \right) - \gamma \frac{r_t (1 - q_l - q_i)}{q_v} \right]}_{(A)} dq_t + \underbrace{\left[ \gamma \left( \frac{q_l + q_i}{q_v} \right) \right]}_{(B)} (dq_l + dq_i)$$

leading to:

$$\boxed{ \overline{w'\theta'_{li}} \approx -K_q \left\{ \underbrace{\left( \text{Le}_{ts2} \right)}_{\neq 1?} \frac{\partial \overline{\theta_{li}}}{\partial z} + \underbrace{\left( \text{Le}_{ts2} - 1 \right) \overline{\theta_{li}} \left[ A \frac{\partial q_t}{\partial z} + B \left( \frac{\partial q_l}{\partial z} + \frac{\partial q_i}{\partial z} \right) \right]}_{\text{additional term if Le}_{ts2} \neq 1?} \right\} \neq -K_h \frac{\partial \overline{\theta_{li}}}{\partial z} } \quad (282)$$

This second-order relationship (282) has been obtained with the main Richardson's  $K$ -gradient hypotheses  $\overline{w'\theta'_{s2}} = -K_{s2} (\partial\theta_{s2}/\partial z)$  and  $\overline{w'q'_t} = -K_q (\partial q_t/\partial z)$  applied to the second-order third-law absolute-entropy variable  $\theta_{s2}$  and the total-water content  $q_t = q_v + q_l + q_i$ , with the second-order Lewis number written as  $\text{Le}_{ts2} = K_{s2}/K_q$ .

Note that the first-order approximation (280) can be logically obtained from (282) with the assumption  $\gamma = 0$  and thus  $B = 0$  and  $A = \Lambda_r$ , and also with  $\theta_{li}$  replaced by  $\theta_l$  and with  $\text{Le}_{ts2}$  replaced by  $\text{Le}_{ts1}$ .

Note that the clear-air case corresponds to  $q_l = q_i = 0$  and  $q_t = q_v$ , with therefore the relationships  $r_t/q_v = (q_t/q_v)/(1 - q_t) = 1/(1 - q_t)$  and  $r_v = q_v/(1 - q_v)$ , and with the following clear-air version of the  $A$  and  $B$  factors:

$$A_{\text{clear}}(q_v) = \Lambda_r - \gamma \ln \left[ \frac{q_v}{(1 - q_v) r_*} \right] - \frac{\gamma}{1 - q_v} \approx \Lambda_r - \gamma \ln \left( \frac{e \times q_v}{r_*} \right) \neq 0 \quad \text{and} \quad B_{\text{clear}} = 0,$$

where  $\Lambda_r \approx 5.865 \pm 0.004$ ,  $\gamma \approx R_v/c_{pd} \approx 0.4594$ ,  $e = \exp(1) \approx 2.718282$  and  $r_* \approx 12.4 \text{ g kg}^{-1}$ .

The first-order relationship (280) may explain that, if  $\text{Le}_{ts} = K_s/K_q \neq 1$ , the turbulent flux of the Betts (1973) variable  $\theta_l$  is no longer proportional to the vertical gradient of it  $\partial\theta_l/\partial z$ , with some kind of counter- or extra-gradient additional term depending on the sign of the vertical gradient of  $q_t$ .

This relationship (280) could therefore explain why the usual exchange coefficient  $K_h$  is ill-defined in almost all present GCM and NWP models, with  $\overline{w'\theta'_l} \neq -K_h \partial\theta_l/\partial z$  and negative (or even infinite) values for  $K_h$  defined as such that cannot be predicted by current theories and parametrizations, namely with the use of  $\text{Le}_{ts1} \equiv 1$  and of same values for the exchange coefficients  $K_h(\theta_l) = K_q(q_t)$  for the two Betts (1973) variables  $\theta_l$  and  $q_t$ .

The same is true for the second-order approximations and with, from (282), the turbulent vertical flux  $\overline{w'\theta'_{li}} \neq -K_h (\partial\theta_{li}/\partial z)$  that is not proportional to the vertical gradient and with and with possible ill-defined (negative) values of  $K_h$  if the lewis number was different from unity,

It was important to check that the first- and second-order approximations  $\theta_{s1}$  and  $\theta_{s2}$  may represent  $\theta_s$  in various conditions. I have already published several results showing that, indeed, the vertical profiles of  $\theta_{s1}$  and  $\theta_{s2}$  remain both very close to those of  $\theta_s$  for several observation campaigns, model and theoretical outputs:

- FIRE-I RF(02,03,04,08)B, ASTEX, EPIC, DYCOMS observations in Marquet (2011a);
- $s$ - $q_t$  diagrams, FIRE-I RF03B in Marquet and Geleyn (2013);
- potential vorticities in Marquet (2014);
- Hurricane DUMILE in Marquet (2017);
- EUREC4-A in Marquet and Stevens (2022);
- a ascent for the Hurricane SEASON (Jordan, 1958) in Marquet (2022).

I recall in the Fig. 35 the vertical profiles for an ascent in the Hurricane SEASON (Jordan, 1958), where it is clearly shown that the very small differences between  $\theta_s$  and  $\theta_{s2}$  (or even between  $\theta_s$  and  $\theta_{s1}$ ) are much smaller than the differences between the third-law absolute value  $\theta_s$  (in red) and the arbitrarily defined liquid-water ( $\theta_l$ , in orange) and equivalent ( $\theta_e$ , in blue) values, with indeed  $\theta_s$  in about a 2/3 position in between  $\theta_l$  and  $\theta_e$ .

This vertical profile for the Hurricane SEASON (like all other observed or simulated profiles) shows that it would be more interesting to use the second order approximation  $\theta_{s2}$  than the first-order approximation  $\theta_{s1}$ . Therefore, accordingly, I will show both the first-order ( $\text{Le}_{ts1/\text{turb}}$ ) and second-order ( $\text{Le}_{ts2/\text{turb}}$ ) Lewis number in the following figures.

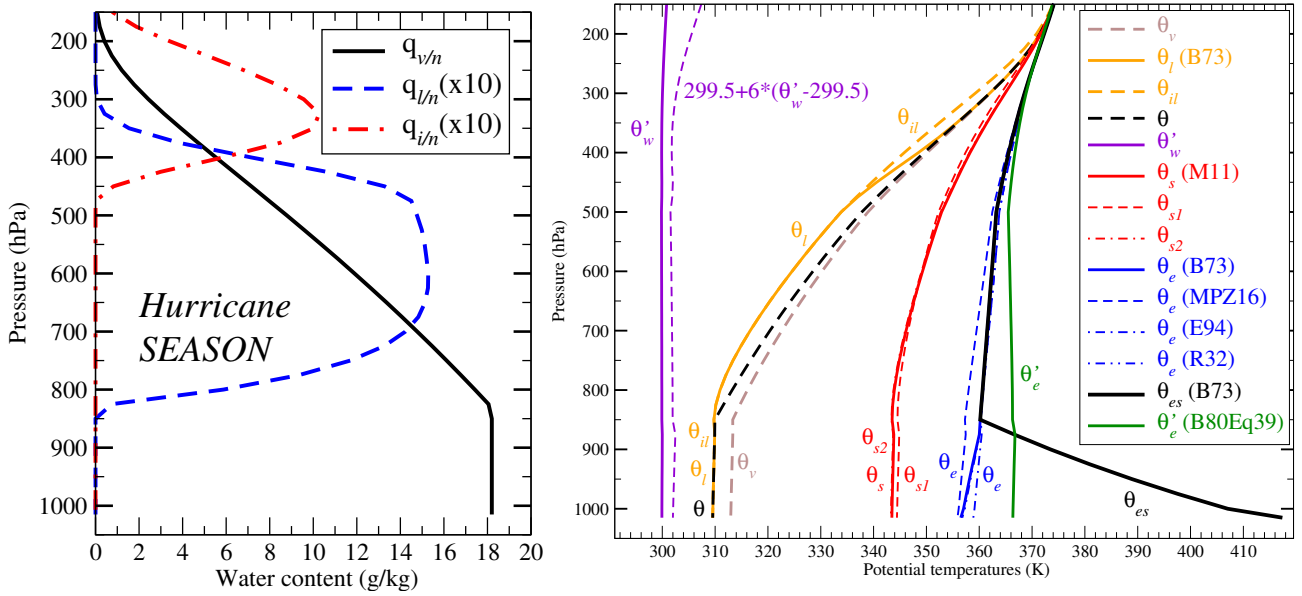


Figure 35: Vertical profiles for an updraft based on the Hurricane “Season” (Jordan, 1958). **On the left:** water vapor ( $q_v$ ), liquid water ( $10 \times q_l$ ) and ice ( $10 \times q_i$ ) specific contents (in g/kg). **On the right:** several dry- and moist-air potential temperatures ( $\theta_v$ ,  $\theta_l$ ,  $\theta_{il}$ ,  $\theta$ ,  $\theta'_w$ ,  $\theta_s$ ,  $\theta_{s1}$ ,  $\theta_{s2}$ ,  $\theta_e$ ,  $\theta_{es}$  and  $\theta'_e$ , in K), with the Betts (1973) variable ( $\theta_l$ ) and Tripoli and Cotton (1981) variable ( $\theta_{il}$ ) in orange, and the third-law absolute values  $\theta_s$ ,  $\theta_{s1}$  and  $\theta_{s2}$  in red.

As a first example, we may rely on the LES outputs for the BOMEX case published by Siebesma et al. (2003), for the average of the last 3 hours of the LES. I have digitized the average vertical profiles for  $\theta$ ,  $q_v$  and  $q_t$  published in the Figs. 3 (a, b, d) of Siebesma et al. (2003, p.1205).

I show the resulting profiles for  $\theta_l$ ,  $\theta_s$ ,  $\theta_{s2}$ ,  $\theta_{s1}$ ,  $q_t$ ,  $q_l = \max(0, q_t - q_{v,sat})$  and  $q_v = q_t - q_l$  in the Figs. 36 (a) to (c), with the vertical gradients of  $\theta_l$ ,  $q_t$ ,  $\theta_{s2}$  and  $\theta_{s1}$  plotted in the Fig. 36 (d).

I have also digitized the vertical profiles for the turbulent vertical fluxes of  $q_t$ ,  $\theta_l$ , and  $q_l$  published in the Figs. 4 (a, b, c) of Siebesma et al. (2003, p.1206), from which the turbulent fluxes of the first- and second-order approximations of  $\theta_{s2}$  and  $\theta_{s1}$  have been computed and also plotted in the Fig. 36 (e).

The turbulent exchange coefficients  $K_h(\theta_l)$ ,  $K_w(q_t)$ ,  $K_{s1}(\theta_{s1})$  and  $K_{s2}(\theta_{s2})$  have then been computed from the respective turbulent vertical fluxes and the vertical gradients of them. The vertical profiles plotted in the Fig. 36 (f) are very similar to those recalled in (g) and published in the Fig.11 of Siebesma et al. (2003, p.1213). This is a validation of the digitalisations of the vertical profiles and for the previous computations of the vertical gradients.

The black curve for  $K_h(\theta_l)$  shows unrealistic negative values in the Fig. 36 (f) in the lower boundary layer between 100 m and 300 m height (in fact  $\rightarrow -\infty$  for  $z \approx 175$  m where the vertical gradient of  $\theta_l$  almost vanish, whereas the turbulent flux is positive). The Fig.11 of Siebesma et al. (2003, p.1213) did not show these unrealistic values for  $K_h(\theta_l)$  below  $z \approx 250$  m.

The last Fig. 36 (h) shows the vertical profiles of the Lewis numbers  $Le_t = K_h/K_w$  (solid black),  $Le_{ts1} = K_{s1}/K_w$  (dashed red) and  $Le_{ts2} = K_{s2}/K_w$  (solid red).

Due to the unrealistic values of  $K_h$  in the lower boundary layer between 100 m and 300 m height, the values of the standard Lewis number  $Le_t = K_h/K_w$  (solid black) are unrealistic too. They even start to become much lower than unity up to  $z \approx 500$  m.

Differently, the third-law absolute entropy values  $Le_{ts1} = K_{s1}/K_w$  (dashed red) and  $Le_{ts2} = K_{s2}/K_w$

(solid red) remain much more realistic within the whole boundary and convective layer up to 1800 m, with positive and in fact  $> 1$  Lewis numbers.

However, due to the digitalization of the vertical profiles of Siebesma et al. (2003) it is difficult to say whether the features  $Le_{ts1} > 1$  and  $Le_{ts2} > 1$  are significant in the Fig. 36 (h), or not. It would be desirable to compute these Lewis numbers from more accurate values, for instance directly from netcdf files of a LES for this BOMEX case, or/and for other cases.

In particular, even if the new third-law absolute-entropy version of the liquid-water turbulent vertical flux  $\overline{w' \theta'_l}$  given by (280), plotted as  $F_{\text{thl/s1}}$  (dashed black line) in the Fig. 36 (e), seems to be different from the usual version  $F_{\text{thl}}$  (solid black line), it is unclear if the difference between  $F_{\text{thl/s1}}$  and  $F_{\text{thl}}$  is relevant, due to the noisy vertical pattern for  $F_{\text{thl/s1}}$ , which is in fact due to the noisy vertical pattern for  $Le_{ts1}$  and  $Le_{ts2}$ .

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In fact, these results suggested from the LES of Siebesma et al. (2003) have been confirmed by the analysis of the same BOMEX (and others) LES prepared during the High-Tune project (ANR, 2017-2021), with these LES provided by Florent Brient and Fleur Couvreux.

In addition to this BOMEX case, I was able to study other LES outputs made available by Florent Brient and Fleur Couvreux during this High-Tune French programme:

- the RICO-composite case (Rauber et al., 2007; van Zanten et al., 2011); and
- the ARM-Cumulus case (Brown et al., 2002; Lenderink et al., 2004).

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In order to properly compute the Lewis numbers  $Le_t = K_h/K_w$ ,  $Le_{ts1} = K_{s1}/K_w$  and  $Le_{ts2} = K_{s2}/K_w$  as outputs of these HIGH-Tune LES with the AROME French model, it was needed to properly compute the exchange coefficients, and thus to separate the impacts of the “thermal” versus the “pure turbulent” processes.

Accordingly, a special care has been taken to separate the “turbulent” part of vertical fluxes from the two “total” and “thermal” parts assumed to be known in the outputs of LES, with first the analysis of passive-scalar tracers to diagnose the “thermal area fraction”  $\alpha_{\text{ther.}}$  at each points and time steps of the LES, and then with the computation of the “turbulent” part from the relationships:

$$(\overline{w' \psi'})_{\text{tot.}} = (1 - \alpha_{\text{ther.}}) (\overline{w' \psi'})_{\text{turb.}} + \alpha_{\text{ther.}} (\overline{w' \psi'})_{\text{ther.}}, \quad (283)$$

$$\text{and thus with } \boxed{(\overline{w' \psi'})_{\text{turb.}} = \frac{1}{(1 - \alpha_{\text{ther.}})} (\overline{w' \psi'})_{\text{tot.}} - \frac{\alpha_{\text{ther.}}}{(1 - \alpha_{\text{ther.}})} (\overline{w' \psi'})_{\text{ther.}}}, \quad (284)$$

where each “total”, “turbulent” and “thermal” Reynolds averages  $(\overline{w' \psi'})_{\text{tot.}}$ ,  $(\overline{w' \psi'})_{\text{turb.}}$  and  $(\overline{w' \psi'})_{\text{ther.}}$  are only computed over the corresponding selected grid points.

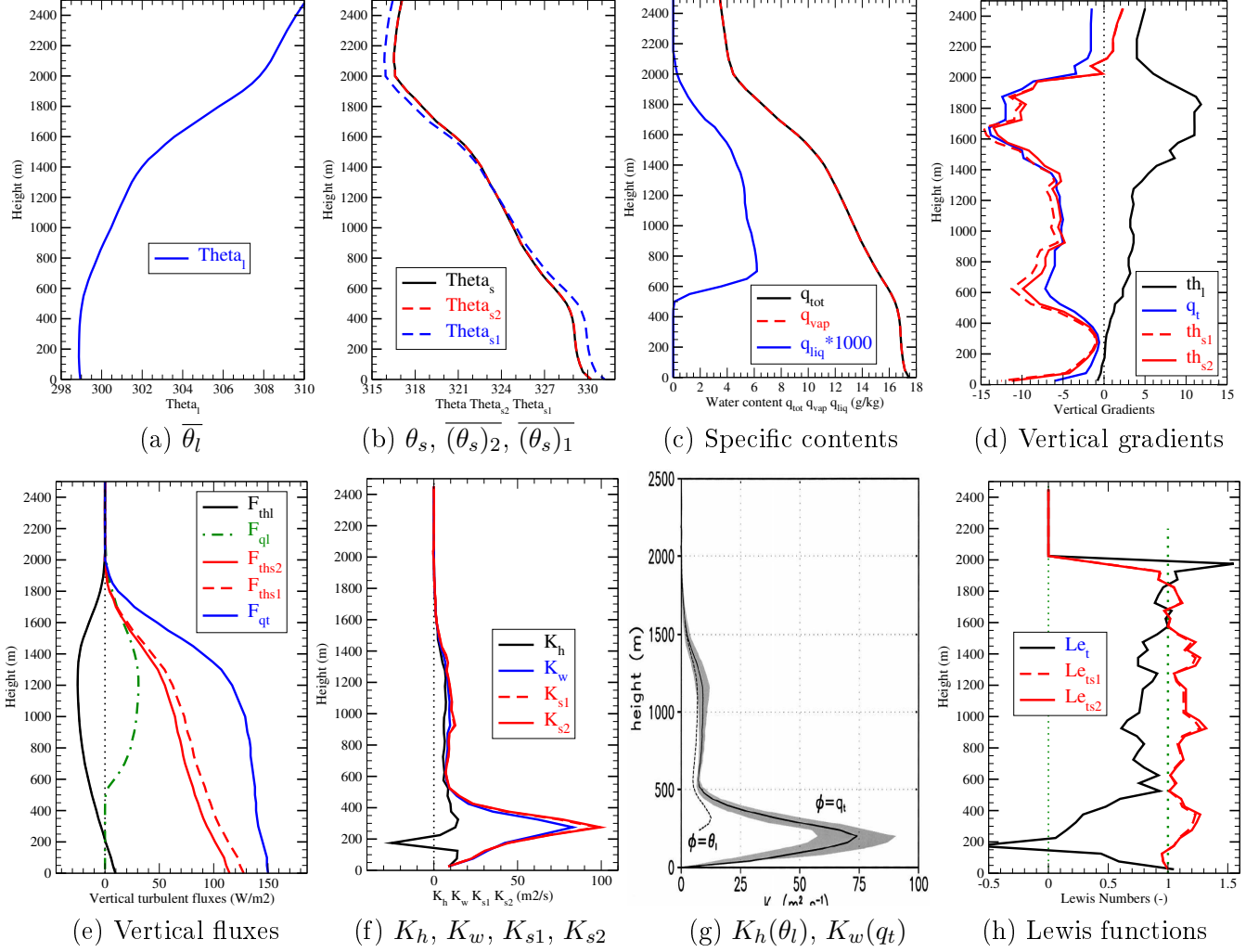


Figure 36: Vertical profiles for the last-3-hours average values of several variables from a Large Eddy Simulation (LES) of the BOMEX case published in Siebesma et al. (2003). The basic vertical profiles for  $\theta$ ,  $q_v$  and  $q_t$  have been digitized from the Figs. 3 (a,b,d) of Siebesma et al. (2003, p.1205), and also for the turbulent vertical fluxes of  $q_t$ ,  $\theta_l$ , and  $q_l$  published in the Figs. 4 (a,b,c), p.1206. The vertical profiles of other variables have been computed from these basic values. The Fig. 11 of Siebesma et al. (2003, p.1213) is reproduced as such in (g) for  $K_h = K(\phi = \theta_l)$  and  $K_w = K(\phi = q_t)$ .



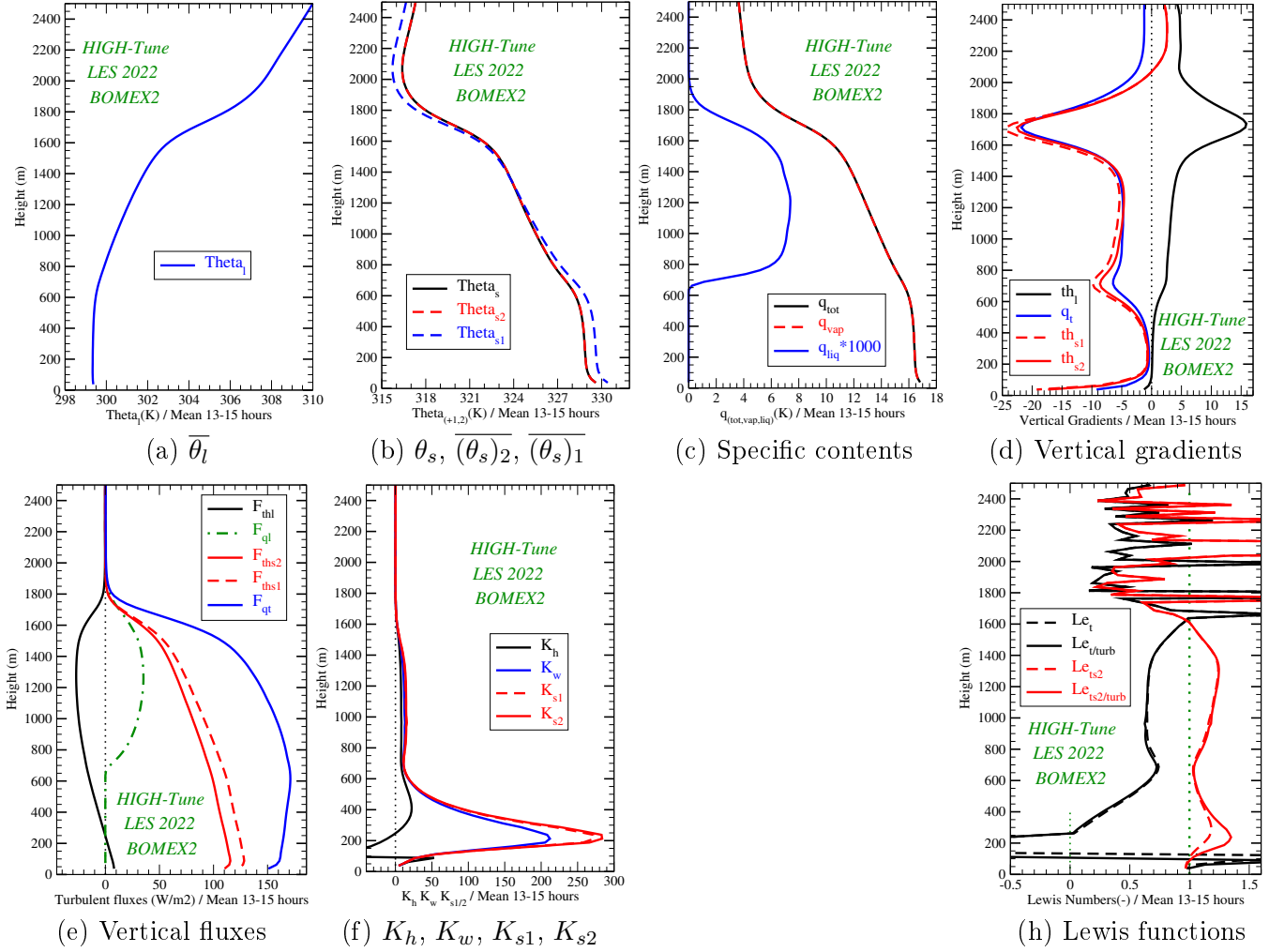


Figure 37: The same vertical profiles as in the Figs. 36, with the same average values for the last 3 hours (13-15h) of the BOMEX case, but for the LES studied during the Hight-Tune project 2017-2021 (outputs provided by Florent Briant and Fleur Couvreur).

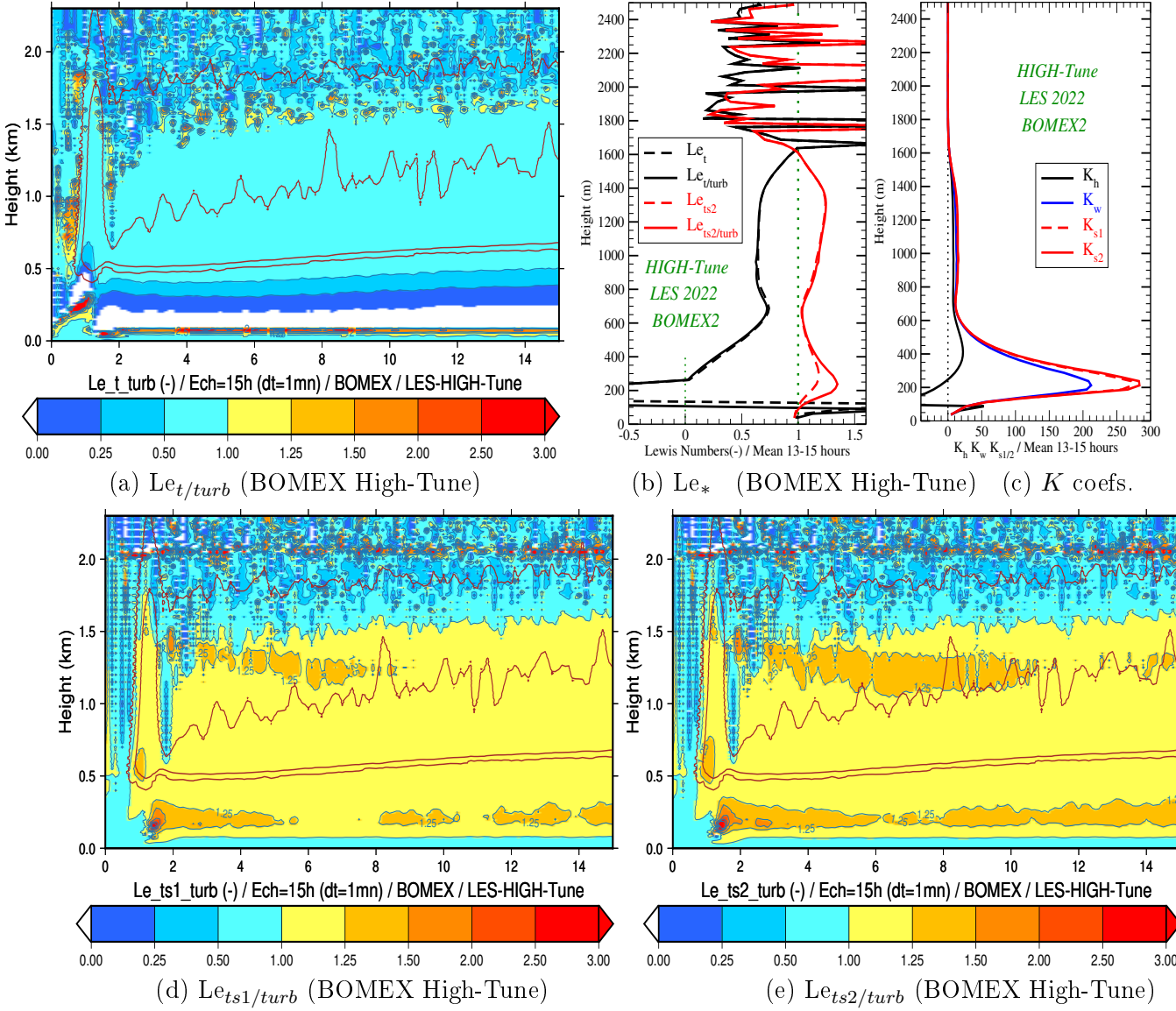


Figure 38: In (a), (d) and (e): the Time-Height sections of the standard Lewis function  $Le_{t/turb}$  and the two approximate (third-law) absolute-entropy values  $Le_{ts1/turb}$  and  $Le_{ts2/turb}$  for the LES of the BOMEX case studied during the Hight-Tune project 2017-2021 (LES outputs provided by Florent Briant and Fleur Couvreur), with the cloud indicated with brown contours (after the initial spin-up period). In (b): the last 3 h average vertical profiles of the same Lewis numbers for this BOMEX High-Tune LES (from 13 h to 15 h). In (c) the exchange coefficients:

- $K_h$  for the first Betts variable  $\theta_l$  (black solid line);
- $K_w = K_q$  for the second Betts variable (total water  $q_t$ , solid blue line);
- $K_{s1}$  and  $K_{s2}$  (dashed and solid red lines, respectively) for the two approximate (third-law) absolute-entropy variables  $\theta_{s1}$  and  $\theta_{s2}$ .

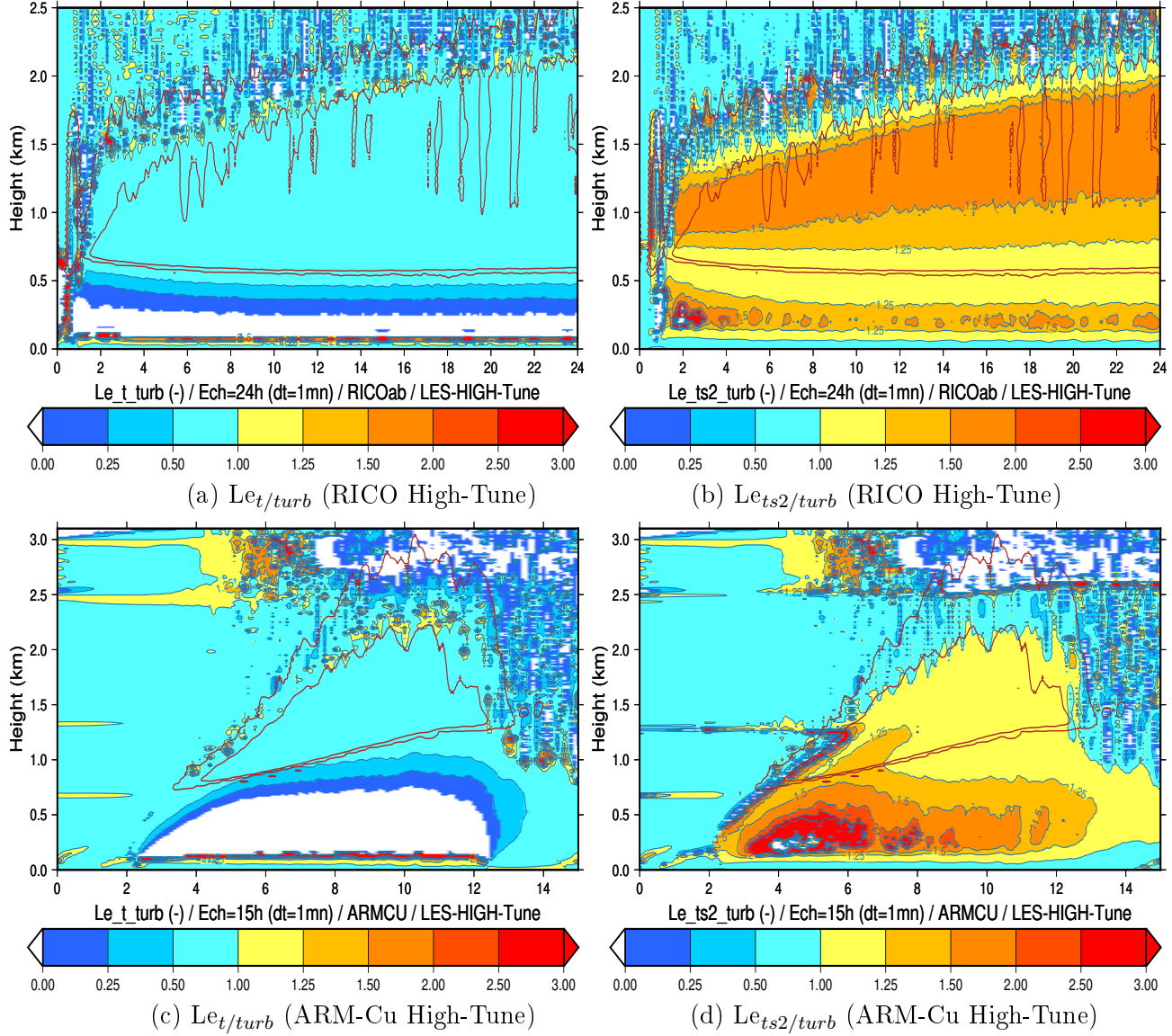


Figure 39: Time-Height sections of Lewis functions for the LES of the RICO (composite) and ARM-Cumulus cases studied during the Hight-Tune project 2017-2021 (LES provided by Florent Briant and Fleur Couvreur).

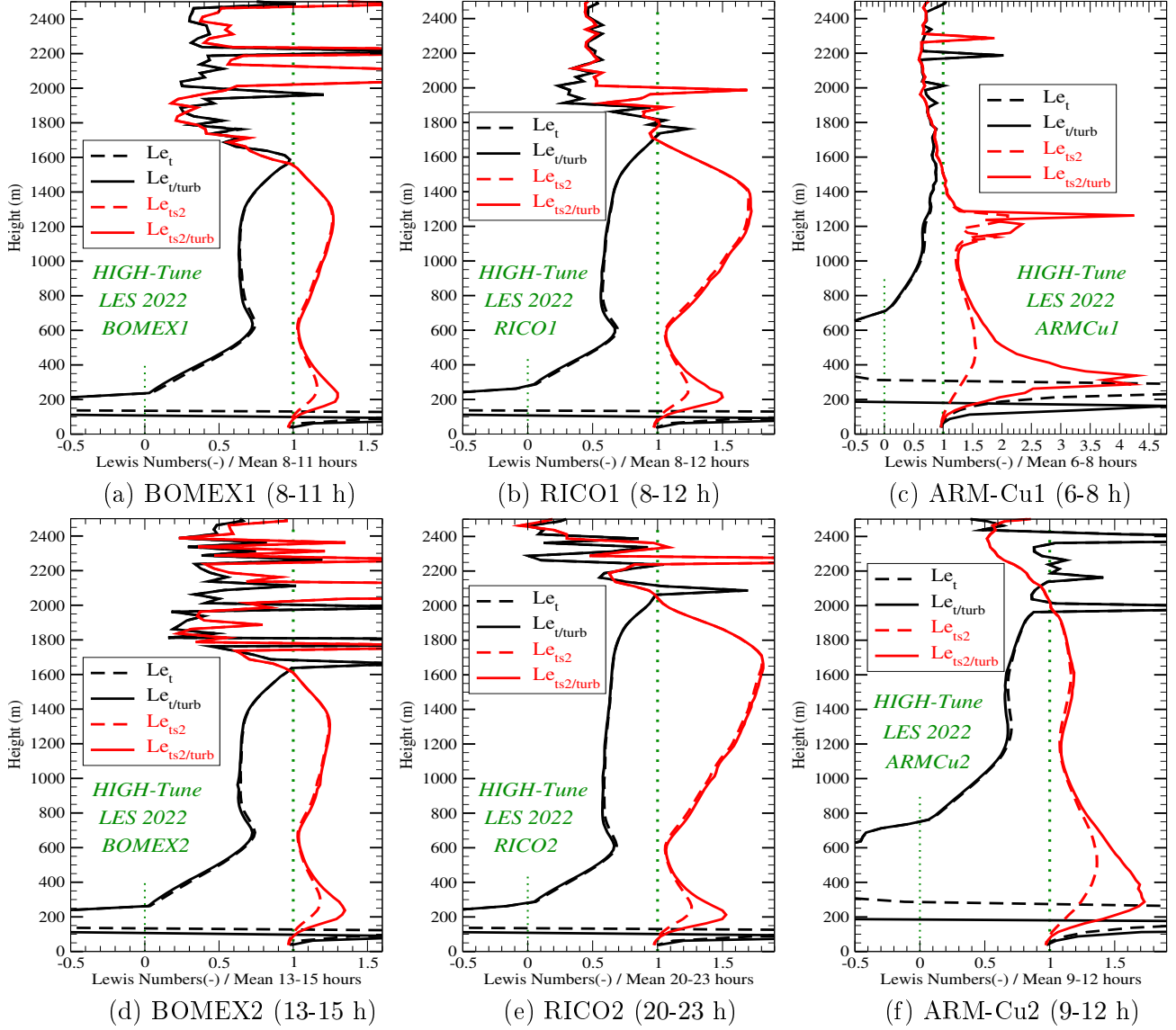


Figure 40: The same vertical profiles of the Lewis numbers as in Fig. 38(b) for the mean 13-15 h time average for the High-Tune BOMEX LES, still for  $Le_t$  (dashed black),  $Le_{t/turb}$  (solid black),  $Le_{ts2}$  (dashed red) and  $Le_{ts2/turb}$  (solid red), but for more LES (RICO, ARM-Cu) and for additional time averages.

The vertical profiles plotted in the Figs. 36 (a) to (h) for the average of the last 3 h of the LES studied by Siebesma et al. (2003) for the BOMEX case can be compared with the high resolution outputs of the HIGH-Tune AROME LES plotted in the Figs. 37 (a) to (h) for the same BOMEX case. The vertical profiles are similar, but logically much smoother with the HIGH-Tune outputs than with the digitized values obtained from the papers by Siebesma et al. (2003).

Even if the HIGH-Tune AROME-LES BOMEX simulation is not absolutely constant and not completely stabilized after 15 h (see the Figs. 38), the Lewis number averaged profiles over the last 3 h (between 13 and 15 h) are almost constant and remain close to unity, with two regions of relative maxima for  $Le_{ts1/turb}$  and  $Le_{ts2/turb}$  between  $z = 100$  and  $300$  m (up to 1.35), on the one hand (in the clear-air boundary layer below the cloud), and between  $z = 900$  and  $1400$  m (up to 1.25), on the other hand (within the cloud region).

We therefore obtained in the Figs. 37 (h) and Figs. 38 (b) similar, but smoother and more accurate results with the HIGH-Tune LES of BOMEX than from the crude digitized values from Siebesma et al. (2003) in the Fig. 36 (h) for the vertical profiles of the average last 3 h values of  $Le_t$  (dashed black),  $Le_{t/turb}$  (solid black),  $Le_{ts2}$  (dashed red) and  $Le_{ts2/turb}$  (solid red). This Fig. 38 (b) clearly shows that the values of  $Le_t$  (dashed black) are unrealistic, with very large values close to the ground (even  $+\infty$  at  $z = 80$  m), then very negative values (even  $-\infty$ ) between  $z = 100$  and  $250$  m, and then values systematically smaller than 1 above up to  $1600$  m.

Differently, both  $Le_{ts2}$  (dashed red) and  $Le_{ts2/turb}$  (solid red) remain positive (as expected) and even larger than 1 from the lowest level up to  $1600$  m (the top of the cloud). The difference between the total ( $Le_{ts2}$ ) and turbulent ( $Le_{ts2/turb}$ ) versions are larger in the lower boundary layer, where the thermal are maximum.

The values of  $Le_{ts1}$  larger than 1.3 in the lower boundary layer ( $z \approx 250$  m) in the Fig. 38 (b) have a large impact on the new (third-law) turbulent vertical flux  $\overline{w'\theta'_l}$  given by (280) or (282) and corresponding to  $\overline{w'\theta'_{s1}} > 0$ ,  $\overline{w'\theta'_{s2}} > 0$ ,  $K_{s1} > 0$  and  $K_{s2} > 0$ :

$$\begin{aligned} \overline{w'\theta'_l} &\approx -K_q \left[ \underbrace{(\text{Le}_{ts1})}_{\neq 1?} \times \frac{\partial \overline{\theta_l}}{\partial z} + \underbrace{(\text{Le}_{ts1} - 1) \overline{\theta_l} \left( \Lambda_r \frac{\partial \overline{q_t}}{\partial z} \right)}_{\text{additional term if } Le_{ts1} \neq 1?} \right] \neq -K_h \frac{\partial \overline{\theta_l}}{\partial z}, \\ \overline{w'\theta'_{li}} &\approx -K_q \left\{ \underbrace{(\text{Le}_{ts2})}_{\neq 1?} \frac{\partial \overline{\theta_{li}}}{\partial z} + \underbrace{(\text{Le}_{ts2} - 1) \overline{\theta_{li}} \left[ A \frac{\partial \overline{q_t}}{\partial z} + B \left( \frac{\partial \overline{q_l}}{\partial z} + \frac{\partial \overline{q_i}}{\partial z} \right) \right]}_{\text{additional term if } Le_{ts2} \neq 1?} \right\} \neq -K_h \frac{\partial \overline{\theta_{li}}}{\partial z} \\ \text{where } A &= \Lambda_r - \gamma \ln \left( \frac{r_v}{r_*} \right) - \gamma \left[ \frac{r_t (1 - q_l - q_i)}{q_v} \right], \\ \text{and } B &= \gamma \left( \frac{q_l + q_i}{q_v} \right), \end{aligned}$$

where  $\Lambda_r \approx 5.865 \pm 0.004$ ,  $\gamma \approx R_v/c_{pd} \approx 0.4594$  and  $r_* \approx 12.4 \text{ g kg}^{-1}$ .

Note that the (third-law) absolute-entropy additional terms depending on the vertical gradient of  $q_t$ ,  $q_l$  and  $q_i$  form some kind of negative counter-gradient negative terms, because  $Le_{ts1} - 1 > 0$  and  $\partial q_t / \partial z < 0$ , whereas  $\partial \theta_l / \partial z$  remains very small (see the Figs. 37).

The fact that  $K_{s2} \approx K_{s1}$  is positive and relevant, whereas  $K_h$  is a negative ill-defined exchange coefficient, can therefore be explained by the need to rely on the advice of Richardson (1919a,b, 1921, 1922), who had anticipated that turbulence should be based on the moist-air variables  $q_t$  (total water) and  $\theta_s$  (third-law absolute entropy potential temperature), but not at all on the (arbitrarily modified) Betts variable  $\theta_l \approx \theta_s \exp(-5.865 q_t)$ .

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The previous results shown for the lewis numbers and for the BOMEX case are also valid for the two other HIGH-Tune LES cases (RICO-composite and ARM-Cumulus) shown in the Figs. 39 and Figs. 40, where:

- both  $Le_t$  (dashed black) and  $Le_{t/turb}$  (solid black) computed from the vertical fluxes and gradients of the Betts variable  $\theta_l$  are ill-defined (negative values) in the lower clear-air boundary layer (from about 100 to 300 m for RICO, from about 200 to 900 m for ARM-Cu);
- with values lower than unity for both  $Le_t < 1$  (dashed black) and  $Le_{t/turb} < 1$  (solid black) in the boundary and cloud regions (up to about 1800 m);
- and, on the contrary, with positive and relevant Lewis number values  $Le_{ts2}$  (dashed red) and  $Le_{ts2/turb}$  (solid red) computed from the vertical fluxes and gradients of the (third-law) absolute-entropy variable  $\theta_s \approx \theta_{s2}$ , with moreover Lewis number larger than unity ( $> 1.5$  for RICO and even  $> 3.5$  for ARM-Cu) over the whole boundary and cloud regions (up to about 1800 m);
- with therefore relevant positive values for the exchange coefficients  $K_{s1}$  and  $K_{s2}$  over the whole boundary and cloud regions (not shown, but valid like for BOMEX for RICO and ARM-Cu).

These results shown for RICO and ARM-Cu provide further validations of the advice by Richardson (1919a,b, 1921, 1922), namely that turbulence should be based on the moist-air variables  $q_t$  (total water) and  $\theta_s$  (third-law absolute entropy potential temperature), but not at all on the (arbitrarily modified) Betts variable  $\theta_l \approx \theta_s \exp(-5.865 q_t)$ .

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- I have shown in this section that the absolute version of the entropy of the atmosphere  $s = c_{pd} \ln(\theta_s) + C_{ste}$  leads to an improvement in the calculation of turbulent exchange coefficients for moist boundary layers, with positive exchange coefficients  $K_s(\theta_s)$  and  $K_w(q_t)$  associated with the absolute-entropy potential temperature  $\theta_s \approx \theta_l \exp(\Lambda_r q_t)$  and the total water content  $q_t = q_v + q_l + q_i$ , where  $\Lambda_r \approx 5.87$ .

Conversely, the use of the presently used Betts (1973) variables  $(\theta_l, q_t)$ , where  $\theta_l$  is contrary to the third law of thermodynamics  $\Lambda_r \approx 0$ , leads to inconsistencies and negative exchange coefficients  $K_h(\theta_l)$ .

In particular, the Lewis number  $Le_t = K_h/K_w$  (noted “ $s = h/k$ ” by Warren K. Lewis, 1922) is set to unity ( $Le_t \equiv 1$ ) in almost all present GCM and NWP models, namely with the use of the same value for the exchange coefficients  $K_h(\theta_l) = K_w(q_t)$  for the two Betts’ variables  $\theta_l$  and  $q_t$ .

Differently, I show that the standard Lewis number  $Le_t = K_h/K_w$  is ill-defined (negative values) for several LES for the BOMEX, RICO, ARM-Cu campaigns, whereas the absolute-entropy version  $Le_{ts} = K_s/K_w$  is well-defined with moderate values in stable layers ( $0 < Le_{ts} < 1$ ) and larger values in convective layers ( $1 < Le_{ts} < 4$ ).

In my opinion, these results clearly indicate that the third law of thermodynamics should prevail to describe the moist-air turbulence since, as Richardson (1919a,b, 1921, 1922) already claimed, we should use the absolute version of the moist-air entropy, and thus the variable  $\theta_s$  as a conservative variable in place of:

- the absolute temperature ( $T$ );
- or the dry-air potential temperature ( $\theta$ );

- or the virtual potential temperature ( $\theta_v$ );
- or the liquid-water potential temperature ( $\theta_l$ );
- or the liquid-ice potential temperature ( $\theta_{li}$ );
- or any other possible thermal variable different from the third-law absolute entropy  $s(\theta_s)$ .

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• The previous results derived for the moist-air turbulence show that the Lewis number  $Le_{ts} = K_s/K_w$  is different from unity, namely that the exchange coefficients  $K_s$  (for the absolute entropy) and  $K_w = K_q$  (for the total-water content) are different from each other, with in particular  $Le_{ts} > 1$  and thus  $K_s > K_w$  in unstable layers. Moreover, none of  $T, \theta, \theta_l, \dots$  moist-air variables correspond to well-defined positive exchange coefficients: this is only true for the absolute-entropy  $\theta_s$  thermal variable. One might legitimately wonder whether such results are also valid for the ocean?

• In fact, we can do more than draw a parallel with the problem of “*double diffusion*” dealing with the joint evolution of temperature and salinity, and thus density gradients in the oceans, with:

- the first studies by Stern (1960); Turner (1965); Shirtcliffe (1973); Turner (1973, 1974); Crapper (1975); Marmorino and Caldwell (1976); Linden and Shirtcliffe (1978); Takao and Narusawa (1980); Newell (1984); Kelley (1984); McDougall and Taylor (1984); Taylor (1988); Kelley (1990);
- followed (for instance) by the next studies by Gargett and Holloway (1992); Large et al. (1994); Ledwell et al. (1998); Zhang et al. (1998); Merryfield et al. (1999); You (2002); Canuto et al. (2001, 2002); ... and
- up to the more recent studied by Carpenter et al. (2012); Radko (2016); Guo et al. (2018); Shibley and Timmermans (2019); Brown and Radko (2019, 2021); Yang et al. (2022); Brown and Radko (2022); Ma and Peltier (2022a,b,c); Middleton (2022); Middleton et al. (2022); Ma and Peltier (2024), ...

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As an example, Canuto et al. (2002) defined the “*diffusivities*” (exchange coefficients)  $K_m, K_h$  and  $K_s$  for the large-scale velocity (momentum), heat (temperature) and salinity, respectively, from the  $K$ -gradient relationships (Eqs. 2d, p.241):

$$\overline{w''u''} = -K_m \frac{\partial U}{\partial z}, \quad \overline{w''T''} = -K_h \frac{\partial T}{\partial z}, \quad \overline{w''s''} = -K_s \frac{\partial S}{\partial z},$$

where the diffusivities (exchange coefficients)  $K_\alpha (\alpha = m, h, s)$  are given (Eq. 2e) as functions of

$$K_\alpha = K_\alpha(R_\rho, N, Ri^T, \epsilon),$$

where  $N$  is the Brunt-Väisälä frequency,  $\epsilon$  the dissipation of energy,  $Ri^T$  the total Richardson number, and  $R_\rho$  the density ratio (also called density anomaly, or stability ratio, or stability number, or Turner’s number associated with the Turner’s angle):

$$R_\rho = \frac{\alpha_s (\partial S / \partial z)}{\alpha_T (\partial T / \partial z)} \quad \text{and} \quad Ri^T = \frac{N^2}{\Sigma_T^2},$$

with  $\alpha_T$  and  $\alpha_s$  the thermal expansion and haline contraction coefficients, respectively.

Note that this definition for the density ratio  $R_\rho$  is the same as  $(\beta \Delta S) / (\alpha \Delta T)$  initially suggested by Shirtcliffe (1973, p.27) and Turner (1973, p.254) and retained in many of subsequent studies, but is the reverse of the ratio defined as  $R_\rho^* = (\alpha \Delta T) / (\beta \Delta S)$  in the same study by Turner (1973, p.281, “... *written here in the inverse sense so that  $R_\rho^* > 1$  denotes static stability*”), and also as  $R_\rho = (\alpha \Delta T) / (\beta \Delta S)$

in the other studies by McDougall and Taylor (1984, p.2), Gargett and Holloway (1992, p.1159), Large et al. (1994, Eq. 30, p.373), Zhang et al. (1998, p.590), Ledwell et al. (1998, Eq. 1, p.21,500), Merryfield et al. (1999, p.1125), You (2002, p.2079), Brown and Radko (2019, Eq. 1.1, p.589), Brown and Radko (2021, Eq. 1, p.1915), Middleton et al. (2022, Eq. 1.1, p.4).

The diffusivities (exchange coefficients)  $K_\rho$  and  $K_c$  that enter the mass flux  $\overline{w''\rho''}$  and the concentration flux  $\overline{w''c''}$  are written by Canuto et al. (2002, Eqs. 3e and 3f, p.242) as

$$K_\rho = \frac{K_h - K_s R_\rho}{1 - R_\rho} \quad \text{and} \quad K_c = \frac{K_s + K_h R_\rho}{1 + R_\rho} ,$$

with the relationship for  $K_\rho$  resulting from  $\rho''/\rho = -\alpha_T T'' + \alpha_s s''$ .

Canuto et al. (2002, Eq. 17a, p.244) arrived at the following formulation for the “*ratio of heat to salt diffusivities (exchange coefficients)*”

$$\frac{K_h}{K_s} = \left( \frac{\pi_4}{\pi_1} \right) \left[ \frac{1 - \pi_1 \pi_3 x R_\rho + \pi_1 \pi_2 x (1 + R_\rho)}{1 + \pi_4 \pi_5 x - \pi_2 \pi_4 x (1 + R_\rho)} \right] ,$$

where large  $x$  means strong stratification and weak turbulence with

$$\frac{K_h}{K_s} \approx \frac{(\pi_2 - \pi_3) R_\rho + \pi_2}{\pi_5 - \pi_2 - \pi_2 R_\rho} ,$$

and vice versa small  $x$  means weak stratification and stronger turbulence with

$$\frac{K_h}{K_s} \approx \frac{\pi_4}{\pi_1} .$$

Constants are  $\pi_1 = \pi_4 = 0.08372$ ,  $\pi_2 = 1/3$ ,  $\pi_3 = \pi_5 = 0.72$  (Eq.B1, p.262).

The ratio  $K_h/K_s$  for the sea-salt oceans is clearly the equivalent of the Lewis number for the moist-air atmosphere  $K_h/K_w$ , but with the salinity replacing the total-water content.

Moreover, in the same way as the Lewis number is different from unity in the HIGH-Tune LES for the BOMEX, RICO and ARM-Cu atmospheric cases, the Figure 5 of Canuto et al. (2002, p.250), recalled in the following Fig. 41, exhibits similar patterns, namely that depending on the three stability parameters:  $R_\rho$  (density ratio),  $N$  (Brunt-Väisälä frequency) and  $Ri^T$  (total Richardson number), the (Lewis number) ratio  $K_s/K_h$  is different from unity (dashed red line) in most regimes.

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The main difference with the advice of Richardson (1919a,b, 1921, 1922) is the use in oceanic studied like in Canuto et al. (2002) of the absolute temperature as the thermal parameter, and not the absolute entropy.

More precisely, the absolute temperature is sometimes replaced by the “*potential temperature*” with, as in the section 16 entitled “*Future improvements of the model*” by Canuto et al. (2002, p.260), the underlying assumption that: “*The presence of non-local terms would change the heat-flux expression to*

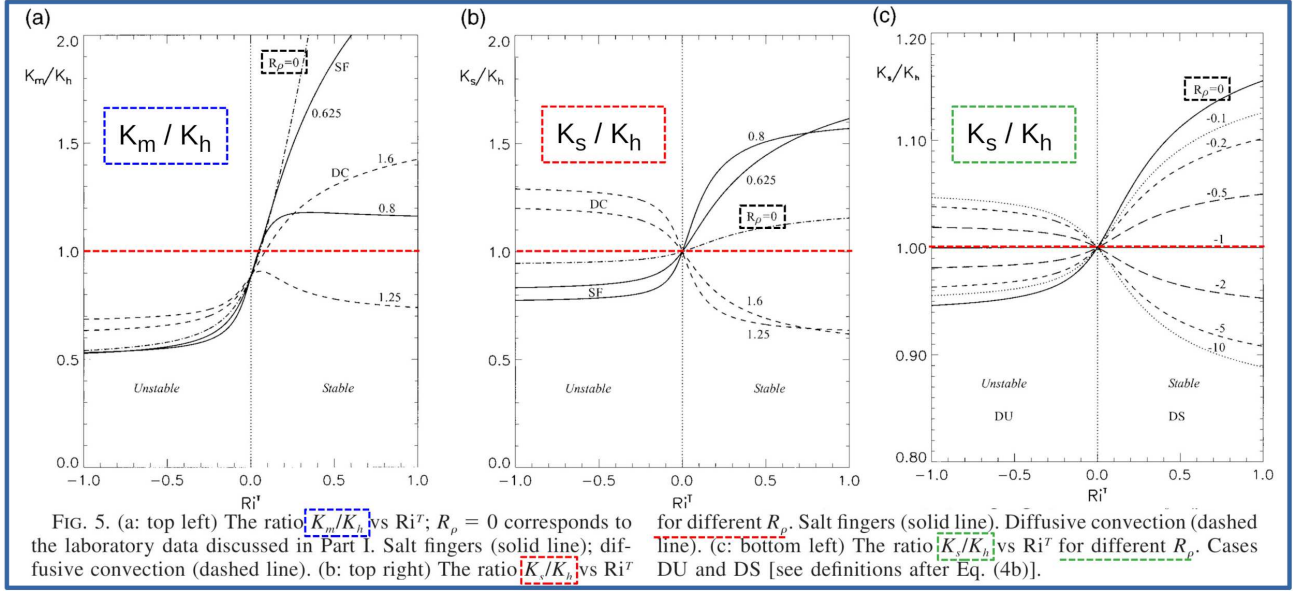
$$\overline{w''T''} = -K_h \left( \frac{\partial T}{\partial z} + \Gamma \right) ,$$

where  $\Gamma$ , known as the counter-gradient term, is a function of the Third-order terms.”

Indeed, this modification agrees with the relationships (280) or (282) I have derived for the “*usual thermal flux of the Betts liquid-water potential temperature  $\theta_l$* ” where a kind of counter-gradient term (similar to  $\Gamma$ ) appears when the turbulence is applied to the absolute moist-air entropy variable  $\theta_s \approx \theta_l \times \exp(\Lambda_r q_t)$ , instead of the liquid-water, arbitrarily modified Betts value  $\theta_l$ .



Figure 41: The Figure 5 of Canuto et al. (2002, p.250) showing the variation of the ratios of diffusivities  $K_m/K_h$  (Prandtl number) and  $K_s/K_h$  (Lewis number) for momentum ( $K_m$ ), heat ( $K_h$ ) and salinity ( $K_s$ ) exchange coefficients.



Other oceanic “non-local transport terms” (counter-gradient terms)  $\gamma_x$  are considered for any variable  $x$  by Large et al. (1994), written in Eq. 9 (p.371) as

$$\overline{w'x'} = -K_x \left( \frac{\partial X}{\partial z} - \gamma_x \right).$$

Similarly, Ledwell et al. (1998) implicitly considered the “potential temperature” (without notation for it) through the stability ratio  $R_\rho$  written in terms of the gradient of the absolute temperature  $T$  plus the adiabatic temperature gradient  $\Gamma$ , leading (Eq. 1, p.21,500) to:

$$R_\rho = \frac{\alpha (\partial T / \partial z + \Gamma)}{\beta (\partial S / \partial z)},$$

where  $\alpha = -\partial \ln(\rho) / \partial T$  and  $\beta = \partial \ln(\rho) / \partial S$ .

Moreover, several studies have explicitly used the potential temperature (often noted  $\theta$  or  $\Theta$ ), instead of the absolute temperature (often noted  $T$ ):

- a potential temperature variable noted  $\theta$  in Kelley (1984);
- a potential temperature noted  $T$ , with the turbulent potential temperature component noted  $\theta$ , by Large et al. (1994);
- a potential temperature variable noted  $\theta$  in You (2002), with (p.2079) the stability (or density) ratio defined as

$$R_\rho = \frac{\alpha (\partial \theta / \partial z)}{\beta (\partial S / \partial z)},$$

where  $\alpha = -\partial \ln(\rho) / \partial \theta$  and  $\beta = -\partial \ln(\rho) / \partial S$ , and with the Turner angle (Tu, in deg) defined from  $R_\rho = -\tan(\text{Tu} + 45)$  and expressed in terms of  $\theta$  in the form

$$\text{Tu} = \tan^{-1} \left[ \left( \alpha \frac{\partial \theta}{\partial z} - \beta \frac{\partial S}{\partial z} \right), \left( \alpha \frac{\partial \theta}{\partial z} + \beta \frac{\partial S}{\partial z} \right) \right];$$

- a potential temperature variable noted  $\Theta$  by Ma and Peltier (2022b,c, 2024);
- (with however a notation  $\theta$  retained by Brown and Radko (2022), but for the anomaly of the absolute temperature  $T - T_0$ , and not for a potential temperature).

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The use of absolute or potential temperature variables as thermal parameter in oceanic studied does not correspond to the recommendations of Richardson (1919a,b, 1921, 1922), who explained that we should use the absolute entropy.

One might therefore legitimately ask whether it would be possible to define a seawater absolute-entropic temperature  $\theta_\eta$ , in the same way as I defined the absolute-entropy potential temperature  $\theta_s$  for the atmosphere as

$$s = s_{d0} + c_{pd} \ln\left(\frac{\theta_s}{T_0}\right) \quad \text{and thus} \quad \theta_s = T_0 \times \exp\left(\frac{s - s_{d0}}{c_{pd}}\right),$$

with the approximate first-order formula

$$\theta_s \approx \theta \times \exp\left(-\frac{L_v q_l + L_s q_l}{c_{pd} T_0}\right) \times \exp\left[\left(\frac{s_{vr} - s_{dr}}{c_{pd}}\right) q_t\right].$$

We can similarly define a seawater absolute-entropic temperature  $\theta_\eta$  as

$$\eta_{abs} = c_w \ln\left(\frac{\theta_\eta}{T_0}\right) \quad \text{and} \quad \boxed{\theta_\eta = T_0 \times \exp\left(\frac{\eta_{std/TEOS10}}{c_w}\right) \times \exp\left[\left(\frac{\eta_{s0} - \eta_{w0}}{c_w}\right) \left(\frac{S_A - S_{S0}}{1000}\right)\right]}, \quad (285)$$

where  $\eta_{std/TEOS10}(t, S_A, p)$  is the standard TEOS10 value of the seawater entropy depending on the temperature, salinity and pressure variables, and with  $T_0 = 273.15$  K,  $c_w \approx 4218$  J K<sup>-1</sup> kg<sup>-1</sup>,  $\eta_{s0} - \eta_{w0} \approx -1880 \pm 17$  J K<sup>-1</sup> kg<sup>-1</sup> and therefore  $(\eta_{s0} - \eta_{w0})/c_w \approx -0.4457 \pm 0.0004$  J K<sup>-1</sup> kg<sup>-1</sup> forming the “*absolute-entropy correction term*” in factor of the salinity departure term  $S_A - S_{S0}$ , with the standard salinity  $S_{S0} = 35.16504$  g kg<sup>-1</sup> defined in TEOS10, for which  $\eta_{std/TEOS10}(0.01^\circ\text{C}, S_{S0}, 0 \text{ dbar}) = 0$ .

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Figure 42: Vertical profiles of temperatures in Celsius units for the three Arctic cases (*sa\_arctic*, *t\_arctic*, *p\_arctic*) available in the subroutine *gsu\_mod\_check\_data.f90* in the TEOS10-GSW software (McDougall et al., 2010), with:

- $\theta(S_A, t, p, p_r)$  the potential temperature (solid blue line);
- $T$  the usual absolute temperature (dashed purple line);
- $\Theta(S_A, t, p)$  the conservative temperature (solid red line);
- $\theta_{\eta\text{-std}}(S_A, t, p)$  the standard seawater entropy temperature with  $\eta_{s0} - \eta_{w0} = 0$  (dashed black line);
- $\theta_{\eta\text{-abs}}(S_A, t, p)$  the absolute seawater entropy temperature with  $\eta_{s0} - \eta_{w0} \neq 0$  (solid orange line).

**Top panels:** zoom for the upper layers; **Bottom panels:** the plots for all the available layers.

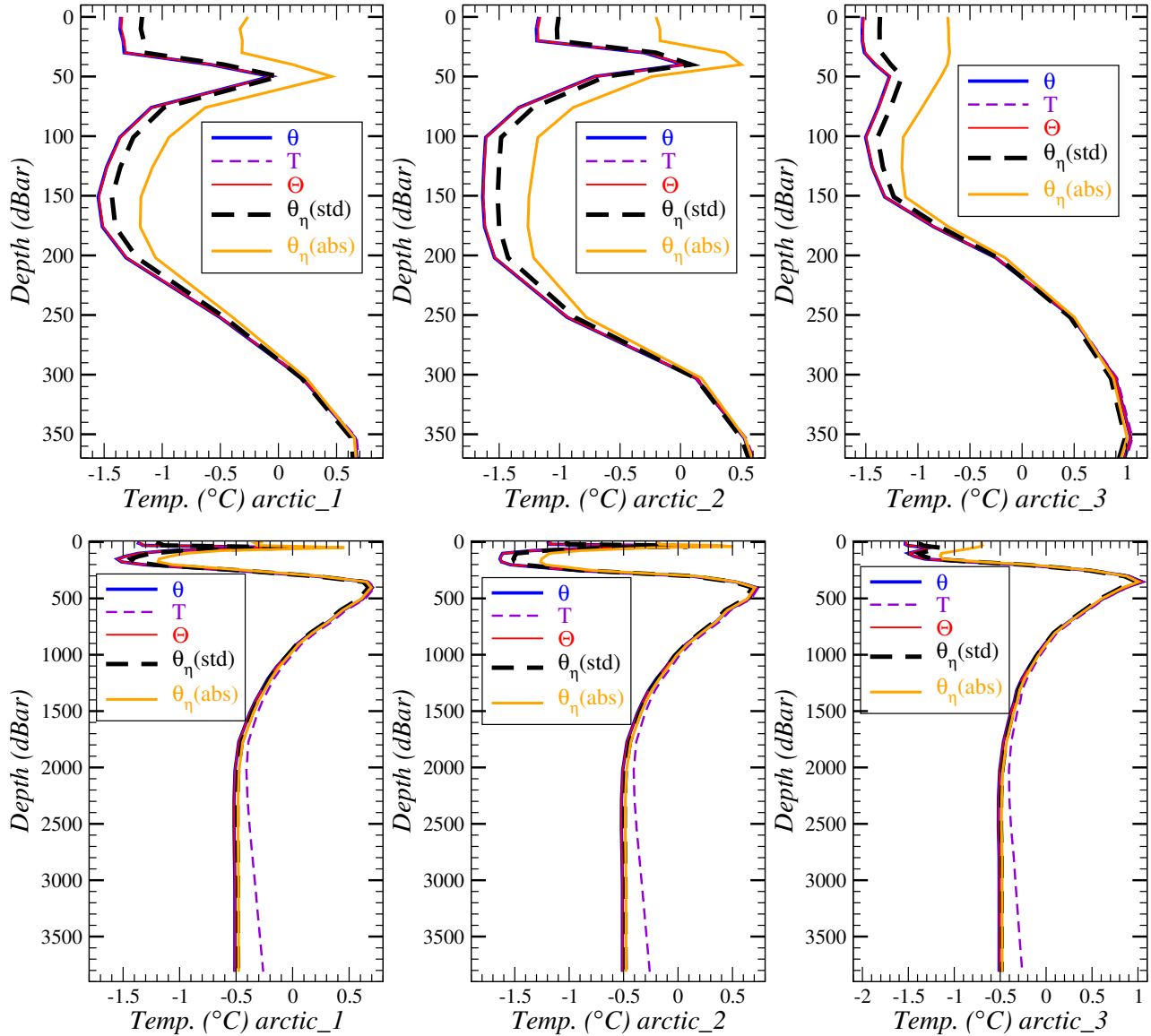


Figure 43: The same as in Figs. 42, but with **On the left:** the Arctic vertical profiles SCICEX96-43 (30th of September 1996; 79.397 deg North; 142.04 West; <https://www.nodc.noaa.gov/archive/arc0021/0000568/1.1/data/0-data/SCICEX-96/Exported%20Data/CTD043.EDF>); **Center:** the vertical profile for the E88-61 case (“Endeavor” cruise E88, station 61, 23 August 1982, 36.667 deg North; 70.993 West) from the CTD profile printed in the document UNESCO-JPOTS (1991, Fig. 2.1 and Tables 2.1 and 2.2, p.40, 49 and 51, available at <https://unesdoc.unesco.org/ark:/48223/pf0000090489>); **On the right:** the vertical profile for the KH-87-1-JT case (“Hakuho Maru” cruise KH-87-1, station JT, 28 January 1987, 33.882 deg North; 141.93 East) from the CTD profile printed in the document UNESCO-JPOTS (1991, Fig. 2.3 and Tables 2.4, p.42 and 55, available at <https://unesdoc.unesco.org/ark:/48223/pf0000090489>);

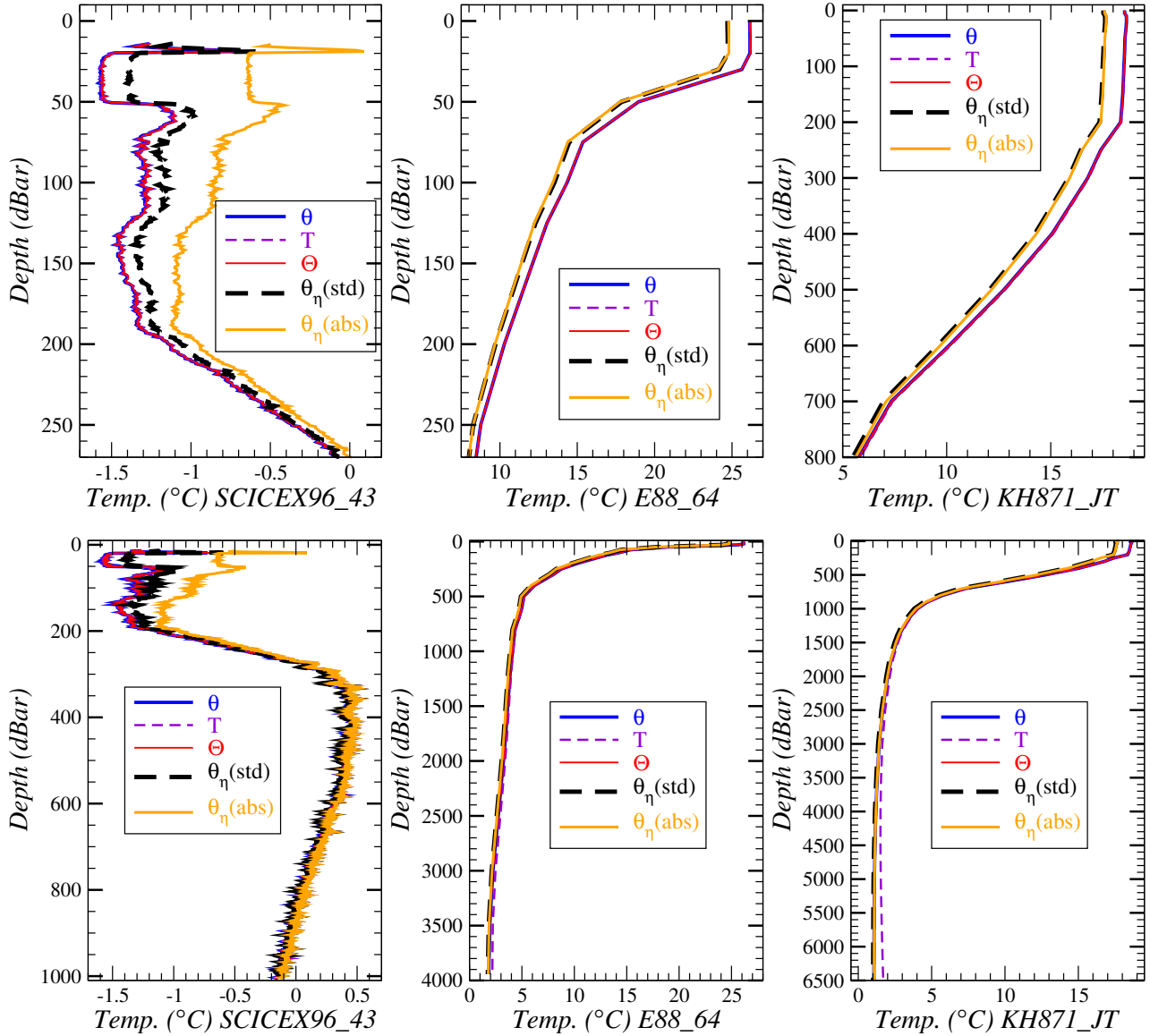
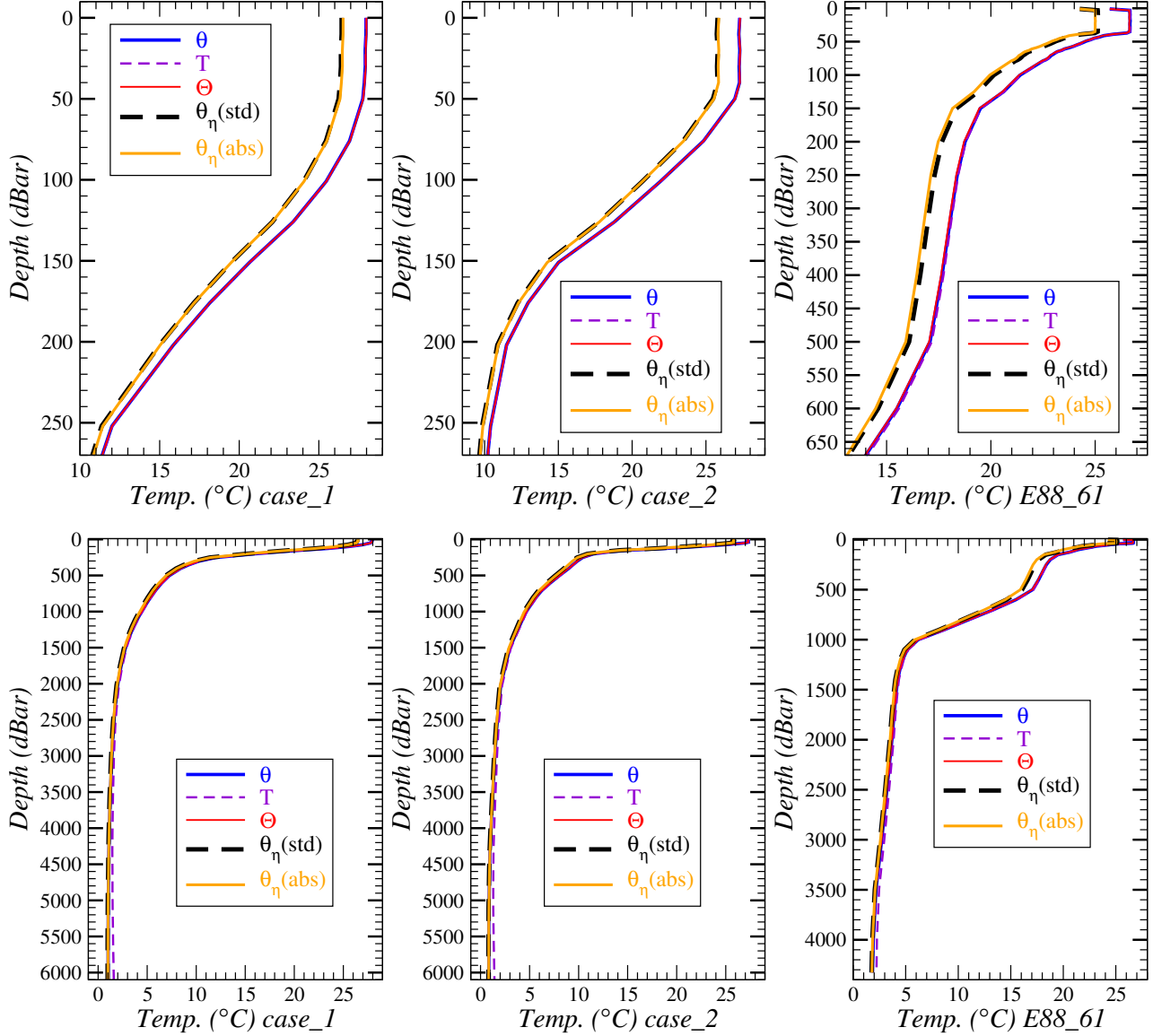


Figure 44: *The same as in Figs. 42, but with* **On the left and center:** *the vertical profiles for the two cases (1, 2) coded into the (*sa*, *t*, *p*) datasets available in the subroutine *gsw\_mod\_check\_data.f90* of the TEOS10-GSW software; **On the right:** *the vertical profile for the E88-64 case (“Endeavor” cruise E88, station 64, 24 August 1982, 37.666 deg North; 71.000 West) from the CTD profile printed in the document UNESCO-JPOTS (1991, Fig. 2.2 and Tables 2.3, p.41 and 53, available at <https://unesdoc.unesco.org/ark:/48223/pf0000090489>).**



I show in the Figs. 42 to 44 vertical profiles for different temperature-like variables (in Celsius unit):

- the potential temperature  $\theta(S_A, t, p, p_r)$  (solid blue line);
- the usual absolute temperature  $T$  (dashed purple line);
- the conservative temperature  $\Theta(S_A, t, p)$  (solid red line);
- the standard seawater entropy temperature  $\theta_{\eta\text{-std}}(S_A, t, p)$  given by (285), but with  $\eta_{s0} - \eta_{w0} = 0$  (dashed black line);
- the absolute seawater entropy temperature  $\theta_{\eta\text{-abs}}(S_A, t, p)$  given by (285) with  $(\eta_{s0} - \eta_{w0})/c_w \approx -0.4457 \pm 0.0004 \text{ J K}^{-1} \text{ kg}^{-1}$  different from 0 (solid orange line).

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The potential temperature  $\theta(S_A, t, p, p_r)$  has been computed, on the one hand, with the more exact TEOS10-GCW subroutine `gsw_pt_from_t(Sa,t,p,pr=0)`, which is very close, on the other hand, to the approximate version `gsw_pt0_from_t(Sa,t,p)`.

It is explained in the section 3.1 by McDougall et al. (2010) that: “*The very useful concept of potential temperature was applied to the atmosphere originally by von Helmholtz (1888, p.652), first under the name of “heat content (Wärmegehalt)”, and later renamed “potential temperature” by (von Bezold, 1888, p.1190). Potential temperature  $\theta(S_A, t, p, p_r)$  is the temperature ( $t = \theta$ ) that a fluid parcel would have if its pressure ( $p$ ) were changed to a fixed reference pressure  $p_r$  in an isentropic (same entropy) and isohaline (same salinity  $S_A$ ) manner. These concepts were transferred to oceanography by Helland-Hansen (1912, The Ocean Waters. Intern. Rev. Hydrobiol. Hydrog., Hydrog. Supp. Ser. 1 No. 2, Leipzig).*” Indeed, Helland-Hansen (1912, Chapter 5, p.220-221, about “Physical oceanography” in “Depths of the ocean”) wrote: “(...) *the temperature that the water would acquire –on account of the reduction of pressure– if it were raised to the surface. This potential temperature has by the author of the present chapter been called the potential temperature, a term used in meteorology.*”

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However, McDougall et al. (2010) forgot to cite the next papers by Bauer (1908, 1910) who started from previous remarks of von Bezold, who showed “... *a striking resemblance to the well-known theorem of Clausius, now commonly known as the second law of thermodynamics, viz.: “that the entropy strives towards a maximum ;” but, he says, “it is not identical with it.”*” Accordingly, Bauer (1908, 1910) arrived at the dry-air relationship

$$s = c_{pd} \ln(\theta) + \text{const.},$$

which “*gives us the relation sought between potential temperature and entropy.*”

This remark of Bauer (1908, 1910) will be serve as a guidance to arrive at the relationship

$$s = c_{pd} \ln(\theta_s) + \text{const.}$$

to define the moist-air absolute entropy potential temperature  $\theta_s$  studied from Marquet (2011a) to Marquet and Stevens (2022), with a similar relationship I used to define in 2025 the seawater absolute entropy potential temperature  $\theta_{\eta}$  by (285) via the formula:

$$\eta_{abs}(S_A, t, p) = c_w \ln\left(\frac{\theta_{\eta}}{T_0}\right) + \eta_{w0} = c_w \ln(\theta_{\eta}) + \overbrace{[\eta_{w0} - c_w \ln(T_0)]}^{(\text{const.})}, \quad (286)$$

with  $\eta_{w0} = 0$  without loss of generality and  $c_w \approx 4218 \text{ J K}^{-1} \text{ kg}^{-1}$  the specific heat capacity for pure liquid water (instead of the dry-air value  $c_{pd} \approx 1004.7 \text{ J K}^{-1} \text{ kg}^{-1}$ ).

Note that this simple logarithmic relationship (286) for  $\eta_{abs}(\theta_\eta)$  leading to the definition for  $\theta_\eta = T_0 \exp [(\eta_{abs} - \eta_{w0})/c_w]$  somehow corresponds to the question asked in the section 4.1 by McDougall et al. (2023, about “An approximate polynomial expression for entropy / An analogy with a perfect gas”), who trusted the definition of the potential temperature ( $\theta$ ) and conservative temperature ( $\Theta$ ) in Celsius units, to wrote (with  $T_0 = 273.15$  K):

“One wonders how accurate a correspondingly simple logarithm expression would be for the entropy of seawater, defined by either

$$c_w \ln(T_0 + \theta) + \text{constant} \quad \text{or by} \quad c_w \ln(T_0 + \Theta) + \text{constant}.$$

The constants can be chosen so that it makes the estimate of entropy zero if  $\theta = 0^\circ\text{C}$  or  $\Theta = 0^\circ\text{C}$  in the two cases respectively, since entropy is zero for Standard Seawater ( $S_A = S_{S0} = 35.16504$  g kg<sup>-1</sup>) at this temperature. That is, we examine the two estimates  $c_w \ln(1 + \theta/T_0)$  and  $c_w \ln(1 + \Theta/T_0)$  as approximations to the entropy of seawater. (Note that for seawater,  $c_w \approx 4218$  J K<sup>-1</sup> kg<sup>-1</sup> is approximately 4 times as large as the isobaric specific gas heat capacity of air,  $c_{pd} \approx 1004.7$  J K<sup>-1</sup> kg<sup>-1</sup>). ”

The important improvement of the definition  $\eta_{abs} = c_w \ln(\theta_\eta) + \text{const.}$  in (285) and (286) is that I have not arbitrarily modified (in the left hand side) the reference liquid-water and sea-salts entropies to define the seawater entropy  $\eta_{abs}(S_A, t, p)$ , and I have not arbitrarily set (in the right hand side) the argument in the logarithm of (286) to either  $\theta$  or  $\Theta$ , but trust this relationship and seek for the value  $\theta_\eta$  (in Kelvin units) of this argument instead.

---

The conservative temperature  $\Theta(S_A, t, p) = h^0(S_A, t, p)/c_p^0$  has been computed with the TEOS10-GCW subroutine `gsw_ct_from_t(Sa, t, p)`, where  $h^0(S_A, t, p)$  is the potential enthalpy and with the (strangely very accurate) numerical TEOS10 constant  $c_p^0 = 3991.86795711963$  J K<sup>-1</sup> kg<sup>-1</sup> “close to the average value of the specific heat capacity at the sea surface of today’s global ocean” (see McDougall et al., 2010, sections 3.2 and 3.3).

The potential enthalpy  $h^0$  defined by McDougall (2003) is described in McDougall et al. (2010, sections 3.2) as: “(...) the enthalpy that a fluid parcel would have if its pressure were changed to a fixed reference pressure  $p_r$  in an isentropic (same entropy) and isohaline (same salinity  $S_A$ ) manner. Because heat fluxes into and out of the ocean occur mostly near the sea surface, the reference pressure for potential enthalpy is always taken to be  $p_r = 0$  dbar (that is, at zero sea pressure” departure  $p = P - P_0$ , with  $P$  the absolute pressure and  $P_0 = 101325$  Pa.)

The differences between  $\theta$  and  $\Theta$  were plotted in the Figs. 2 (a) and (b) of McDougall (2003, p.952), with typical small values of  $\pm 0.2^\circ\text{C}$  for realistic ranges of temperatures ( $t$ ) and salinities ( $S$ ). More precisely, McDougall (2003, p.952) wrote : “The temperature difference,  $\theta - \Theta$ , is quite small when the temperature ( $t$ ) is close to  $0^\circ\text{C}$  and, because of our choice of  $c_p^0$ , also when  $S$  is close to 35 psu. We can read off Fig. 2a that  $\theta - \Theta$  is zero for one parent water mass and is about  $0.22^\circ\text{C}$  for the other (...)” Larger differences  $\Theta - \theta > 1.5^\circ\text{C}$  exist, but mainly for small values of salinities ( $S < 10$  psu) and large values of  $\Theta > 30^\circ\text{C}$ .

McDougall (2003, p.954) further explain that: “One handy way of expressing the error involved with using potential temperature (namely  $\theta$  instead of  $\Theta$ ) is to note that 0.5 % of the annual-mean SST values in the ocean atlas have  $\theta - \Theta < -0.15^\circ\text{C}$  and 0.5 % have  $\theta - \Theta > 0.10^\circ\text{C}$ . That is, 1 % of the annual-mean SST data lie outside an error range of  $0.25^\circ\text{C}$ . In salty water potential temperature  $\theta$  tends to be larger than it should be if it were to accurately represent heat content, while for freshwater,  $\theta$  is less than  $\Theta$ .”

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The Figs. 42 to 44, plotted for the (1, 2, 3) + SCICEX-96-43 Arctic and (E88-64, KH-87-1-JT) + (1, 2, E88-61) Tropical cases, show that:

- the potential ( $\theta$ ) and conservative ( $\Theta$ ) temperatures remain very close to each others up to less than  $\pm 0.05^\circ\text{C}$  at all depth and for all the cases (overlapping curves), as previously shown by McDougall (2003);
  - the potential ( $\theta$ ) and conservative ( $\Theta$ ) temperatures remain close to the usual absolute temperature ( $T$ ), with zero deviations from  $T$  at the surface which become progressively negative with depth, but without exceeding  $-0.6^\circ\text{C}$  at 6000 dbar for the non-Arctic cases (1, 2, E88-61, E88-64 and KH871-JT), with the dashed purple  $T$ -lines that do not overlap the other  $\theta$  and  $\Theta$  blue and red lines only for the deep layers below the 2000 dbar depth;
  - the difference between the seawater entropy potential temperatures  $\theta_\eta$  (standard and absolute) and both  $\theta$  or  $\Theta$  are very small at large depths (less than  $-0.05^\circ\text{C}$  at 4000 dbar), but with some systematic smaller values of  $\theta_\eta$  (standard and absolute) in the upper layers of non-Arctic cases (1, 2, E88-61, E88-64 and KH871-JT), up to  $-1.5^\circ\text{C}$  close to the surface;
  - the differences between the TEOS10 standard values of  $\theta_\eta$  and those for both  $\theta$  or  $\Theta$  remain small at all depths for the Arctic cases (1, 2 and SCICEX-96-43), with differences of less than  $0.2^\circ\text{C}$ ;
  - the values of the absolute seawater entropy temperature  $\theta_\eta$  are larger than all other values for  $T$ ,  $\theta$ ,  $\Theta$  and  $\theta_\eta$  (std.) for the upper layers of the Arctic cases (1, 2 and SCICEX-96-43, between the surface and the depth of 200 dbar), with differences reaching  $+0.8^\circ\text{C}$  to  $+1^\circ\text{C}$  close to the surface.
- 

We can therefore see that the absolute seawater entropy temperature  $\theta_\eta$ , like the absolute seawater entropy, exhibits special behaviours and properties that are different from those of all other variables  $T$ ,  $\theta$  and  $\Theta$ .

However, these differences remain small and consistent enough with an important and peculiar impact of gradients in salinity (in particular close to the surface and with almost unchanged deep layers properties) that we can a priori comply with the requirements given by Richardson (1919a,b, 1921, 1922), who explained that we should use the absolute entropy as the thermal variable on which turbulent and mixing processes should be applied.

These considerations must be able to be taken into account via the current oceanic turbulent double-diffusion formalisms, but based on the absolute seawater entropy variable  $\theta_\eta$  on the one hand, and on the absolute salinity  $S_A$  on the other, with likely a ratio of the corresponding exchange coefficients  $K_\eta/K_s \neq 1$  for the seawater (namely likely as in the Fig. 41, and in a way similar to the Lewis number  $\neq 1$  for the atmosphere shown in the Figs. 36 to 40).

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## 12.10 Validations and physical meaning of absolute entropies / Non-linearities?

A reviewer seems to have questioned my ability to have thoroughly investigated how non-linear aspects might prevent the proper consideration of reference values for the entropies of liquid water and sea salts, and thus may prevent the absolute definition of the entropy of seawater :

*“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.”*

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- In fact, I have followed a scientific methodology, and my approach did not rely on the sole comparison between Millero’s and TEOS10’ fits, and I know the motivations and origins of the hypotheses concerning the thermodynamics of electrolytes used to establish the formulation in TEOS10, and 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  $a_2 + a_4 S$  in TEOS10's documents and since Fofonoff (1962).

- I have recalled in my last 2025 paper that, for TEOS10:

*“The specific free enthalpy  $g = G/m$  (with  $m = 1$  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*

$$g = (1 - C) \times \mu_w^0(T, P) + C \times \mu_s^0(T, P) + \sum_a \frac{X_a}{M_s} R T C \ln \left[ X_a \frac{C}{1 - C} \frac{M_w}{M_s} \right] - \frac{[\sum_a N_a Z_a^2 e^2 / D(T, P)]^{3/2}}{\sqrt{36 \pi \nu(T, P) k T N_w}}. \quad (287)$$

where:  $C = 1.00488 S = S_A/1000$  is the sea-salts concentration (...)

This relationship (287) is indeed another way to write the Eq. (4.9) of Feistel and Hagen (1995, p.266), as shown in the Fig. 45.

- 
- This Eq. (4.9) is at the basis of the other Eq. (4.10) of Feistel and Hagen (1995, p.266), written in terms of a series of:

- a constant term (pure water properties);
- a linear term depending on the salinity  $S$  (ideal solution, solvation effects);
- and other higher-order terms like  $S \ln(S)$  (ideal solution);
- and  $S\sqrt{S}$  (Debye-Hückel limiting laws), ...

Therefore, according to Feistel (1993, p.105), the salinity part of the Gibbs function is a series of the terms 1,  $S \ln(S)$ ,  $S$ ,  $S\sqrt{S}$ , ..., or equally with  $S = x^2 \times 40 \text{ g kg}^{-1}$  a series of 1,  $x^2 \ln(x)$ ,  $x^2$ ,  $x^3$ :

$$g_{sw}(S_A, t, p) = g_{sw}(x, y, z) = (g_0 + g_1 y) x^2 \ln(x) + \sum_{(i \neq 1, j, k)} g_{(i, j, k)} x^i y^j z^k, \quad (288)$$

where  $x = \sqrt{S/40 \text{ g kg}^{-1}}$ ,  $t = y \times 40^\circ\text{C}$  and  $p = z \times 100 \text{ MPa}$ .

- 
- I really 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).

In particular, I may provide the following detailed historical items I have learned and checked in the old papers and book.

- Debye and Hückel (1923a, p.185) studied the osmotic pressure  $P = f_0 P_k$ , where  $P_k$  is the classical value and  $P$  the smaller observed value due to the osmotic coefficient  $f_0 < 1$ . In fact, Debye and Hückel did not study the osmotic pressure itself, but the “freezing point depression” or “boiling point increase” instead, by assuming the same impact on them of this osmotic coefficient  $f_0$ . Debye and Hückel (1923a, p.197) arrived at the “*Theorem 1: For all electrolytes, in the limit (Grenze) for low concentrations the percentage deviations of the freezing point depression from the classical value*

Figure 45: Excerpts from the book, papers and manual by Lewis and Randall (1961), Falkenhagen and Ebeling (1971), Feistel and Hagen (1995) and Feistel and TEOS10 (2010, TEOS10) showing some of the hypotheses concerning the theories of electrolytes.

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

are proportional to the (squared) root (Wurzel) of the concentration.” This limit law (Eq. 40, p.197) was written as

$$1 - f_0 \propto \sqrt{n}, \quad (289)$$

where  $n$  is the volume concentration of the dissolved molecules. The same limit law valid for small concentrations of the electrolytes (see Eqs. 46', 48, 50 and 53, p.200 to 202) was also written as

$$\Theta = 1 - f_0 \propto \sqrt{\nu \gamma}, \quad (290)$$

with a theoretical value provided for the proportionality coefficient, where  $\gamma$  is the concentration and with  $\nu = 2$  for the binary electrolytes KCl and MgSO<sub>4</sub>,  $\nu = 3$  for K<sub>2</sub>SO<sub>4</sub>, etc

- In a second paper, Debye and Hückel (1923b, Eq. 59, p.323) studied the “*molecular conductivity*”  $\Lambda$  and defined a “*conductivity coefficient*”  $f_{\lambda}$  similarly to the earlier osmotic coefficient  $f_0$ , namely such that  $\Lambda = f_{\lambda} \Lambda_0$ , where  $\Lambda_0$  means the same quantity as  $\Lambda$  but in the vanishing concentration limit. The same (squared) root law (Wurzelgesetz) derived by Debye and Hückel (1923b, Eq. 49, p.317) was written as

$$1 - \frac{\Lambda}{\Lambda_0} = 1 - f_{\lambda} \propto \sqrt{\nu \gamma}, \quad (291)$$

$$\text{which is equivalent to } \Lambda = \Lambda_0 - \alpha \sqrt{\nu \gamma}, \quad (292)$$

with another theoretical value for the proportionality coefficient ( $\alpha$ ). These relationships (291) are only limit laws (Grenzgesetz) from which the deviations grow with increasing concentration. Therefore, Debye and Hückel (1923b, Eq. 55, p.319) have also represented  $\Lambda$  by the new, more accurate formula

$$\Lambda = \Lambda_0 - \alpha \sqrt{\nu \gamma} + \beta (\nu \gamma), \quad (293)$$

where the coefficients  $\Lambda_0$ ,  $\alpha$  and  $\beta$  must be determined from observations by the method of least squares (with still  $\nu = 2$  for KCl and  $\text{MgSO}_4$ ,  $\nu = 3$  for  $\text{K}_2\text{SO}_4$ , etc).

- In his first paper about the “*theory of electrolytes*” Onsager (1926a, Eqs. 1 and 2, p.388) recalled and studied the formulas  $g = 1 - \alpha \sqrt{c}$  for the osmotic coefficients derived by Debye and Hückel (1923a,b), who attempted to theoretically justified the empirically long known formula for the conductivity coefficients  $f_\lambda = 1 - k \sqrt{c}$ , which is valid for sufficiently diluted solutions and with the coefficients  $\alpha$  and  $k$  to be taken from the measurements themselves.
- In his second paper, Onsager (1926b, Eqs. 62, p.290 and p.293) derived and studied the same relationships as (293), but written as

$$\Lambda = \Lambda_0 - \alpha \sqrt{\mu} - \left( \frac{\Lambda_0}{k} \right) \mu \quad (294)$$

$$\text{and } \Lambda = \Lambda_0 - \alpha \sqrt{2 \gamma} + \beta (2 \gamma), \quad (295)$$

where  $\mu$  is the equivalent concentration,  $\gamma$  the molar concentration of binary electrolytes, and  $k$  the constant of dissociation. Onsager (1926b, p.290) explained that “*A certain uncertainty remains in the calculation, because the consideration of the viscosity changes with the concentration, and with the finite ion diameter and the mathematical simplifications of the calculation impacting the linear members in  $\mu$ , which can be estimated only approximately.*”

- In a next paper of Onsager (1927, Eq. 1, p.341 and p.345) about a “*revision of the conductivity theory*” he studied the same limiting formula for the molar conductivity as in (292) and the improved formula (293), but rewritten as

$$\Lambda = \Lambda_0 - \alpha \sqrt{\Gamma}, \quad (296)$$

$$\Lambda = \Lambda_0 - \alpha \sqrt{\Gamma} + \beta \Gamma, \quad (297)$$

where  $\Lambda$  is the molar conductivity and  $\Gamma$  “*twice the ionic strength.*”

- I have not found the copies of the papers by Debye and Falkenhagen (1928) and Bennewitz, Wagner and Küchler (1929) cited by several other authors...
- The two first formulas recalled in Onsager and Fuoss (1932) took into account how, “*in an electrolyte, the Coulomb forces between the ions will affect the thermodynamic and other physical properties of the system (... where ...) these effects can be calculated, because the force law is known.*” The first formula (Eq. 1.1.1, p.2689) is the same square-root Debye-Hückel’s limiting law

$$F(c) = F(0) - \alpha \sqrt{c}, \quad (298)$$

where the term  $-\alpha \sqrt{c}$  represents “*the influence of the ionic forces,*”  $F(0)$  and  $\alpha$  “*are two constants*” and  $F(c)$  “*stands for any one of the usual molecular properties (freezing-point depression, conductance, viscosity, etc)*” expressed in terms of the concentration  $c$ . Other “more exact computations (...) would (...) lead to expressions of the type” (Eq. 1.1.2, p.2689)

$$F(c) = F(0) - \alpha \sqrt{c} + \gamma c + \beta c \ln(c) + \dots, \quad (299)$$

where a new term proportional to “ $c \ln(c)$ ” appears in addition to the known squared-root and linear terms. Onsager and Fuoss (1932, p.295) were interested in formulating “*the most general*

*description of the laws of diffusion (and conduction) in a multi-component systems. The theory of electrolytes furnishes a good example in that all the terms in the phenomenological equations are important.*” Then Onsager and Fuoss (1932, p.295) explained that they “*shall only be concerned with the formulation of the differential equations (...) and make no attempt to integrate them for any practical case.*”

- In the summary section of Fuoss and Onsager (1957) they explained that in their paper “*the conductance equation is obtained (...) with retention of higher order terms (...) which has the limiting form*”

$$\Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) \sqrt{c} + D c \ln(c) + (J_1 c - J_2 c \sqrt{c}) (1 - \alpha \sqrt{c}) , \quad (300)$$

“*in which the constants  $J_1$  and  $J_2$  are explicit functions of the ion size,  $\Lambda_0$  and properties of the solvent;  $D$  is independent of ion size.*” When the last product term of (300) is developed, the linear and higher order non-linear terms appear in the form

$$\Lambda = \Lambda_0 + D c \ln(c) - (\alpha \Lambda_0 + \beta) c^{1/2} + J_1 c - (\alpha J_1 + J_2) c^{3/2} + \alpha J_2 c^2 , \quad (301)$$

made of the constant term  $\Lambda_0$ , the mixed term  $c \ln(c)$  and the start of a power series of  $c^{1/2}$ . This more general formula (301) for  $\Lambda$  did not explicitly appear as such in the paper, but we can find many approximation of it:

$$\text{(Eq. 1, p.668)} \quad \Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) \sqrt{c} , \quad (302)$$

$$\text{(Eqs. 7.7 and 7.7', p.675)} \quad \Lambda = \Lambda_0 - (\alpha \Lambda_0 + \beta) \sqrt{c} + (B_1 \Lambda_0 + B_2) c , \quad (303)$$

$$\text{(Eq. 8.3, p.676)} \quad \Lambda''' (\approx \Lambda_0) = \Lambda'' - (J_1 c - J_2 c^{3/2}) , \quad (304)$$

$$\text{(Eq. 8.4, p.676)} \quad \Lambda'' (1 - \alpha c^{1/2}) = \Lambda + \beta c^{1/2} - (\alpha' \Lambda_0 - \beta') c \ln(c) . \quad (305)$$

Note that the more general formula (300) is obtained with  $\Lambda$  given by (305) and  $\Lambda''$  given by (304), leading to  $D = \alpha' \Lambda_0 - \beta'$ .

- In the summary section of Fuoss et al. (1965) it is explained that “*Using the potential of total directed force on charged spheres moving in a continuum under an external field and correcting for electrophoresis, the conductance equation*

$$\Lambda = \Lambda_0 + (E' c) \ln(6 E'_1 c) - S c^{1/2} + (L - A f^2 \Lambda_0) c , \quad (306)$$

*is derived*” with theoretical relationships for the constants  $E'$ ,  $E'_1$ ,  $S$ ,  $L$ ,  $A$  and  $f^2$  computed in terms of the observed known values  $D$ ,  $T$ ,  $\gamma$ ,  $N$ ,  $a$  and  $\eta$  depending on the thermodynamic properties of the electrolyte solution. The formula for the “*conductance of symmetrical electrolytes (...) using the model of rigid charged spheres in a hydrodynamic and electrostatic continuum*” is then recalled in Fuoss et al. (1965, Eq. 1, p.2581):

$$\Lambda = \Lambda_0 + (E c) \ln(c) - S c^{1/2} + J c . \quad (307)$$

Note that the concentration  $c$  is replaced by  $\gamma c$  to derived Eq. 4a, p.2583 of Fuoss et al. (1965) “*For solvents of lower dielectric constant (...) ad hoc hypothesis that pairs of oppositely charged ions in contact, in concentrations determined by the dielectric constant and the stoichiometric concentration, would not contribute to (d.c.) transport of charge*” leading to

$$\Lambda = \Lambda_0 + E (c \gamma) \ln(c \gamma) - S (c \gamma)^{1/2} + (J - K_A f^2 \Lambda) (c \gamma) , \quad (308)$$

where  $\gamma = \Lambda/\Lambda_i$  is “*the Arrhenius hypothesis*” ( $\Lambda_i$  is “*the conductance of the free ions*”) and if “*the concentration of ion pairs is given by the mass action equation*”  $1 - \gamma = K_A f^2 c \gamma^2$ . Fuoss et al. (1965, p.2583) recalled that “*It was found that (308) reproduced experimental data for solutions in both aqueous and nonaqueous mixtures of solvents for all the 1-1 electrolytes.*”

- Fuoss and Hsia (1967, Eqs. 2 and 3, p.1550) considered the same type as (306) for the “*linearized conductance equation for unassociated (or slightly associated) salts*”

$$\Lambda = \Lambda_0 + E' c \ln(c) - S c^{1/2} + (J - K_A \Lambda_0) c. \quad (309)$$

However, Fuoss and Hsia (1967, Eq. 4, p.1551) recalled that “*Consideration of a large number of recent data of high precision ( $\pm 0.02\%$ ) for several alkali halides in water showed that the experimental data could be reproduced within the experimental error by a semi-empirical equation of the form*”

$$\Lambda = \Lambda_0 + E c \ln(c) - S c^{1/2} + A c + B c^{3/2}, \quad (310)$$

“*where  $E$  and  $S$  are given by theory.*” (namely like in (301) but without the last term proportional to  $c^2$ ). Then, according to Fuoss and Hsia (1967, p.1551) “*A test of equation (310) is shown in Figure 1. Conductance data for potassium chloride, cesium iodide, sodium chloride, and cesium bromide were analyzed by a least-squares procedure to obtain the corresponding values of  $\Lambda_0$ ,  $A$ , and  $B$ . Then the quantity*”

$$Y = \frac{[\Lambda(\text{obs}) - \Lambda_0 - E c \ln(c) + S c^{1/2}]}{c}, \quad (311)$$

“*was plotted against square root of concentration. The resulting plots are linear as required by equation (310) (namely it should be equal to  $A + B c^{1/2}$ ). The solid circles represent Shedlovsky’s earlier results for potassium and sodium chlorides; perfect agreement appears.*”

- Barthel (1968, Eq. 13, p.257) considered the same Fuoss-Onsager-Hsia’s relationship as (310) or (301), but without the last quadric term, to describe the “*conductivity of fully dissociated electrolytes,*” but written as

$$\Lambda(c) = \Lambda_0 + E c \ln(c) - S c^{1/2} + J_1 c - J_2 c^{3/2}, \quad (312)$$

where  $E'$  and  $S$  are given by the theory, and  $J_1$  and  $J_2$  are to be determined experimentally. The check of the validity of the simplified version (Eq. 46, p.262, without the term  $c^{3/2}$ ) of (312)

$$\Lambda(c) \approx \Lambda_0 + E c \ln(c) - S c^{1/2} + J_1 c \quad (313)$$

(with  $E = 0.4343 E'$ ), is shown in the Fig. 5 of Barthel (1968, p.262) where

$$\Lambda_1(c) = \Lambda - E' c \ln(c) + S c^{1/2} (\approx \Lambda_0 + J_1 c?) \quad (314)$$

This quantity  $\Lambda_1(c)$  is therefore plotted against  $c$ , the concentration, to test the expected linear relations  $\Lambda_0 + J_1 c$  for the electrolytes of  $\text{CsOCH}_3$  and  $\text{CH}_3\text{OH}$ , with the linear law validated in the Fig. 5 of Barthel (1968, p.262). Note that this test is made only for very small concentrations ( $c < 0.0013 \text{ mol l}^{-1}$ ), whereas the previous test was conducted up to  $c \approx 0.12$ , this likely explaining the need of the extra term proportional to  $c^{3/2}$  if “ $c \times \Lambda(c)$ ” deduced from (311) can indeed be represented by  $c \times (A + B c^{1/2}) = A c + B c^{3/2}$ .

- Justice (1975, Eq. 20, p.456) considered about the same formula as (312), but where (p.455) “ *$c$  must be replaced by  $c\gamma$* ” leading to the same type of relationship as (308):

$$\Lambda(c) = \gamma \left[ \Lambda_\infty + E (c\gamma) \ln(c\gamma) - S (c\gamma)^{1/2} + J (c\gamma) + J_{3/2} (c\gamma)^{3/2} + O(c^2) \right]. \quad (315)$$

- Then I may describe some of the results published by Reiner Feistel about electrolytes and prior to his paper Feistel (1993).
- In the paper by Ebeling, Feistel, Kelbg and Sändig (Ebeling et al., 1978, Eqs. 1 and 4, p.11 and 13), they recalled and studied the formulas

$$\text{(Eq. 1, p.11)} \quad \Lambda = \Lambda_0 - S c^{1/2}, \quad (316)$$

$$\text{and (Eq. 4, p.13)} \quad \Lambda = \Lambda_0 - S c^{1/2} + E c \ln(c) + B c + D c^{3/2}, \quad (317)$$

where “*the constants  $B$  and  $D$  are rather complicated functions of the potential parameter (...)*” whereas  $S$  and  $E$  may be known from theoretical arguments. As an example, Ebeling et al. (1978, p.13) recalled the following values for “*binary symmetrical electrolytes*”

$$S = \frac{\kappa l}{\sqrt{c}} \left[ \frac{\Lambda_0}{3(2 + \sqrt{2})} + 8H \right] \quad \text{and} \quad E = \frac{(\kappa l)^2}{2c} \left[ \frac{\Lambda_0}{12} - H \right], \quad (318)$$

where “*the coefficients  $l$ ,  $\kappa$  and  $H$  are defined as follows*”

$$l = \frac{z_1 z_2 e^2}{D_0 k_B T}, \quad \kappa^2 = \frac{4\pi N_A e^2}{1000 D_0 k_B T} (\nu_1 z_1^2 + \nu_2 z_2^2) c \quad \text{and} \quad H = \frac{D_0 k_B T N_A \delta}{24\pi \eta_0} \quad (319)$$

from the basic constants:  $N_A$  the Avogadro’s number;  $k_B$  the Boltzmann number;  $D_0$  the dielectric constant of the pure solvent;  $\eta_0$  the viscosity of the pure solvent;  $T$  the absolute temperature;  $e = 4.80223 \cdot 10^{-9}$  esu the charge of the ion; and  $\delta = 10^9/(c_L)^2 \approx (1/9) \cdot 10^{-7} \text{ s m}^{-1} \Omega^{-1}$  with  $c_L$  the speed of light in the vacuum. As for  $\nu_i, i = (1, 2)$  they are the numbers of moles of ions formed from one mole of the electrolyte.

All the results presented by (Ebeling et al., 1978, p.13-14) “*were obtained in the framework of the semi-phenomenological theory. In the pure statistical theory corrections are to be expected.*”

- The aim of Feistel (1978) was to discuss the relationship for  $E$  in (318) for 1-1-valent strong electrolytes, with (317) rewritten as

$$\text{and (Eq. 4, p.13)} \quad \Lambda = \Lambda_0 - S c^{1/2} + E c \ln(c) + F c + J c^{3/2} + \dots \quad (320)$$

In some papers

$$E = \frac{(\kappa l)^2}{2c} \left[ \frac{\Lambda_0}{12} - H \right] \quad \text{is replaced by} \quad E = \frac{(\kappa l)^2}{2c} \left[ \frac{\Lambda_0}{12} - \textcolor{red}{2} H \right], \quad (321)$$

but Feistel (1978, Eq. 18, p.371) arrived at the new formula

$$E = \frac{(\kappa l)^2}{2c} \left[ \frac{\Lambda_0}{12} - \textcolor{red}{\frac{3}{2}} H \right], \quad (322)$$

with “*the new value of  $E$ , e.g. for KCl in water at 25°C, is about 20 % less than the old one. This deviation becomes greater of course for salts with small limiting conductivity.*”

- The new factor 3/2 in (321) is confirmed in the next paper by Ebeling, Feistel and Sändig (Ebeling et al., 1979). However, they explained (p.68) that: “*numerically the influence of the new correction terms due to hydrodynamic interactions is not very strong. For example, the influence of the correction terms on the conductivity  $(\Lambda - \Lambda_0)$  of KCl at 25°C is less than 2 %. Therefore in the following comparison with experimental data the correction term (...) will be neglected*” (namely 3/2 versus 1 or 2).
- Sändig and Feistel (1979, p.411) recalled that, in

$$\Lambda = \Lambda_0 - S c^{1/2} + E c \ln(c) + B c + \dots, \quad (323)$$

“*the coefficients  $S$  and  $E$  result only from the long-range Coulombic and hydrodynamic interactions between the ions*” whereas “*the short-range interactions influence  $B$  and the coefficients following.*” Sändig and Feistel (1979, p.412) explained that “*the "traditional" value for  $E$  appears to be incorrect. The first correction was found by Chen and Onsager (1977) and Chen (1977)* (namely like in (321) with the factor 2). *Later, Feistel (1978) derived a new value for  $E$  different from that of Chen (1977)*” (namely like in (322) with the factor 3/2). Sändig and Feistel (1979, p.424) arrived at the same result, with the coefficient 3/2 “*in the case of symmetrical electrolytes.*”

- But what is the link between the sea-water Gibbs energy function  $g_{sw}(S, t, p)$  and the osmotic pressure  $P = f_0 P_k$  and osmotic coefficient  $f_0$ , with the first limit law (289) with  $1 - f_0 \propto \sqrt{c}$  derived by Debye and Hückel (1923a, p.185) in terms of the concentration  $c$  playing the role of the salinity  $S$  for the sea water? And what is the link between  $g_{sw}(c = S_A, t, p)$  and the more and more general laws for the conductance  $\Lambda$  derived by Onsager and Fuoss (1932) including in (299) new terms in  $c$  and  $c \ln(c)$ ? And then by Fuoss and Onsager (1957) including in (301) new terms in  $c^{3/2}$  and  $c^2$ ?
- Debye and Hückel (1923a, p.185) suggested that this limit law proportional to  $\sqrt{c}$  should be equally valid for the freezing point depression or the boiling point increase. However, Feistel (1993, p.105) explained that “ (...) *from statistical thermodynamics (?) we know that for any electrolyte the series expansion of  $g_{sw}(S)$  does not contain terms  $\sqrt{S}$ .*” (...) and that “*Lowest powers in the series expansion with respect to ion concentration are 1 (pure water properties),  $S \ln(S)$  (ideal solution),  $S$  (ideal solution, solvation effects) and  $S \sqrt{S}$  (Debye-Hückel limiting laws).*”

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• Therefore, I think 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. This is not the case, and 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. 45).

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• Similarly, the non-ideal features for the liquid-water and water-vapour thermodynamic states can be fully taken into account, as done via non-linear terms in the two SIA and GSW parts of the TEOS10 software.

And in the end, there remain the reference values for the entropy of pure water, the absolute value of which can be easily determined and imposed in accordance with the third law of thermodynamics.

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## 12.11 Validations and physical meaning of absolute entropies / Observables?

• Several referees and opponents to my studies of the moist-air and seawater absolute entropy explained to me that no physical meaning should exist for such absolute entropies (versus other definitions of moist-air and seawater entropy), not only because there exist no “*entropy thermometers*” and thus I cannot prove that the absolute version could be more realistic than the conventional other versions (see the Section 12.7), or in other words because the absolute entropy is not an “*observable quantity*” and thus cannot acquire a physical meaning.

---

• For the ocean, it is true that most “*observable seawater quantities*” do not depend on reference values of pure-water and sea-salts entropy (specific volumes, heat capacities, expansion coefficients, sound speeds, osmotic pressure, etc) provided in the output of TEOS10.

However, as a first answer to the criticisms of referees and opponents, the absolute-entropy reference values impact at least the seawater entropy itself, which deserves to be precisely calculated and studied as one of the major thermodynamic state functions, this implying the use of the absolute reference entropies.

Similarly, for the moist-air atmosphere, the need to take into account the absolute values of the entropy for dry air and water vapour is mandatory for the computations of the moist-air entropy function itself (or the related potential temperature  $\theta_s$ ).

Indeed, since the difference in entropy between two points of a state function (like the entropy) must have a unique value, because the value of a state function at a given point must be entirely determined by the local state variables like the temperature, pressure, and concentrations of the minor constituents (water vapour for the atmosphere and sea-salts for the oceans), the value of the moist-air and seawater entropies cannot be left undetermined up to functions of the water-vapour or sea-salt contents for variables values of the water vapour and sea-salt contents. This means that there is no other possibility than the use of the absolute values of the moist-air and seawater entropies, with the absolute values of the entropies of all moist-air and seawater components given in all thermodynamic Tables.

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- As another answer to these criticisms, I would like to recall that we can recognize here the same issue that Marcelin Berthelot and his followers (in particular Henry Le Chatelier) insisted that the laws of chemistry should be based exclusively on observational facts at the macroscopic scale (i.e. that of the laboratory). Following this principle, they criticized the fact that atoms were not observable, and therefore atoms should not exist... It is probably useful to reread, in this regard, what Max Planck (1932, p.170-200) wrote in the chapter VI entitled “*From the relative to the absolute*” and about atomic weights, energies and the entropy concepts.

Fortunately, not everyone followed Berthelot’s principle of “*observable quantities*” and others had a premonition of the atomic nature of matter, as well as the atomic composition of molecules and their weights, which were deduced well before Jean Perrin’s proof of this atomic nature of matter.

The same applies to what I consider to be an overly restrictive requirement that “*absolute entropy should be an objective fact which can be perceived by our senses*” (such as the temperature and the sensations of hot and cold).

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- It is also possible to answer to these criticisms by recalling the results shown in the Section 12.1, with the relationship (171) allowing the computation of the theoretical Sackur-Tetrode absolute entropy constant  $i_0$  from measurements or knowledge of the saturation pressure  $p_s$ , the absolute temperature  $T$ , the latent heat of change of phase  $\lambda_0$  and the molar mass, via:

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

I show in the Fig. 28 that Nernst (1918), Nernst (1923) and Nernst (1926) 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  $C_0 \approx -1.62 \pm 0.03$ . This validation was obtained for  $C = C_0 + 1.5 \ln(M)$  depending on the molar mass for:

- dihydrogen ( $H_2$ , with  $M \approx 2$ );
- Mercury ( $Hg$ , with  $M \approx 40$ ); and
- Argon ( $Ar$ , with  $M \approx 200$ ).

I think that these validation clearly show that the theoretical Sackur-Tetrode absolute entropy constant  $i_0$  can be measured from the local physical properties  $p_s$ ,  $\lambda_0$ ,  $T$  and  $M$ .

---

- Another way so show that the absolute entropies has a physical meaning is given in the Section 12.3, where I recall that the “difference in third-law entropies”

$$\delta\eta(T_0, p_0) = \eta_{v/3rd}^{stat.}(T_0, p_0) - \eta_{i/3rd}^{calor.}[T_0, p_{sat}(T_0)] \approx 8023 \pm 2.5 \text{ J K}^{-1} \text{ kg}^{-1} ,$$



computed for a system of saturation water vapour at  $T_0 = 273.15$  K and  $p_0 = 1000$  hPa obtained via a sublimation of ice-Ih, is related to the latent heat of sublimation  $L_s(T_0)$  and the saturation pressure  $p_{\text{sat}}(T_0)$  via the relationships (191) and (192).

This means that  $L_s(T_0)$  and  $p_{\text{sat}}(T_0)$  are not independent variables, since they are linked through the difference  $\delta\eta(T_0, p_0)$  and the two way to compute the absolute entropies:

- the third-law statistical-quantum entropy  $\eta_{v/3\text{rd}}^{\text{stat.}}(T_0, p_0) \approx 10318 \pm 0.63 \text{ J K}^{-1} \text{ kg}^{-1}$  for water vapour at  $0^\circ\text{C}$  and  $1000\text{hPa}$ , computed with the relationship  $\eta = k \ln(W)$  represented by the blue arrow and path up to the blue disk in the Fig. 30(b), and with  $W$  corresponding to the translational, rotational and vibrational degrees of freedom of the 3D molecule  $\text{H}_2\text{O}$ ;
- the absolute calorimetric entropy  $\eta_{i/3\text{rd}}^{\text{calor.}}(T_0) \approx 2295 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$  for  $\text{H}_2\text{O}$  ice-Ih at  $0^\circ\text{C}$  computed with via the relationship  $\eta_0 + \int_0^T c_p(T') d\ln(T')$  represented by the red arrow and path up to the red disk in the Fig. 30(b), with the values of  $c_p(T)$  plotted in the Fig. 30(a) and where  $\eta_0 \approx 189 \text{ J K}^{-1} \text{ kg}^{-1}$  is the Pauling-Nagle residual entropy at  $0^\circ\text{K}$ .

Said differently, the relationship (190)

$$\eta_{v/3\text{rd}}^{\text{calor.}}(T_0, p_0) = \eta_{i/3\text{rd}}^{\text{calor.}}[T_0, p_{\text{sat}}(T_0)] + \frac{L_s(T_0)}{T_0} - R_v \ln \left[ \frac{p_0}{p_{\text{sat}}(T_0)} \right]$$

allow the comparison of the calorimetric values I have computed in the Section 5.5

$$\eta_{v/3\text{rd}}^{\text{calor.}}(T_0, p_0) \approx 10320 \pm 13 \text{ J K}^{-1} \text{ kg}^{-1}$$

from the other variables in the right-hand-side of (190), and this calorimetric value is almost the same than the third-law statistical-quantum value I have computed in the Section 4.6, which depends on the same constant  $i_0$  previously validated (see Nernst, 1918, 1923, 1926):

$$\eta_{v/3\text{rd}}^{\text{stat.}}(T_0, p_0) \approx 10318 \pm 0.63 \text{ J K}^{-1} \text{ kg}^{-1}$$

This means that this absolute statistical entropy for water vapour can be either computed from calorimetric datasets or predicted by the quantum-statistical theory. This corresponds to all what is needed for validating the physical meaning of the water absolute entropy, and the same is true for the absolute value of all other atoms and molecules like  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{CO}_2$ , and thus the dry-air, as shown in the Sections 3 and 4.

---

• Another physical consequence of the third-law absolute entropy principle is the “*principle of unattainability of the absolute zero of temperature (Prinzip von der Unerreichbarkeit des absoluten Nullpunktes)*” first put forward by Nernst (1912), and then studied by Simon (1927), in particular.

I recalled in the Fig. 46 (published in Marquet, 2019c, Fig. 3) that if the third law of thermodynamic were nor valid, i.e. if  $S_{01} \neq S_{02}$  in (a), then it would be possible to reach the 0 K limit by a finite-steps sequence of processes involving changes in an internal state  $X$  of the system (for instance the magnetization state).

Differently, the third law defined in (b) by Planck (1911, 1914, 1917) prevents this possibility to reach the 0 K limit, by setting the entropy of the more stable solid state to a universal value (say  $S_0$ ) close to 0 K, a value independent of the substances and of the internal parameters  $X$  (in fact independent of everything), with therefore the third-law valuable possibility to set to 0 this absolute universal value  $S_0$ , without loss of generality.

Therefore, the third law of thermodynamics implies the principle of “*unattainability of absolute zero*” (even if the reverse may not be true), and this unattainability principle provides to the third law of

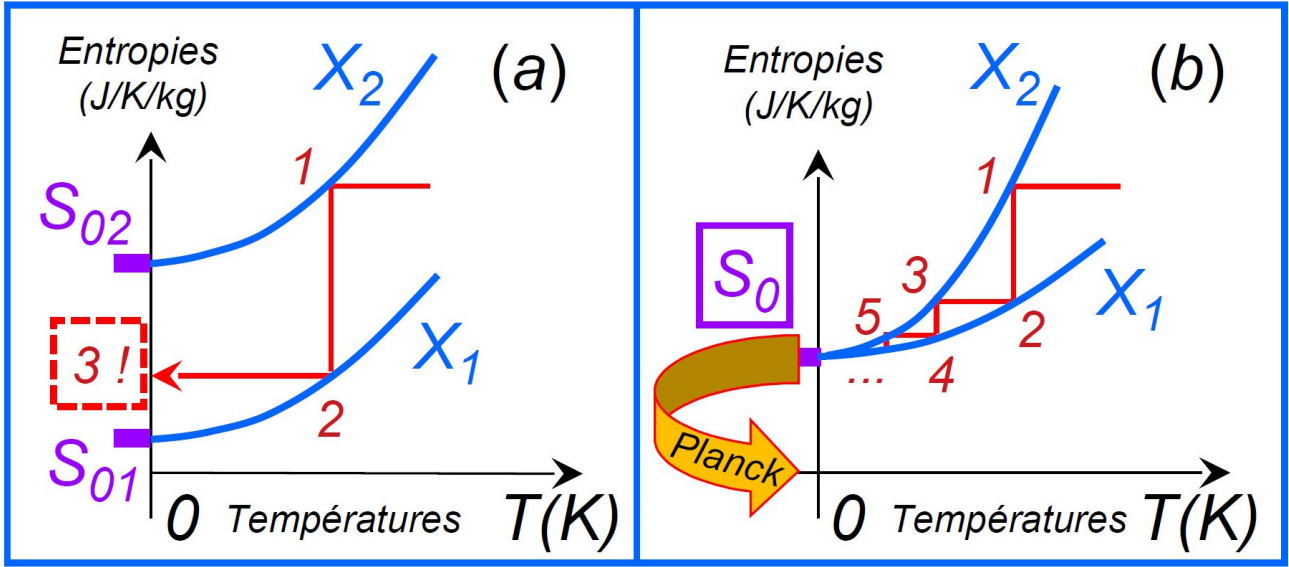


Figure 46: The entropy curves ( $S$ ) are plotted as ordinates as a function of the absolute temperature ( $T$ ) as abscissa. The aim is to provide a graphical illustration of the principle of “unattainability of absolute zero” as expressed by Nernst (1912), and then studied by Simon (1927). This principle means that  $S_{01} = S_{02}$  in (a). Then, Planck (1917) postulated that this common value is a universal value  $S_0$  like in (b) for the more stable solid state of all species at  $T = 0$  K. The next contribution of Planck (1917) was to postulate a zero entropy  $S_0 = 0$  for  $T = 0$  K for all species, without loss of generality (the yellow arrow).

thermodynamics a clear physical justification and meaning, just like the absolute temperature scale for which lord Kelvin considered the 0 K as: “(...) a point which cannot be reached at any finite temperature, however low.”

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- I show in the Section 12.9 that the exchange coefficients  $K_s(\theta_s)$  computed as required by Richardson (1919a,b, 1921, 1922) with the absolute third-law moist-air entropy  $s = c_{pd} \ln(\theta_s) + C_{ste}$  are more relevant than those  $K_h(\theta_l)$  presently computed in the GCM and NWP models with the Betts (1973) variable  $\theta_l$  (or proxies of it), therefore with the water-vapour and dry-air values of the reference entropies arbitrary cancelled.

The fact that  $K_h(\theta_l)$  has negative or even infinite values for different LESs like BOMEX, RICO, and ARM-Cu has a physical meaning that should discredit the use of  $\theta_l$  as a turbulent variable. But then, why bother continuing to use this arbitrarily defined Betts’ variable? And why not consider the only other variable  $\theta_s$  consistent with the third law of thermodynamics, as a proxy of the absolute moist-air entropy  $s = c_{pd} \ln(\theta_s) + C_{ste}$ , which above all has the clear physical property that the exchange coefficient  $K_s(\theta_s)$  is positive?

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## 12.12 Validations and physical meaning of absolute entropies / Residual values?

- The discovery of existing residual entropy for some crystals at 0 K is not a failure of the third law of thermodynamics. It is on the contrary a great success and a validation of the theoretical derivation of the Sackur-Tetrode formula, with an explanation of the discrepancy between the theoretical and observed absolute values of the entropies.

Pauling (1935) explained that: “(...) *phenomenon of rotation of molecules in crystals was found to be not uncommon. The entropy values of carbon monoxide (CO) and nitrous oxide (N<sub>2</sub>O) show that in crystals of these substances the molecules are not uniquely oriented, but have instead a choice between two orientations, presumably the opposed orientations CO and OC or NNO and ONN along fixed axes.*”

Moreover Pauling (1935) explained that: “(...) *the observed entropy of ice at low temperatures provides strong support for a particular structure of (H<sub>2</sub>O) ice, and thus gives an answer to a question which has been extensively discussed during the past few years.*”

---

Indeed, for the entropy of water vapor (steam) at  $T_0 = 298.15$  K and  $p_0 = 1$  atm (in E.U. units of cal K<sup>-1</sup> mol<sup>-1</sup> with  $R \approx 1.9872$  E.U.):

- Giauque and Ashley (1933) computed the value 44.23 E.U. from thermal data and the calorimetric method  $S(T_0, p_0) = \int_0^{T_0} c_p(T) d\ln(T) + \sum_k L(T_k)/T_k - R \ln(p_0/p_{sat})$ ;
- Gordon (1934) computed the value 45.101 E.U. by using the spectroscopic method  $S = k \ln(W)$  with the impacts of the translational Sackur-Tetrode plus other rotational and vibrational degrees of freedom;
- Pauling (1935) explained the difference of about 0.87 E.U. by the impacts  $R \ln(3/2) \approx 0.805$  E.U. of the hydrogen bonds of the H<sub>2</sub>O molecules previously computed by Latimer and Rodebusch (1920);
- Nagle (1966) updated this impact of hydrogen bounds with the more accurate value of about  $R \ln(1.50685 \pm 0.00015) \approx 0.8145 \pm 0.0002$  E.U, which is in an even closer agreement with the difference between statistical and calorimetric values more recently evaluated to about  $0.82 \pm 0.05$  E.U. by Pauling (1960, p.468);
- Modern values recalled in the Table 2 and in the Section 3.5 show that the residual entropy of  $189.17 \pm 0.05$  J K<sup>-1</sup> kg<sup>-1</sup> or  $0.8145 \pm 0.0002$  cal K<sup>-1</sup> mol<sup>-1</sup> of Nagle (1966), with a molar mass of 18.0153 g mol<sup>-1</sup> and 4.184 J cal<sup>-1</sup>, is in full agreement with the calorimetric values (personal computations) of  $10293 \pm 13$  J K<sup>-1</sup> kg<sup>-1</sup> or  $44.319 \pm 0.06$  cal K<sup>-1</sup> mol<sup>-1</sup> and the statistical values (Chase, 1998) of  $10482 \pm 2.3$  J K<sup>-1</sup> kg<sup>-1</sup> or  $45.133 \pm 0.01$  cal K<sup>-1</sup> mol<sup>-1</sup>.

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• Despite the validations described above, Feistel (2019) recently decided to revive the debate on the physical meaning of residual entropy of ice at 0 K. More precisely, Feistel (2019, p.19) explains that:

*“There exists the hypothesis that ice Ih is metastable at temperatures below about 100 K (Johari and Jones, 1975). The stable phase of ice at the zero point is assumed to be ice XI, a proton-ordered crystal without residual entropy (Knight et al., 2006). Note that such an assumed phase transition is inconsistent with formulations of the 3rd law that claim the zero-point entropy to be not only invariant with respect to changes of density or pressure, but also against phase transitions, modifications or different states of aggregation, including metastable condensed phases if those states may exist at least (Planck, 1911, Gutzow and Schmelzer, 1995, 2013), see Appendix A. Again, by contrasting the distinct entropies, the invariance of the zero-point entropy with respect to alternative molecular configurations is assumed to be obeyed by the Clausius entropy but may be violated by the Boltzmann entropy. Various zero-point entropies for substances other than water have meanwhile be determined (Gutzow and Schmelzer, 1995, 2013).”*

• I confess I do not know if and how it would be appropriate to modify the “calorimetric” computations for H<sub>2</sub>O and for the integral  $\int_0^{100} c(T) d\ln(T)$  in the range  $0 \leq T \leq 100$  K, to include a new more stable form of ice as well as the impact of a new term  $L(T_k)/T_k$  due to the Ih/XI and/or VII/VIII phase transitions...

• Differently, I show in the Fig. 47 what Knight et al. (2006, p.12, cited by Rainer Feistel) plotted in their Fig. 13b, where it is explained that the proposal would not be to modify the Pauling value

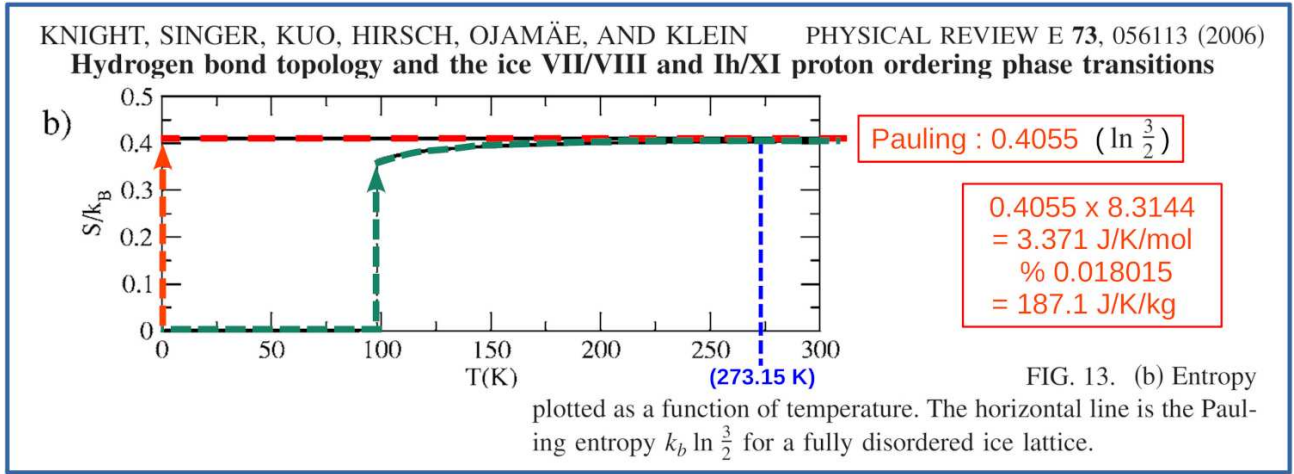


Figure 47: The Figs. 13b of Knight et al. (2006, p.12), with (in red) the inclusion of the Pauling-Nagle residual entropy at 0 K and (in green) the more progressive inclusion from 100 K to 300 K.

$\ln(1.5) \approx 0.4055$  “entropy unit” (or the next enhanced Nagle values form  $\ln(1.507) \approx 0.4101$ ,  $\ln(1.51) \approx 0.4121$  to the “observed” one  $\ln(1.540) \approx 0.4318$ ?).

In fact, the proposal would be to include more gradually the residual entropy, which only occurs at 0 K in the Pauling-Nagle version (in red), by including a change occurring mainly at 100 K (in green) and then with a small increase from 100 K to the room temperatures 273.15 K and up to 300 K. However, the two versions lead to the same value of about 0.4055 “entropy unit” suggested by Pauling-Nagle, but reached in an asymptotic way at 273.15 K (the blue line) by Knight et al. (2006).

Therefore, the version of Knight et al. (2006) recalled in the Fig. 47 leads to the same standard entropy for Ice-Ih at 273.15 K for both the “calorimetric” (or “Pauling + Clausius”  $S_P + S_C$ , in terms of the Feistel’s words) values of about  $2295.5 \text{ J K}^{-1} \text{ kg}^{-1}$  and for the “statistical-quantum physics” (or “Boltzmann”  $S_B$ , in terms of the Feistel’s words) value of about  $2293.5 \text{ J K}^{-1} \text{ kg}^{-1}$ .

This shows that it was logical and relevant to include the residual entropy at 0 K, in agreement with the value  $2296 \text{ J K}^{-1} \text{ kg}^{-1}$  suggested in Hauf and Höller (1987, p.2891), with the value  $2295.70 \pm 1.8 \text{ J K}^{-1} \text{ kg}^{-1}$  retained in Feistel and Wagner (2006, Table. 8, p.1035), and with the other value  $2293.2 \text{ J K}^{-1} \text{ kg}^{-1}$  corresponding to the value  $37.99 \text{ J K}^{-1} \text{ mol}^{-1}$  retained in the more recent entry by Atkins and de Paula (2014, Table. 2C.5, p.975) for the standard absolute entropy  $S_m^\ominus(\text{H}_2\text{O}_{(s)}) \approx 37.99 \text{ J K}^{-1} \text{ mol}^{-1}$ , and thus  $37.99/0.0180153 \approx 2108.8 \text{ J K}^{-1} \text{ kg}^{-1}$  given at 298.15 K, plus a correction of about  $-2106 \times \ln(273.15/298.15) \approx +184.4 \text{ J K}^{-1} \text{ kg}^{-1}$  to give the 0 Celcius value at 273.15 K.

Rainer Feistel’s writings are aimed solely at discrediting the third law of thermodynamics and the possibility of calculating and studying the absolute entropies of the atmosphere and the ocean.

### 12.13 Validations and physical meaning of absolute entropies / IFS model

Peter Bechtold (at ECMWF) was a referee of several of my papers and was able to quickly understand the interest of the absolute entropy variable  $\theta_s$  derived in Marquet (2011a) and studied in my next papers.

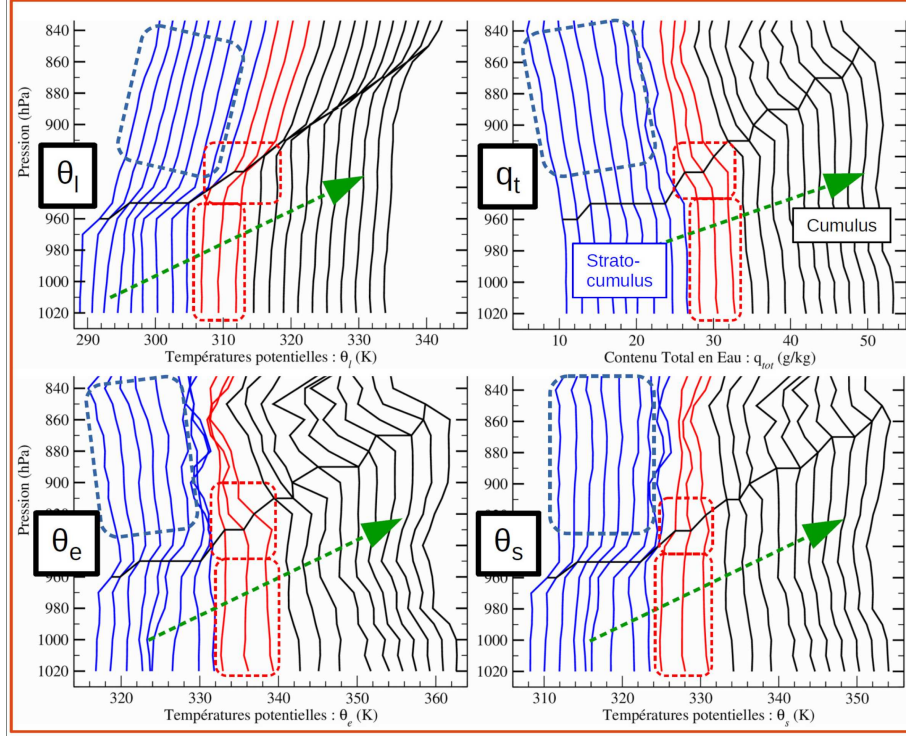


Figure 48: The Fig. 3 of Marquet (2019d). Vertical profiles corresponding to the aircraft measurements studied in Bretherton and Pincus (1995) for the “ASTEX Lagrangian” campaign (digital data available at: <https://atmos.washington.edu/~breth/astex/lagr/README.hourly.html>). The profiles for stratocumulus are in blue (to the left), those for non-precipitating cumulus are in black (to the right), with in the middle (in red) those for the transition regime. For better visibility, only half (one in two) of the 43 aircraft flight are shown, and the successive profiles are shifted by 2 K for  $\theta_l$ ,  $\theta_e$  and  $\theta_s$ , and 2 g/kg for  $q_t$ . The height of the top of the boundary layer is indicated by the broken solid line (in black) which is increasing from left to right.

I studied since Marquet (2011a,b) several “FIRE” “DYCOMS” “EPIC” “EUCLIPSE” ... vertical profiles, with the hope to use the neutral vertical profiles of  $\theta_s$  as a predictor of the threshold separating the stable versus unstable marine-stratocumulus regimes.

Peter Bechtold acted, again, as a referee of my two papers in French in the revue “La Météorologie” (Marquet, 2019c,d) where I showed the beautiful results obtained with the “ASTEX Lagrangian” campaign (see the Fig. 48).

After several discussions, Peter Bechtold found 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  $\theta_s$  absolute entropy variable (Marquet and Bechtold, 2020; Bechtold et al., 2020; Bechtold, 2021)<sup>9</sup>.

The variable  $S(K) = S_m/c_{pd}$  used by Peter Bechtold as a proxy of the first-order formulation of the absolute-entropy potential temperature variable

$$\theta_s \approx T \left( \frac{p_0}{p} \right)^\kappa \exp \left[ - \frac{L_v q_l + L_s q_i}{c_{pd} T} \right] \exp(\Lambda_r q_t)$$

I derived in 2011, with  $\Lambda_r \approx 5.87$ , is based on the Moist-Static-Energy version  $S_m$  I derived in Marquet

<sup>9</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.

(2011a, Eq. 74, p.782)

$$S(K) = \frac{S_m}{c_{pd}} \approx (1 + 5.87 q_t) T - \frac{L_v q_l + L_s q_i}{c_{pd}} + \frac{g z}{c_{pd}} .$$


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The important feature in the application found by Peter Bechtold in the IFS model corresponds to a clear physical process via the use of the EIS variable: the turbulent entrainment at the top of the boundary layer of marine stratocumulus.

Therefore, since  $S(K) = S_m/c_{pd}$  depends on

$$\Lambda_r = \frac{s_{vr}(T_r, p_{vr}) - s_{dr}(T_r, p_r - p_{vr})}{c_{pd}} \approx 5.865 \pm 0.004 ,$$

which fully depends on the two reference values of the third-law absolute entropies for water vapour ( $s_{vr}$ ) and dry air ( $s_{dr}$ ), the daily application of  $S(K) = S_m/c_{pd}$  in the IFS model must be understood as a physical meaning for the moist-air absolute entropy.

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## 12.14 Validations and physical meaning of absolute entropies / Solitary position?

It has often been said that I am alone to work on the subject of the absolute definition of the moist-air entropy.

As an example, a reviewer tried to prevent the publications of my two French papers Marquet (2019c,d) in the revue “*La Météorologie*” with the following words:

*“Marquet’s views on many aspects of atmospheric thermodynamics are often at odds with that of the rest of the community (...) the third law of thermodynamics endows  $\theta_s$  with special properties not possessed by other variables (...) this is in sharp contrast with the prevailing view in the community that the knowledge of the reference constants entering the definition of the various master thermodynamic potential such as entropy or enthalpy is not needed for the study of atmospheric (or oceanic) motions, which among other things implies that the third law of thermodynamics is irrelevant for understanding the observed properties of the atmospheric and oceanic circulations, including those linked to turbulence (...) The incompatibility between Dr. Marquet’s views and those of the rest of the community is important to stress here (...) Dr. Marquet’s interpretation is based on incorrect reasoning and premises.”*

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Differently, faced with the beautiful results I first obtained at the end of 2009 for the study of the absolute moist-air entropy with the FIRE-I campaign dataset, Jean-François Geleyn (who died in 2015) was immediately more than enthusiastic at the beginning of 2010, and I was able to carry out with him, despite his illness, several years of very fruitful work between 2010 and 2014, in a way echoing the period from 1989 to 1993 when he was able to help me during my PhD period on the subject of the definition of the exergy of moist air.

Moreover, Peter Bechtold was a reviewer and allowed the publication of most of my second set of papers in the QJRMS, where  $\theta_s$  was first defined and studied from 2011 to 2015. Peter was thus able to quickly understand the interest of this variable  $\theta_s$ , which represents the moist-air entropy and with an application found in 2020 at ECMWF in the IFS model, where the criterion used to distinguish between Sc and Cu topped boundary layers is now based on a revised version of the EIS (Estimated Inversion

Strength) with the use of a  $\theta_s$ -like variable (Marquet and Bechtold, 2020; Bechtold et al., 2020; Bechtold, 2021).

This already shows that two internationally renowned scientists understood and supported my work on the study of the absolute moist-air entropy of the atmosphere.

Unfortunately, despite all the very nice results obtained and published concerning the constancy of entropy (and  $\theta_s$ ) in the boundary layers and in the entrainment zone at the tops of marine stratocumulus, most of the reactions were: “wait-and-see” or even much more “hostile”.

Indeed, the generally accepted idea (without wanting to redo, understand nor verify my calculations published in 2011) was that the previous studies done with the potential-temperature variables  $\theta$  (dry-air),  $\theta_l$  (liquid-water) and  $\theta_e$  (equivalent) were largely sufficient and well-founded, with  $\theta_l$  and  $\theta_e$  already representing the moist-air entropy of the atmosphere, and that the third law of thermodynamics (which is used to define  $\theta_s$ ) should not have any impact on the atmosphere’s behaviour and evolution.

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Despite the astonishment of discovering the incomprehension of many about the evidently general scope of my results, and about the tenacious lack of confidence of so many in the third law to study the atmosphere (as if the question was to “believe in” it, or not...), I was nevertheless able to continue my work with the main help of Jean-François Geleyn for 4 years between 2010 and 2014, and then with the help of a few other people during my last 10 years from 2013 until my retirement in 2022:

- Etienne Blot and Patrick Santurette (applications of  $\theta_s$  for forecasters, see Blot, 2013; Marquet, 2022);
- Rachel Honnert, Xavier Lamboley, William Maurel and Guylaine Canut ( $\theta_s$ -Lewis factor in turbulence from Meteopole-Flux observations and from an LES of IHOP, see Marquet et al., 2017);
- Sophie Belamari, Yves Bouteloup, Aurore Voldoire (test to use  $\theta_s$  in the bulk oceanic scheme EC-UME, see Marquet and Belamari, 2017);
- Thibaut Dauhut (diagnostic of  $\theta_s$ -isentropic steam functions with the Hector mega-LES, see Marquet and Dauhut, 2018);
- Frédéric Ferry, Catherine Freydier, Didier Ricard, Ludovic Delannoy, Alan Demortier, Rémi Dupont, Thomas Orti (study of  $\theta_s$  in the Sting-Jet Zeus simulated with the AROME model);
- Peter Bechtold (who found an operational application of the vertical gradients of a proxy of  $\theta_s$  in the ECMWF NWP model, to improve the “criterion used to distinguish between Sc and Cu topped boundary layers” via a new version of the “EIS” for “Estimate Inversion Strength”, see Marquet and Bechtold, 2020; Bechtold et al., 2020; Bechtold, 2021, in the IFS-cy47r3 documentation, p.41-42)<sup>10</sup>;
- Peter Bechtold and Michael Mayer (to possibly understand and improve the “MSE surface fluxes” in ERA5 by using the new moist-air enthalpy formulation, see the IFS-cy47r3 documentation Bechtold, 2021, p.212-213);
- Adriana Bailey (to show that H<sub>2</sub>O-pathways follow preferentially surfaces of same values of  $\theta_s$ , namely the true moist-air isentropes, and not those of the equivalent-proxy values of  $\theta_e$ , see Marquet and Bailey, 2021);
- Antoine Hubans (to compute and compare the tendencies of a crude proxy of  $\theta_s$  in ARPEGE and IFS simulations);
- Jean-François Mahfouf, Pauline Martinet, Alina Barbu (use of  $\theta_s$  in a 1D-ENVar AROME simulation and generate more stable B-matrix, see Marquet et al., 2022);
- Bjorn Stevens (to better define and compare the three potential temperatures  $\theta_l$ ,  $\theta_e$  and  $\theta_s$ , see Marquet and Stevens, 2022).

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<sup>10</sup> 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.

## 12.15 Validations and physical meaning of absolute entropies / Wrong citations?

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— Rainer Feistel’s (2020) citations of Planck —

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Feistel and Hellmuth (2020) provided an English translation of a presentation they made at the colloquium “Climate Change & Evidence, Causes, Consequences” on 13 February 2020 at the Leibniz Society in Berlin.

Rainer Feistel stated in this presentation (p.42-43) that “*In TEOS-10, energies and entropies are defined relative to arbitrarily specified, metrologically advantageous reference states (Feistel et al., 2008; Feistel, 2018). The claim that these definitions lead to incorrect results in atmosphere models (Marquet, 2015a) and a resulting call for a related revision of TEOS-10 are, however, empirically ill-founded (Feistel, 2019). The “arbitrary additive constant [of the entropy has] no physical meaning and may be omitted at will” (Planck, 1906: p. 137). “That these additive terms, if considered absolutely, have no physical relevance at all is related to the fact that during processes in nature always exclusively differences of energy, entropy, free energy etc. between different states of a substance play a role, and that those additional terms compensate each other upon forming the differences” (Planck, 1911: p. 267). Absolute values of the entropy are available only from mathematical models of statistical thermodynamics; they cannot be determined from empirical measurements (Feistel, 2019).*”

These criticisms clearly concerned my work carried out and published since 2011, following numerous email exchanges where we were unable to understand each other Rainer Feistel and me, when I tried in vain to explain to him the possibility, the need and especially the interest of defining, calculating and studying the absolute (Third-law) values of the entropy of the atmosphere and the ocean.

I can of course admit that I could be wrong, and other arguments than those of Rainer Feistel may be right. However, it is a matter of fact that all the claims by Rainer Feistel are unfounded, because these statements are based on anachronistic sentences partly written before 1906 and before Planck could have known, and then taken into account, the heat theorem of Nernst (1906). Other parts were written by Rainer Feistel before Planck had fully taken into account consequences of this theorem. In addition, other parts have been extracted in a truncated or irrelevant manner. And finally, Rainer Feistel’s comments are not logical, as he refuses on principle to modify his calculations in the TEOS10 program, even though this is easily possible.

Indeed it is first possible to simply activate an existing commented line in the FORTRAN code of TEOS10 to compute the absolute dry-air entropy as suggested by Lemmon et al. (2000) and to modify another line to compute the absolute entropy of water species (ice-Ih, liquid and vapour), these joint modifications leading to the same moist-air entropy I have studied since 2009, published in 2011 and corresponding to the absolute moist-air entropy suggested first by Hauf and Höller (1987). It is moreover possible to make other changes to compute the absolute entropy for sea-salt water and to take into account what were already suggested by Millero and Leung (1976) and Millero (1983), a co-authors of previous Feistel papers.

Since these changes largely modify the TEOS10 results, with large differences in the numerical values of the moist-air and sea-salt entropies, Rainer Feistel cannot claim that the arbitrary choices he made –to get away from the thermodynamic absolute third-law definition of entropy– have no impact on plotting vertical profiles and vertical cross-sections, in particular.

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— Rainer Feistel’s (2020) and radiation (Planck, 1914) —

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First, Rainer Feistel and Hellmuth (2020) do not cite the English book of Planck (1914) based on the second German edition on theory of heat radiation, nor the fifth English edition of the book by Planck



(1917) on thermodynamics, based on the seventh German edition. Differently, Rainer Feistel (likely intentionally) stays with the first German edition on radiation, and he uses truncated quotes from the 1911 third German edition of Planck's book on thermodynamics. Moreover, Rainer Feistel uses only Planck's quotes that seems to support his point, these quotes being however irrelevant to the subject of variable-composition moist air, simply because Planck clearly promoted and believed in the third law of thermodynamics since he is the man who generalized the Nernst's theorem and precisely invented the concept of the third law.

Indeed, in the preface (of Nov. 1912) to the second edition of his book about "*The theory of heat radiation*" Planck (1914) describes the new features and additions (that Rainer Feistel could not take into account, since he likely intentionally only considered the first German edition unpublished in English of the Planck's book) to the first edition: "(...) *there has been added, as a further strong support of the hypothesis of quanta, the heat theorem which has been in the meantime announced by W. Nernst, and which seems to point unmistakably to the fact that, not only the processes of radiation, but also the molecular processes take place in accordance with certain elementary quanta of a definite finite magnitude. For the hypothesis of quanta as well as the heat theorem of Nernst may be reduced to the simple proposition that the thermodynamic probability (Sec. 120) of a physical state is a definite integral number, or, what amounts to the same thing, that the entropy of a state has a quite definite, positive value, which, as a minimum, becomes zero, while in contrast therewith the entropy may, according to the classical thermodynamics, decrease without limit to minus infinity. For the present, I would consider this proposition as the very quintessence of the hypothesis of quanta.*"

This already undermines Rainer Feistel's claim, since Planck described here the importance he attached to Nernst's theorem, i.e. the necessity of assuming that entropy is zero at 0 K, and that this was related to quantum theory!

In saying this, Planck (1914) was precisely going against the ideas put forward by Rainer Feistel, which are to be classified under the heading of "classical thermodynamics" where, as Olivier Pauluis et al. (2010) still maintained, "entropy could decrease to infinity at absolute zero temperatures" (what the third law prevent because it applies to solids only, and not to the gases at 0 K).

In a different way, Planck discovered and fully understood the importance of Nernst's theorem between the two editions of his book on radiation. One can even consider that Planck understood better what Nernst had discovered, in the same way that Planck was the one who best understood and applied Boltzmann's discoveries and formalism, to the point of writing the formula  $S = k_B \ln(W)$  which Boltzmann never wrote down in this way, and to the point of calculating the value of the two constants  $k_B$  and  $h$ , whereas Boltzmann had neither defined nor calculated the value of  $k_B$  (Planck himself having decided to give Boltzmann's name to  $k_B$  in honour to him).

More precisely, Planck (1914) explained (in that section 120, p.141-142, cited by him in the introduction): "*Secondly, and this is of greater consequence, Boltzmann leaves an additive constant undetermined in the entropy  $S$  [namely  $S_0$  in  $S = k \ln(W) + S_0$ ] as is done in the whole of classical thermodynamics, and accordingly there is a constant factor of proportionality, which remains undetermined in the value of the probability  $W$ .*

*In contrast with this we assign a definite absolute value to the entropy  $S$ . This is a step of fundamental importance, which can be justified only by its consequences. As we shall see later, this step leads necessarily to the "hypothesis of quanta" and moreover it also leads, as regards radiant heat, to a definite law of distribution of energy of black radiation, and, as regards heat energy of bodies, to Nernst's heat theorem. [namely to the third law of thermodynamics and to  $S_0 = 0$ ]*

*From  $S = k \ln(W) + S_0$  it follows that with the entropy  $S$  the probability  $W$  is, of course, also determined in the absolute sense."*

Here, Planck (1914) explained that the entropy of (black-body) radiation would be modified if arbitrary choices other than  $S_0 = 0$  would be made in the Planck-Boltzmann (statistical physics) formula

$S = k \ln(W) + S_0$ , because since Planck (1901) there is a need to use  $S = k \ln(W)$  to evaluate  $S$  by computing the number complexions  $W$  by using some quanta of exchange of energy, and by doing so to arrive at the Planck's formula for the black-body radiation.

I agree with Rainer Feistel that in the first German edition Planck (1906) wrote at the end of the section 134 (p.137): “*Die universelle Integrationskonstante  $k$  ist für ein ein irdisches System dieselbe wie für ein kosmisches, und wenn ihr numerischer Wert für dieses bestimmt ist, gilt et auch für jenes. Die zweite, additive, Integrationskonstante hat, weil die Entropie  $S$  eine willkürliche additive Konstante enthält, keine physikalische Bedeutung, und kann nach Belieben fortgelassen werden.* / *The universal integration constant  $k$  is the same for a terrestrial system as for a cosmic one, and if its numerical value is determined for the latter, it is also valid for the former. The second, additive, integration constant, because entropy  $S$  contains an arbitrary additive constant, has no physical meaning and can be omitted at will.*”

However, the second sentence (cited by Rainer Feistel) has been removed in the second edition, where Planck (1914) wrote instead, about the relationship  $S = k \ln(W) + S_0$ : “*The second additive constant ( $S_0$ ) of integration may, without any restriction as regards generality, be included as a constant multiplier in the quantity  $W$ , which here has not yet been completely defined, so that the equation reduces to  $S = k \ln(W)$ .*” ... before to add the sentences I have previously recalled (“... Secondly, and this is of greater consequence, ...”) where  $S$  and  $W$  are defined by Planck with the (Nernst) hypothesis  $S_0 = 0$ .

It is clear here how Rainer Feistel has chosen to discredit what I have written in all my papers about entropy (Marquet, 2011a; Marquet and Geleyn, 2013; Marquet, 2014; Marquet and Geleyn, 2015; Marquet, 2017; Marquet and Dauhut, 2018; Marquet, 2019c,d), and not solely about the thermal enthalpy (Marquet, 2015a) as wrongly cited by Rainer Feistel, by going back to a Planck's anachronistic and irrelevant sentence written from before Nernst's 1906 paper.

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— Rainer Feistel's (2020) and thermodynamics (Planck, 1917) —

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As for subject of thermodynamics, Rainer Feistel should have read the fifth English version by Planck (1917), which is likely based on the fifth (1917) German edition (and not the seventh German version by Planck, 1922). Instead, Rainer Feistel cite the third German edition of 1911, where the “*heat theorem*” of Nernst is only partly taken into account by Planck.

These are not matters of detail, but of great importance, since Planck explained in the prefaces from the third (1910) to the ninth (1930) German editions that he had added sections dealing essentially with the consequences of this theorem by Nernst (1906), in that providing an ultimate proof of the importance of the third law in the mind of Max Planck.

Preface to the third edition (Berlin, November, 1910).

“*The plan of the presentation and the arrangement of the material is maintained in the new edition. Nevertheless, there is to be found in this edition, apart from a further revision of all the numerical data, a number of explanations and additions, which, one way or another, have been suggested. These are to be found scattered throughout the whole book. (...)*

*A real extension of fundamental importance is the heat theorem, which was introduced by W. Nernst in 1906. Should this theorem, as at present appears likely, be found to hold good in all directions, then Thermodynamics will be enriched by a principle whose range, not only from the practical, but also from the theoretical point of view, cannot as yet be foreseen.*

*In order to present the true import of this new theorem in a form suitable for experimental test, it is, in my opinion, necessary to leave out of account its bearing on the atomic theory, which to-day is by no means clear. The methods, which have otherwise been adopted in this book, also depend on this point of view.*

*On the other hand, I have made the theorem, I believe, as general as possible, in order that its applications may be simple and comprehensive. Accordingly, Nernst's theorem has been extended both in form and in content. [namely that  $S = 0$  at 0 K for all solids] I mention this here as there is the possibility of the extended theorem not being confirmed, while Nernst's original theorem still be true."*

Preface to the fifth edition (Berlin, March, 1917).

*"For the fifth 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 has in the interval received abundant confirmation and may now be regarded as well established. Its atomic significance, which finds expression in the restricted relations of the quantum hypothesis, cannot, of course, be estimated in the present work."*

Preface to the sixth and seventh editions Planck (1930, p.8 and 9).

*"Among the additions to the new edition, I mention here (...) Debye's equation of state of solid bodies, which contains both the temperature dependence of the specific heat and Grüneisen's theorem for the coefficient of thermal expansion (section 285)."*

Preface to the eighth edition. Berlin-Grünwald, January 1927. Planck (1930, p.8 and 9).

*"The presentation of the thermodynamics of strongly dissociated electrolytes (section 273) has also undergone a considerable improvement, since the works of P. Debye and E. Hückel, which have appeared in the meantime, have led a significant step beyond the results achieved by Ghosh by their deeper grasp of the problem. (...) Finally, I would like to mention here as particularly noteworthy the fact that in recent times, through measurements by F. Simon, the zero point entropy of a solution (section 291) has not only been proven perfectly for the first time, but has also been found to be in marked agreement with the theory."*

Just reading these prefaces by Max Planck shows the importance that this great universal scientist brought to the Nernst's theorem and to the third law of thermodynamics he invented (as being the "extended heat theorem of Nernst"), namely to the fact that for systems of variable composition the entropy of solid bodies at 0 K is a constant and universal value, which for simplicity's sake should be set equal to zero.

It is these crucial contributions of Max Planck, added between 1911 and 1930, that Rainer Feistel strives not to take into account, choosing to quote only the anachronistic passages of the older versions of Planck's writings which go in the direction of Rainer Feistel's credo that it would be possible to define the zero of the entropies of gaseous or liquid bodies at ambient temperatures (zero Celsius), and this independently for the different species making up the atmosphere or the ocean (for the dry air, on one side, for liquid water or water vapour, on the other).

These choices made by Rainer Feistel are clearly in contradiction with the last versions of Max Planck's book on thermodynamics, as well as with the later books of Lewis and Randall (1923, 1961) on which, however, Rainer Feistel says he based his approach, whereas in these books the entropies are defined and calculated in perfect agreement with Planck's formulation.

In particular (as I recalled in the Table 3) the Table 2 (p.464) of Lewis and Randall (1923) already listed the non-zero (Third-law, absolute) "*Entropy of the elements at 25°C*" for Nitrogen, Oxygen, Argon, even if the aim of Lewis and Randall (1923) was mainly to compute the free energy  $F = U - T S$ .

In a more general way, Lewis and Randall (1961) listed the third-law entropies of all atmospheric and oceanic atoms, molecules, cations and anions, with the entire Chapter 12 (p.128-137) devoted to the subject of "*The third law of thermodynamics*" (as defined by Planck) and written as (p.130): "*If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy; but at the absolute zero of temperature the entropy may*

become zero, and does so become in the case of perfect crystalline substances. We shall see, in the later chapter, the great utility of this principle in the prediction of chemical equilibrium constants and therefore in the direction of chemical reactions.”

Lewis and Randall (1961) provided the non-zero absolute (Third-law, absolute) entropies at 25°C:

- in the Table 12.3 (p.137) for N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, ...;
- in the Tables 25-7 (p.400-401) for aqueous ions (Na<sup>+</sup>, Cl<sup>-</sup>, K<sup>+</sup>, Sr<sup>2+</sup>, Mg<sup>2+</sup>, SO<sub>4</sub><sup>-</sup>, ..., with  $S = 0$  for H<sup>+</sup>);
- in the Table 27-1 (p.421) for noble gases (Ar, ...);
- in the Tables A7-1 to A7-10 (p.671-685) for solid, liquid and gaseous elements (like NaCl, MgCl<sub>2</sub>, ...), where the standard entropy is written as  $-(F^0 - H^0)/T_0 = S^0$  in terms of the standard free energy  $F^0 = H^0 - T_0 S^0$  and enthalpy  $H^0$  given at  $T_0 = 25^\circ\text{C}$ .

Rather than engage in a sterile and undue controversy, Rainer Feistel therefore had all the elements to trust the theoretical contributions of Planck (1917) and the numerical data of Lewis and Randall (1961), and of course other more recent data such as those from NIST (Chase, 1998) as shown in the Table 3, to calculate the absolute entropy of the ocean and the atmosphere. The same is true for Olivier Pauluis (and others) for the atmosphere.

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— Rainer Feistel’s (2019) about thermodynamics (Planck, 1917) —

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Another paper previously written by Feistel (2019) aimed to discredit the idea that we can be interested in the absolute values of the entropy of the atmosphere and the ocean, and that these values resulting from the third law can have the least influence on the atmosphere and the ocean.

Feistel (2019) suggested (in the introduction p.1) that: “(...) *entropy is a quantity that may be calculated by different methods, for example experimentally from heat capacities (following Clausius) or statistically from numbers of microscopic quantum states (following Boltzmann and Planck). It had turned out that these methods do not necessarily provide mutually consistent results, and for equilibrium systems their difference was explained by introducing a residual zero-point entropy (following Pauling), apparently violating the Nernst theorem.*” (...) and that (...) “*it is suggested to consider Clausius, Boltzmann, Pauling and Shannon entropies as distinct, though related, physical quantities with different key properties, in order to avoid confusion by loosely speaking about just “entropy” while actually referring to different kinds of it. For instance, zero-point entropy exclusively belongs to Boltzmann rather than Clausius entropy, while the Nernst theorem holds rigorously for Clausius rather than Boltzmann entropy.*”

Feistel (2019) defines (p.5) the Planck’s isobaric entropy (Eq. 3) as

$$S_C(T, p) = \int_0^T \frac{C_p(T', p)}{T'} dT', \quad (324)$$

and the isochore Clausius entropy (Eq. 4) as

$$S_C(T, V) = \int_0^T \frac{C_v(T', V)}{T'} dT', \quad (325)$$

where “*For the existence of the integrals (324) and (325), it is necessary that both  $C_p$  and  $C_v$  vanish at  $T = 0$ . This is evidently not the case, however, for ideal gases with constant heat capacities, for which entropy diverges logarithmically at the zero point.*”

This is the example of remarks that make discussions obscure, since Planck himself (and then Richardson) explained that his third law only applies to solid forms and not at all to gases, leading to finite values of the absolute entropy and for which we can duly set  $S = 0$  at 0 K!

Feistel (2019) also explains (still p.5) that “*definitions formally deviating from Equation (325) may be considered elsewhere for certain reasons, such as specifying [the lower limit 0] by the triple point of water in order to reduce the uncertainty of empirical equations, or by the melting temperature of metastable, glass-like solids. Such arbitrary definitions, if deviating from Equation (325) by merely a numerical constant, do neither affect any measurable thermodynamic properties nor the physical description of natural processes.*”

Feistel (2019, p.17) further explained that: “*For clarity it should be emphasized finally again that in this paper, the Nernst theorem is identified with the 3rd law, both valid, without any known exceptions among local-equilibrium systems, for empirical thermodynamics and thermal processes, and for the Clausius entropy ( $S_C$ ). On the contrary, residual or zero-point entropy are considered here as quantities that belong to statistical thermodynamics, or Boltzmann ( $S_B = S_C + S_P$ ) and Pauling ( $S_P$ ) entropies, and do not contribute to measurable heat capacities. In the literature, however, the 3rd law, the Nernst theorem and the residual entropy are often set in mutual relations other than here.*”

It is true that I have used in all my paper the name “third-law entropy” to describe the absolute version corresponding to  $S_B = S_C + S_P$ , thus including the Pauling-Nagle residual entropy.

The scientific process would require that the different hypotheses be studied and the different versions be compared (namely  $S_B$  versus  $S_C$ ; with zero entropies set at 0 K or 0 ° C), to know if differences exist when one traces for example the vertical profiles of the different entropies in the atmosphere and the ocean, and also when the heat capacity are computed.

atmosphere and the ocean, and also when the heat capacity are computed.

For the choice of reference values I was able to find very noticeable differences when changing the zero point from 0 K or 0 ° C for both dry air and water vapour, with several recent applications founded:

- to improve the EIS in the IFS model (Marquet and Bechtold, 2020) by using the absolute entropy;
- to show that increase in CO<sub>2</sub> at Mauna-Loa modifies the dry-air absolute entropy only (Marquet, 2021);
- to show that the H<sub>2</sub>O pathways depend on these arbitrary choices (Marquet and Bailey, 2021);
- to show that B-Matrices can be better defined with the absolute moist-air entropy (Marquet et al., 2022);
- with several impacts of these arbitrary choices shown in Marquet and Stevens (2022); and
- with most of meteorological impacts studied between 2011 and 2022 described in Marquet (2022).

The fact is that Rainer Feistel (and many other influential people) refused and still refuses even the possibility of calculating the absolute entropies for the atmosphere and the ocean. This is not a constructive attitude and it has deprived the scientific community of great discoveries since 2011.

As for the “*Boltzmann entropy*” Feistel (2019) uses the same definition  $S_B = k_B \ln(W)$  derived by Planck but considers that, except for ideal gases,  $S_B$  is different from  $S_C$  and that: “*Boltzmann entropy is more relevant than Clausius entropy in the sense that statistical thermodynamics is richer than empirical thermodynamics by including also molecular information. The entropy that such systems exhibit has, of course, a statistical meaning, but not a thermodynamic one.*”

I have shown, indeed, the equality of these two versions  $S_B$  and  $S_C$  for N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub> and Ar in the Fig. 1, where the “calorimetric” method (called “Clausius” by Feistel) leads to similar results as the “statistical and quantum physics” method (called “Boltzmann” by Feistel).

This equality is valid in the Fig. 1 for H<sub>2</sub>O only if the “residual entropy” at 0 K of Pauling (1935) and Nagle (1966) is added to the “calorimetric” value. This corresponds to the addition “*perfect crystalline substances*” added by many to amend the initial definition of the Third law of Planck, and in particular in Lewis and Randall (1961, p.30), namely in the paper cited by Feistel as a basis of IAPWS and TEOS10 software. Moreover I have shown in the Table 3 that all recent (absolute) entropies for H<sub>2</sub>O include the residual entropy of  $R_* \ln(3/2) \approx 0.4055 R_*$  or 3.37 J K<sup>-1</sup> mol<sup>-1</sup> or 189 J K<sup>-1</sup> kg<sup>-1</sup> for Ice-Ih of H<sub>2</sub>O.

But again, Feistel (2019) confuses things by defining (p.10) a third kind of entropy called “*Pauling Entropy*” by him, an entropy  $S_P$  that would represent the same residual entropy as that at 0 K for Ice-Ih of  $H_2O$ , but defined for all other positive absolute temperatures and leading to his Eq. 17 and to  $S_B = S_C + S_P$ , with the difference  $S_P = S_B - S_C$  “*generalized here to be valid for arbitrary temperatures, this way defining the Pauling entropy, originally defined only at the zero point,  $S_P(T = 0) \equiv S_P^0$ .*”

Note that adding the same value  $S_P(T = 0)$  at all temperature  $T > 0$  K for Ice-Ih absolute entropy of  $H_2O$ , and then to the liquid and vapour states after adding the impact of change of state on entropy  $L_f(T_r)/T_r$  and  $L_v(T_r)/T_r$  at  $T_r = 273.15$  K, is exactly what I have plotted in the Fig. 1, with indeed the same results for the “Boltzmann-Statistical-Quantum” value  $S_B$  and the “Calorimetric-plus-Pauling” value  $S_c + S_P$ .

Note also that the agreement between the standard values of  $S_B$  and  $S_C + S_P$  is very good for all atmospheric species, including water:

- see the Table 3 for comparison with old thermodynamical Tables; and
- see the Table 1 for the computations I have made on my own in 2022.

These Tables clearly show that we can trust in the values published by Hauf and Höller (1987) and Lemmon et al. (2000) for water vapour and dry-air components, also in values of Ice-Ih and liquid-water entropies by Millero (1983) and Feistel and Wagner (2006).

So I don’t see the practical interest for the atmosphere and the ocean in Rainer Feistel’s proposal to distinguish three types of entropy, with the common values  $S_B = S_P + S_C$  already used and studied in many studies, and in particular in all those I have published since 2011 about moist-air thermodynamics and absolute values for the entropies of dry air and water vapour.

As far as I may understand the proposal of Rainer Feistel, the issue would be to discard the Pauling(-Nagle) entropy  $S_P$  because neither the Boltzmann ( $S_B = S_C + S_P$ ) nor Pauling ( $S_P$ ) entropies should “*contribute to measurable heat capacities?*”

I confess I do not understand this proposal, because statistical physics explains that all physical quantities can be computed starting from the partition function  $Z$ , with the (absolute) Boltzmann entropy  $S_B$  corresponding with  $\beta = 1/(R_* T)$  to formula like  $S_B = R_* (\ln(Z) - \beta [\partial \ln(Z)/\partial \beta]_{N,V})$  for the molar entropy (used in (25), (35) and (36) for defining the Sackur-Tetrode translational molar entropy), with the molar internal energy given by the first-order derivative  $U = -[\partial \ln(Z)/\partial \beta]_{N,V}$  and the molar specific heat given by the second-order derivative  $c_v = (\beta/T) [\partial^2 \ln(Z)/\partial \beta^2]_{N,V}$ . This means that the Pauling residual entropy for the water Ice-Ih corresponds to the constant term  $Z_P = 3/2$ , leading to the expected additional term  $R_* \ln(3/2)$  for the molar entropy, but without contribution for the internal energy  $U$  nor for the specific heat  $c_v$  (as expected by Rainer Feistel) simply because the first and second derivatives of the constant term  $\ln(Z_P)$  cancels out in the formula for  $U$  and  $c_v$ . But then: what is the problem?

I think there is no issue, nor irrelevant physical consequence for the specific heat, to consider the (absolute, third-law) molar entropy  $S_B$  derived from the Boltzmann statistical physics partition function  $Z_B$  including the Pauling part  $Z_P = 3/2 = 1.500$  for water Ice-Ih. Moreover, this residual entropy  $Z_P$  should be modified with the new values due to Nagle (1966) corresponding to the enhanced values from 1.507 for “square ice” to 1.534 for “real ice” with the in between “experimental result” of about 1.511 and the value 1.506 I have retained to get the rounded residual entropy of  $3.4049 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $189 \text{ J K}^{-1} \text{ kg}^{-1}$  for water Ice-Ih.

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Feistel (2019, p.19) also added: “*There exists the hypothesis that ice Ih is metastable at temperatures below about 100 K (Johari and Jones, 1975). The stable phase of ice at the zero point is assumed to be ice XI, a proton-ordered crystal without residual entropy (Knight et al., 2006). Note that such an assumed phase transition is inconsistent with formulations of the 3rd law that claim the zero-point*

entropy to be not only invariant with respect to changes of density or pressure, but also against phase transitions, modifications or different states of aggregation, including metastable condensed phases if those states may exist at least (Planck, 1911, Gutzow and Schmelzer, 1995, 2013), see Appendix A. Again, by contrasting the distinct entropies, the invariance of the zero-point entropy with respect to alternative molecular configurations is assumed to be obeyed by the Clausius entropy but may be violated by the Boltzmann entropy. Various zero-point entropies for substances other than water have meanwhile been determined (Gutzow and Schmelzer, 1995, 2013)."

I confess I don't know if and how it would be appropriate to modify the "calorimetric" computations for  $\text{H}_2\text{O}$  and for the integral  $\int_0^{100} c(T) d\ln(T)$  in the range  $0 \leq T \leq 100$  K, to include a new more stable form of ice as well as the impact of a new term  $L(T_k)/T_k$  due to the Ih/XI and/or VII/VIII phase transitions.

Differently, I show in the Fig. 47 (see in the Section 12.12) what Knight et al. (2006, p.12, cited by Rainer Feistel) plotted in their Fig. 13b, where it is explained that the proposal would not be to modify the Pauling value  $\ln(1.5) \approx 0.4055$  "entropy unit" (or the next enhanced Nagle values from  $\ln(1.507) \approx 0.4101$ ,  $\ln(1.51) \approx 0.4121$  to the "observed" one  $\ln(1.540) \approx 0.4318?$ ). In fact, the proposal would be to include more gradually the residual entropy, which only occurs at 0 K in the Pauling-Nagle version (in red), by including a change occurring mainly at 100 K (in green) and then with a small increase from 100 K to the room temperatures up to 300 K. However, the two versions lead to the same value of about 0.4055 "entropy unit" suggested by Pauling-Nagle, but reached in an asymptotic way at 273.15 K (the blue line) by Knight et al. (2006).

Therefore, the version of Knight et al. (2006) recalled in Fig. 47 leads to the same standard entropy for Ice-Ih at 273.15 K for both the "calorimetric" (or "Pauling + Clausius"  $S_P + S_C$ ) values of about  $2295.5 \text{ J K}^{-1} \text{ kg}^{-1}$  (see the section 3.5) and for the "statistical-quantum physics" (or "Boltzmann"  $S_B$ ) value of about  $2293.5 \text{ J K}^{-1} \text{ kg}^{-1}$ , thus including the residual entropy at 0 K and in agreement with the value  $2296 \text{ J K}^{-1} \text{ kg}^{-1}$  suggested in Hauf and Höller (1987, p.2891), the value  $2295.70 (\pm 1.8) \text{ J K}^{-1} \text{ kg}^{-1}$  retained in Feistel and Wagner (2006, Table. 8, p.1035), and the value  $2293.2 \text{ J K}^{-1} \text{ kg}^{-1}$  corresponding to the value  $37.99 \text{ J K}^{-1} \text{ mol}^{-1}$  retained in the more recent entry by Atkins and de Paula (2014, Table. 2C.5, p.975) for the standard absolute entropy  $S_m^\ominus(\text{H}_2\text{O}_{(s)}) \approx 37.99 \text{ J K}^{-1} \text{ mol}^{-1}$  and thus  $37.99/0.0180153 \approx 2108.8 \text{ J K}^{-1} \text{ kg}^{-1}$  given at 298.15 K, plus a correction of about  $-2106 \times \ln(273.15/298.15) \approx +184.4 \text{ J K}^{-1} \text{ kg}^{-1}$  to give the 0 Celcius value at 273.15 K.

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— Rainer Feistel's (2020, 2019) and thermodynamics: conclusion —

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I still do not understand Rainer Feistel's 2019-2020 (among many others) criticisms and proposals to remove the residual entropy and/or to arbitrarily modify the zero of standard entropies in atmospheric and oceanic science.

The only honest scientific attitude would be to calculate the different versions of what are called "moist-air entropy" in atmospheric science and compare them with each other, choosing numerical applications that are convincing and representative of the atmosphere. This is precisely what I have done since 2009 with most of the existing and available formulations, but on his side Rainer Feistel has always refused to calculate the absolute value of the moist-air entropy with his TEOS10 software (McDougall et al., 2010; Feistel et al., 2010b; Feistel, 2012, 2019; Feistel and Hellmuth, 2020). This forced me to make these calculations and comparisons myself, where I show large differences in the results).

I prefer to remain admiring and favour the wonderful numerical agreement of the two ways of calculating the standard entropies ( $S_B$  on the one hand,  $S_P + S_C$  on the other). Moreover, it is this common standard entropy (including the residual entropy at 0 K for water ice-Ih) that is used to describe all chemical reactions and that is measured via the study of changes with temperature of the constants of reaction  $K(T)$ . If Rainer Feistel's (and so many others) criticisms and proposals were right, this would

likely amount to modify and redefine the constants of all reactions including  $N_2$ ,  $O_2$ ,  $CO_2$  and  $H_2O$  in the atmosphere and in the ocean, and this is not possible.

To be honest, this agreement between the two “calorimetric” (called  $S_P + S_C$  by Feistel) and “statistical+quantum physics” (called  $S_B$ ) methods seems a bit mysterious and somehow “magical” to me, as nothing explicitly includes the residual entropy in the partition function for water  $Z = Q_{\text{trans.}} \times Q_{\text{rot.}} \times Q_{\text{rot./dist}} \times Q_{\text{vibr.}}$ , namely the product of only translational, rotational, distortion and vibrational parts, as shown in the subsection 4.6.

However, just because you don’t understand everything doesn’t mean you shouldn’t apply such convincing, if mysterious, results! Similarly, no one really “knows” how quantum physics works, nor why the speed of light has an absolute limit value, but our world is based on the use of radio waves, electronic devices, laser as well as GPS that use space-time corrections in the earth’s gravitational field!

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## 12.16 Validations and physical meaning of absolute entropies / General physics?

There have been several attacks against the idea that an “absolute” version of entropy can be defined for crystals, liquids, and gases. Some of these reasons concern general principles of physics which should be commented on.

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- In the last section entitled “So-called Absolute Entropies” 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 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.*

*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.

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- The words of Fofonoff (1962, p.8) were different, with an acceptance of the concept of absolute version of the entropy, although with some arbitrariness:

*“To determine the Gibbs function,  $g$ , completely –except for an arbitrary constant– we would have to know absolute values of the three first derivatives, i.e. the entropy, specific volume and chemical potential difference as functions of temperature, pressure and salinity.*

*(...) However, this cannot be done as neither entropy nor chemical potential difference is completely specified in terms of equilibrium-state properties. (...) This implies that the Gibbs function is arbitrary to the extent of a function of the form ‘ $g = aT + bTs + cs + d$ ’, where  $a, b, c$  and  $d$  are constants. Conversely, it is clear that we do not require a knowledge of this arbitrary function to describe the equilibrium state (...) entropy  $\eta = -\partial g/\partial T$ , can be determined except for a linear function of salinity.”*

- This means that the entropy  $\eta = -\partial g/\partial T$  depends on the linear function of the salinity  $-a - bs$ , and that the enthalpy  $h = g - T \partial g/\partial T$  (and thus the internal energy) depends on another linear function of the salinity  $d + cs$ .

It is true that both  $a$  and  $d$  have no impact on the enthalpy and entropy, and thus can indeed be set to any arbitrary values (for instance to 0, for sake of simplicity).

It is also true that, except for computing and studying the enthalpy and entropy functions themselves, all other derived variables [like the heat capacity  $-T \partial^2 g/\partial T^2$ , the specific volume  $\partial g/\partial p$  or the isothermal compressibility  $-(1/V) \partial^2 g/\partial p^2$ ] do not depend on the other two constants  $c$  and  $d$ . Therefore, these two constants  $c$  and  $d$  can also be set to any arbitrary values as far as only derived quantities are considered (for instance set to 0, for sake of simplicity).

However, who can believe and impose on others that it would be uninteresting to calculate the 3 fundamental thermodynamic state functions which are: the internal energy, the enthalpy and the entropy?

Differently, it should be our goal to ensure that these 3 fundamental state functions could be computed accurately and without arbitrariness. Moreover, since these 3 fundamental state functions depend on the salinity via the two terms  $b$  and  $c$ , it is needed to know in some way or another these two terms if we want to compute the changes in time or the turbulent fluxes of energy, enthalpy and entropy, with for instance the second law depending on  $d\eta/dt$  and  $\overline{w'\eta'}$ , and thus on  $-b ds/dt$  and  $-b \overline{w's'}$  which both depends on  $b$ .

This means that, depending on the sign of  $b$ , the change and fluxes of entropy could be positive (increase) or negative (decrease)? This would amount to abandoning the spirit and the letter of the Clausius principle (i.e. the possibility to compute the change in entropy within a domain and at the boundary of this domain).

Similarly, the changes in time and the turbulent fluxes of enthalpy  $dh/dt$  and  $\overline{w'h'}$ , with  $h$  depending on  $d + cs$ , depends on  $c ds/dt$  and  $c \overline{w's'}$  which both depends on  $c$ . This means that, if  $c$  could be arbitrary defined with an arbitrary sign, it would be impossible to know if the enthalpy (and thus the internal energy) increases or decreases within a domain and at the boundary of this domain.

Therefore, Fofonoff (1962) cannot say in general that the constants  $b$  and  $c$  can be defined arbitrarily, except for defining the derived quantities, and only those quantities. Fofonoff (1962) overlooked the fact that it is also important that internal energy, enthalpy, and entropy can be calculated precisely, like all thermodynamic state functions and in addition to the derived quantity. In this sense, Fofonoff (1962) has a great responsibility because of his major impact on later studies, as we shall see.

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- Similarly, Feistel (1993, p.103-105) explained:

“(...) In other words, in our (Gibbs)  $G(S, t, p)$  solvation enthalpy, solvation entropy at 0°C and 1 atm, absolute enthalpy and absolute entropy of pure water at 0°C and 1 atm are ignored. This simplification is possible and reasonable because these energy contributions are never freed or converted during oceanic processes (Fofonoff, 1962), and so do not falsify any thermodynamic calculations of hydrodynamic thermohaline properties.

If we exaggerate the problem for clarity, the same argument can be applied to other energy contributions such as the electromagnetic binding energy of the electron shell of ions and the relativistic rest energy of nuclei (namely  $m_0 c^2$ ).

(...) 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 (Robinson and Stokes, 1955).

Therefore every energy definition in this field should be accompanied by the definition of the state, assumed to have 'no energy'. Our reference state is the following hypothetical situation. A solution of an infinite amount of seawater with an infinite number of ions of sea salt, but in the limit of zero salinity, is in equilibrium at 0°C and under the pressure of 1 atm with no external (electromagnetic or gravitational or inertial) field applied to the volume (only to the surface to maintain the pressure).

All molecules and ions of the solute are infinitely far from each other such that even their long range Coulomb interaction forces are not felt. Each ion is surrounded by its undisturbed hydration shell. At this state, enthalpy and entropy of 1 kg of this solution are assumed to be zero.”

- We can recognize in the assumptions retained by Feistel (1993) those of Fofonoff (1962), duly cited by Rainer Feistel, with however the additional mention to the other forms of energy: electromagnetic binding energy (to create the electron configurations of atoms) and the relativistic rest energy (to create the electrons, neutrons, protons).

I am sorry to see that Feistel (1993) continued and extended the previous misinterpretations by Fofonoff (1962). Indeed, the intend of the third-law absolute definition of the entropy by Nernst, Planck and others was not at all to take into account the whole physical effects, like the binding energy or the relativistic rest energy. The third-law absolute entropy only takes into account the thermal translational, rotational, vibrational and electronic degrees of freedom of atoms and molecules, nothing less, but nothing more.

- Note that the reference made by Feistel (1993) to the first edition of the book of Robinson and Stokes (1955) about “*Electronic Solutions*” should have been replaced by the reference to the more recent second edition by Robinson and Stokes (1959).

Above all, Feistel (1993) could have recalled that, in these 1955-59 books by Robinson and Stokes, the “*Conventional Ionic Entropies at 25°C*” derived by Powell and Latimer (1951) were listed in the Table 3.3 (p.67), as shown in the Fig. 49.

Robinson and Stokes (1959, p.67) also recalled that Powell and Latimer (1951): “*point out that the (ion entropy) values can be represented with very fair accuracy by the equation:*

$$\bar{S}^\circ = \frac{3}{2} R \ln(M) + 37 - 270 \frac{|z|}{r_e^2},$$

*where  $M$  is the atomic weight,  $|z|$  the valency treated as positive regardless of sign, and  $r_e$  an effective radius of the ion in solution (...)*”

And furthermore, Feistel (1993) could also have mentioned that Robinson and Stokes (1959, p.67-68)

*Table 3.3*  
*Conventional Ionic Entropies at 25°C (298·16°K), computed relative to  $\bar{S}_{\text{H}^+}^0 = 0$  in the hypothetical standard state of one gram-ion per kg of water.*

<i>Ion</i>	$\bar{S}^0$ cal deg <sup>-1</sup> mole <sup>-1</sup>	<i>Ion</i>	$\bar{S}^0$ cal deg <sup>-1</sup> mole <sup>-1</sup>	<i>Ion</i>	$\bar{S}^0$ cal deg <sup>-1</sup> mole <sup>-1</sup>
H <sup>+</sup>	(0·00)	Mg <sup>++</sup>	− 28·2	Al <sup>+++</sup>	− 74·9
Li <sup>+</sup>	3·4	Ca <sup>++</sup>	− 13·2	Cr <sup>+++</sup>	− 73·5
Na <sup>+</sup>	14·4	Sr <sup>++</sup>	− 9·4	Fe <sup>+++</sup>	− 70·1
K <sup>+</sup>	24·5	Ba <sup>++</sup>	3·0	Ga <sup>+++</sup>	− 83
Rb <sup>+</sup>	29·7	Mn <sup>++</sup>	− 20	In <sup>+++</sup>	− 62
Cs <sup>+</sup>	31·8	Fe <sup>++</sup>	− 27·1	Gd <sup>+++</sup>	− 43
Tl <sup>+</sup>	30·4	Cu <sup>++</sup>	− 23·6	U <sup>+++</sup>	− 36
Ag <sup>+</sup>	17·67	Zn <sup>++</sup>	− 25·45	Pu <sup>+++</sup>	− 39
F <sup>−</sup>	− 2·3	Cd <sup>++</sup>	− 14·6	U <sup>++++</sup>	− 78
Cl <sup>−</sup>	13·17	Sn <sup>++</sup>	− 5·9	Pu <sup>++++</sup>	− 87
Br <sup>−</sup>	19·25	Hg <sup>++</sup>	− 5·4		
I <sup>−</sup>	26·14	Pb <sup>++</sup>	5·1		
OH <sup>−</sup>	− 2·5	S <sup>−−</sup>	− 6·4		
SH <sup>−</sup>	14·9				

Data from POWELL, R. E. and LATIMER, W. M., *J. chem. Phys.*, 19 (1951) 1139.

Figure 49: *The Table 3.3 (p.67) in the book by Robinson and Stokes (1959), from Powell and Latimer (1951).*

trusted the third-law Sackur-Tetrode definition for the absolute entropy for monoatomic gases, which was written as:

$$\bar{S}_{(g)} = R \left[ \frac{5}{2} \ln(T) - \ln(P) + \frac{3}{2} \ln(M) + \ln(Q_e) - 1.164 \right]$$

by Robinson and Stokes, where  $T$  is the absolute temperature,  $M$  is the atomic mass (molar mass, noted  $W$  by Robinson and Stokes),  $P$  the pressure (in atm),  $Q_e$  the multiplicity of the ground state, and 1.164 the Sackur-Tetrode constant for the given unit of pressure (atm).

Similarly, Robinson and Stokes (1959, p.64-65) explicitly wrote that: “*The third law of thermodynamics provides a basis for the calculation of absolute entropies of pure substances from the heat capacity data extending down to low temperatures:*

$$\bar{S} = \int_0^T \bar{C}_P d\ln(T) .$$

*Allowance can also be made for any phase transitions occurring below the temperature of interest, so that the absolute entropies of the pure substances composing the electrodes of the cell discussed above, or of the solid potassium chloride are determinable.”*

- All these reminders show that Feistel (1993) could not continue to indicate that the entropies of the elements (liquid water for the ocean) and of the ions (sea salts  $\text{Na}_{aq}^+$ , ...,  $\text{Cl}_{aq}^-$ , ...) were unknown and could be arbitrarily defined. Differently, the absolute values for the entropies were already available in the books and tables published by Powell and Latimer (1951), Rossini et al. (1952), Robinson and Stokes (1959) and Lewis and Randall (1961), among others.

Differently to what was written by Feistel (1993), I think that he hid things behind a veil of mystery, and that the need to use the absolute definition of the thermal entropies cannot be at all a matter of ‘scientific taste’.

No one can avoid applying the third law of thermodynamics, in particular for variable composition mixtures (like the moist-air atmosphere and the sea-salt oceans). It is only for the trivial case of a single substance of invariable composition (pure water for the ocean of zero salinity, dry air for the atmosphere without humidity) that, of course, the Sackur-Tetrode constant does not intervene in physical properties.

Feistel (1993) could have recalled that, for the seawater, these absolute entropies intervene in the two constants  $c$  and  $b$  of Fofonoff (1962) and thus impact the entropy and the enthalpy via the linear function of the salinity  $-a - b s$  and  $d + c s$ , respectively. As a consequence, the seawater entropy and the enthalpy should be defined, computed and studied by using the third-law absolute values.

- Other general-physic comments were made by Feistel and Hagen (1995, p.267-268), who explained:

*“(...) the four (energy and entropy) constants  $CO00$ ,  $CO10$ ,  $C200$  and  $C210$ , however, have no influence on measurable thermodynamic properties of seawater and cannot be determined from experiments with seawater only (Fofonoff, 1962).  $CO00$  and  $CO10$  are related to absolute energy and absolute entropy of water molecule,  $C200$  and  $C210$  to absolute energy and absolute entropy of salt particles.*

*One possibility to fix these numbers could be the reference to solid salt, as used for ionic standard entropies (Lewis and Randall, 1961).*

*Very theoretically, energy could be fixed relativistically by mass measurements with more than 13 valid digits, and entropy by the Third Law, if seawater thermodynamics were to be valid down to  $-273^\circ\text{C}$ , but in practice this is neither possible nor necessary for seawater equilibrium thermodynamics.*

*As a consequence, for use in the oceanographic context all four constants  $CO00$ ,  $CO10$ ,  $C200$  and  $C210$  can be chosen quite arbitrarily.*

*We emphasize that their adjustment is not a question of right or wrong, but simply of taste, usefulness, or common agreement.*

*The most natural way to fix them is the definition of one or more reference states (i.e. triples  $S, t, p$ ), at which certain quantities like enthalpy or entropy are supposed to have zero value.*

*Changing this "reference frame" can be done at any time by the "transformation" (Fofonoff, 1962) (for the Gibbs function)*

$$G' = G + (A + B t) + (C + D t) S$$

*with suitable numbers of  $A, B, C, D$ , where  $G'$  is physically as correct as  $G$ , only possessing another reference state.”*

I can provide the following comments about these remarks of Feistel and Hagen (1995).

- What a relief to see that it was already possible to rely on the third-law absolute energy and absolute entropy of water molecule and ionic standard entropies published in Powell and Latimer (1951) and Lewis and Randall (1961), for instance!
- It is wrong to say that “(...) the four (energy and entropy) constants  $CO00$ ,  $CO10$ ,  $C200$  and  $C210$  (...) have no influence on measurable thermodynamic properties of seawater and cannot be determined from experiments with seawater only (...)” Indeed, I recalled in Equation (192) in the Section 12.3 that the knowledge of the difference  $\delta\eta$  in the statistical and calorimetric absolute entropies for water vapour and ice-Ih (at  $T_0 = 273.15$  K and 1 atm) may allow the computation of the saturation pressure  $p_{\text{sat}}(T_0)$  if we know the latent heat of sublimation  $L_s(T_0)$ , and vice versa. Said differently, the knowledge of the third-law values  $\delta\eta$  corresponds to a constraint on the values of  $p_{\text{sat}}(T_0)$  and  $L_s(T_0)$  that is possible to check (191) or (192) via experimental processes. Therefore, the third-law of thermodynamics implicitly gives constraints on the saturation pressure at the sea surface that “influence on measurable thermodynamic properties of seawater.”
- It is meaningless to explain that we can compute the “(...) entropy by the Third Law” only “if seawater thermodynamics were to be valid down to  $-273^\circ\text{C}$  (...)” Indeed, like in Millero and Leung (1976) and Millero (1983), I have computed in my 2025 papers (submitted to the Comptes Rendus Geosciences) the third-law entropy of seawater from the absolute values of its constituents, namely from the values for liquid water and sea-salts ions given at  $0^\circ\text{C}$  in Thermodynamic Tables, without any hypothesis made at  $-273^\circ\text{C}$  for the seawater!

- Therefore, all four constants C000, CO10, C200 and C210 cannot be chosen quite arbitrarily, since the (third-law) absolute entropy values can be set to the values available in all Thermodynamic Tables at 0°C or 25°C for liquid water or water vapour, on the one hand, and the sea-salt ions ( $\text{Na}_{aq}^+$ , ...,  $\text{Cl}_{aq}^-$ , ...), on the other hand.
- It is incorrect to claim that the choice of reference values of entropies, absolute or arbitrary, would: not be a question of right or wrong, but simply of taste, usefulness, or common agreement. It is true that, since Fofonoff (1962), there has been a common agreement that applies to everyone that would authorize the choice of arbitrary values for the reference entropies for the ocean, just as for the atmosphere since Normand (1921), ..., Rossby (1932), ..., Iribarne and Godson (1973), ..., Emanuel (1994), ..., Pauluis et al. (2010), ... But an agreement should be able to be challenged and modified if the underlying assumptions were to be invalidated, as here to allow the entropy of the ocean and the atmosphere to be calculated in all cases, including those where salinity (in the ocean) or water content (for the atmosphere) are variable.

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- More recently, Feistel and Hellmuth (2020, p.42) explained that:

*“In TEOS-10, energies and entropies are defined relative to arbitrarily specified, metrologically advantageous reference states (Feistel et al., 2008; Feistel, 2018). The claim that these definitions lead to incorrect results in atmosphere models (Marquet, 2015a, about the moist-air enthalpy) and a resulting call for a related revision of TEOS-10 are, however, empirically ill-founded (Feistel, 2019).”*

- The conclusions of Feistel (2019, p.24) was:

*“Deviating from common practice in thermodynamic textbooks which consider entropy as a unique quantity that may be estimated by different methods, it is suggested here to consider the entropy formulas of Clausius, Boltzmann, Planck or Pauling as describing distinct but related properties, namely, a thermal, empirical Clausius entropy, a statistical Boltzmann entropy, and their difference, the “frozen” Pauling entropy.”*

- I strongly disagree with these conclusions of Feistel (2019), with a proof published in Marquet and Stevens (2022, Figure B1) and recalled in the above Fig. 1, with also the numerical values in the above Table 1, where the statistical absolute entropies (the Planck’s version with Feistel’s terminology) for  $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ , are very similar to the calorimetric absolute entropies (the sum of Clausius and Pauling-Nagle versions with Feistel’s terminology).

Therefore, the paper by Rainer Feistel (2019) appears to be a kind of somewhat desperate attempt to save the current system imposing arbitrary choices, without providing a relevant thermodynamic vision. This paper by Feistel (2019) appears as a kind of somewhat desperate attempt to save the current system imposing arbitrary choices, without providing a relevant thermodynamic vision and which seems to have the sole aim of discrediting my approaches which aim to explain that only the absolute definitions of entropies have a clear thermodynamic meaning, and that they are available in all thermodynamic tables.

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- Even more (and very) recently, Feistel (2024, p.1372) explained that:

*“Thermodynamic potentials include certain adjustable constants expressing the absolute energies and entropies of the particular substances, which are not available from measurement Planck (1906); Feistel (2019) and have, in turn, no effect on measurable properties derived from those potentials.*

*(...) the International Conference on the Properties of Steam in London in 1967 defined the common triple point of water as the reference state at which those absolute values were arbitrarily set. Since then, no evidence has appeared for putative conflicts caused by such settings with any technical or scientific applications of the equations.*

(...) *Despite this, Feistel and Wagner (2006); Feistel et al. (2008) discuss the implementation of alternative residual entropies of water, if that should be of interest in exceptional applications of TEOS-10.*

I can provide the following comments about these remarks of Feistel (2024), for which I wrote a Comment (see CC1: 'Comment on egusphere-2024-1243' by Pascal Marquet on <https://egusphere.copernicus.org/preprints/2024/egusphere-2024-1243/>).

- I explain in the Section 12.15 that Feistel (2024) wrongly cited the book of Planck (1906) on the theory of thermal radiation, written before the Nernst's theorem was published, instead of citing the next book on radiation by Planck (1914), as well as the thermodynamic books of Planck (1911, 1917) where he invented the third law of thermodynamics! This is a bit of a dishonest attitude, as I have explained these facts many times by email to Rainer Feistel over the years...
- As previously explained, I think I have shown that the knowledge of the difference  $\delta\eta$  in the statistical and calorimetric absolute entropies for water vapour and ice-Ih (at  $T_0 = 273.15$  K and 1 atm) may allow the computation of the saturation pressure  $p_{\text{sat}}(T_0)$  if we know the latent heat of sublimation  $L_s(T_0)$ , and vice versa. Therefore, the third-law of thermodynamic do have "effect on measurable properties"
- I explain in the Section 12.5 that, in fact, there were two resolutions accepted at the 5th International Conference on the Properties of Steam in London in 1956 (Schmidt, 1956, see the Fig. 32), with only the first of it recalled in the 1965 proceeding cited by Rainer Feistel (Haywood, 1965): there was a first trivial proposal by Prof. Schmidt (recalled by Rainer Feistel) with a need to set to zero the enthalpy and entropy of pure liquid water at the triple point ( $0.01^\circ\text{C}$ ); but these was also a second proposal by the Dr. Weir to also indicate the absolute version of the liquid-water entropy to be computed at  $0.01^\circ\text{C}$ .
- Moreover, these two 1956 resolutions were only valid for a unique substance of constant composition (the liquid state or steam of  $\text{H}_2\text{O}$ ), without any word about the recommendation for the best way to set the entropy of water vapour or pure liquid water when they are in a mixture of gases (atmosphere) or with solved sea salts (seawater). Differently, only the second resolution must be retained (with the need to compute absolute, third-law version of the entropies) for the cases of a mixture of variable compositions like the moist-air atmosphere and the sea-salt oceans (as already stated by Gibbs, Planck, ...).
- Anyhow, I am happy that we are allowed to: “ (...) *discuss the implementation of alternative residual entropies of water, if that should be of interest in exceptional applications of TEOS-10.*” Even if the sentence is a little bit ambiguous, I have defined, computed and studied the (alternative) absolute moist-air entropy since Marquet (2011a), and more recently the (alternative) absolute seawater entropy like in Millero and Leung (1976) and Millero (1983) in my 2025 papers (submitted to the Comptes Rendus Geosciences). However, the (alternative) absolute seawater entropy amount to modify more than the “ *residual (part of the) entropies of water*” ( $189 \text{ J kg}^{-1} \text{ K}^{-1}$ ) but, in fact, both the liquid-water entropy ( $3513.4 \pm 1.7 \text{ J kg}^{-1} \text{ K}^{-1}$ ) and sea-salts entropies ( $633.3 \pm 15 \text{ J kg}^{-1} \text{ K}^{-1}$ ).

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• More generally, I think that the term “absolute entropy” can likely be understood in the same way as for the “absolute temperature” as stated by William Thomson (1848, next Lord Kelvin), who introduced the “*absolute scale*” of temperature for which (p.104):

(...) “*all degrees have the same value*” and (...) “*give out the same mechanical effect*” for which (...) “*characteristic is quite independent of the physical properties of any specific substance.*”

• Indeed, similarly, the Sackur-Tetrode and Planck entropy constant was derived as an “*independent-of-the-substances*” value, which can be set to 0 without loss of generality.

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- William Thomson (1848, next Lord Kelvin) also introduced (see the footnote p.316 in the Phil. Mag., and p.104 in the Math. and Phys. Papers):

(...) the “*absolute temperature scale*”  $T = 273 + t$ , where  $t$  is in degree Celsius and “*where the air-thermometer*”  $t = -1/0.00366 \approx -273^\circ\text{C}$  “*is a point which cannot be reached at any finite temperature, however low.*”

- This last remark is analogous to the “*principle of unattainability of the absolute zero*” put forward and studied by Nernst (1912) and Simon (1927), which is often considered as an equivalent of the third law of thermodynamics (in fact, a consequence of it).

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- Moreover, for those who still have doubts about the generality or even the physical basis of the third law of thermodynamics and its application to the atmospheric and oceanographic sciences, I would like to remind that the same applies to many general principles of physics, such as the existence of the Michelson-Morley-Lorentz-Einstein’s limiting velocity ( $c$ ) of physical phenomena in a vacuum, or the existence of the Planck’s quantum of action ( $h$ ).

There is no demonstration in the logical, mathematical or physical senses of these facts, which are simply observed, never disproved and therefore elevated to the status of general principles.

The same applies to the third law and the principle of unattainability of the absolute zero of temperature, subject to amending Planck (1911, 1917) formulation by adding possible residual entropies at 0 K in the calorimetric computations for some species like  $\text{H}_2\text{O}$ .

However, just because you don’t understand everything doesn’t mean you shouldn’t apply such convincing, if mysterious, results! Similarly, no one really “knows” how quantum physics works, nor why the speed of light has an absolute limit value, but our world is based on the use of radio waves, electronic devices, laser as well as GPS that use space-time corrections in the earth’s gravitational field!

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## 12.17 Validations and physical meaning of absolute entropies / specific values?

- It is worth mentioning another way of suggesting that the reference values for enthalpy and entropy may have no impact on the moist-air thermodynamics.

Perhaps the most emblematic is the influential book by Kerry Emanuel (1994) about “*Atmospheric Convection*” where quantities are often expressed “*per unit mass of dry air*” and with the impression (or even the aim) that this is the way to explain why the dry-air and water-vapour (or liquid-water) reference values for enthalpy and entropy cannot have any physical impact due to the use of mixing ratio as content.

- The aim of this section is, for instance, to extend the answers published in the Section 6 of Marquet and Dauhut (2018, p.3344) about “*The budgets per unit mass of “dry or moist” air?*” to the Comments published by Pauluis (2018), where he wrote (p.3731-3732):

“... Under the framework of per unit mass of dry air, water can be added or removed, but the amount of dry air remains unchanged. (...) In the steam cycle proposed by Pauluis (2011), water vapor is added at warm temperature and removed at cold temperature, with no change in the amount of dry air. As the mass of dry air through the cycle is constant, the per-unit-mass-of-dry-air framework should be used to correctly assess the thermodynamic transformations (...) From a physical point of view, the per-unit-mass-of-dry-air framework is the correct one to assess the atmospheric overturning of precipitating convection. A cycle based on this framework assumes that there is not net upward mass transport of dry

air. This is consistent with the fact that mass conservation ensures that, on average, there is no net upward mass flux of dry air. (...) the use of the per-unit-mass-of-moist-air framework can result in a large error in the estimate of the work done by the atmospheric circulation”.

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- For sake of simplicity, let us consider that the moist-air is made of a mixture of dry air, water vapour and liquid droplets (i.e. without ice crystals) with, respectively, the elementary small masses:

- $m_d$  for the dry air;
- $m_v$  for the water vapour;
- $m_l$  for the liquid water; and
- $m_t = m_v + m_l$  for the total water.

The specific (i.e. per unit mass of the mixture) moist-air enthalpy ( $h$ ) and entropy ( $s$ ) were already defined by Gibbs (1875-1878), and more recently for instance by Iribarne and Godson (1973, 1981), leading to the weighted sums

$$h = q_d h_d(T) + q_v h_v(T) + q_l h_l(T), \quad (326)$$

$$s = q_d s_d(T, p_d) + q_v s_v(T, p_v) + q_l s_l(T), \quad (327)$$

depending on the absolute temperature  $T$ , the partial pressure  $p = p_d + p_v$  and the specific contents verifying  $1 = q_d + q_v + q_l = q_d + q_t$  with  $q_t = q_v + q_l$ , where:

- $q_d = m_d / (m_d + m_v + m_l)$  for the dry air;
- $q_v = m_v / (m_d + m_v + m_l)$  for the water vapour;
- $q_l = m_l / (m_d + m_v + m_l)$  for the liquid water; and
- $q_t = m_t / (m_d + m_v + m_l) = (m_v + m_l) / (m_d + m_v + m_l)$  for the total water.

Differently, Emanuel (1994, Eqs. 4.5.2 and 4.5.6) defined the “*specific moist-air enthalpy and entropy*” (written as  $k$  and  $s$  in his book, but rewritten as  $h^*$  and  $s^*$  in the following) “*per unit mass of dry air*” according to:

$$h^* = \frac{h}{q_d} = h_d(T) + r_v h_v(T) + r_l h_l(T),$$

$$s^* = \frac{s}{q_d} = s_d(T, p_d) + r_v s_v(T, p_v) + r_l s_l(T),$$

where the mixing ratios were defined as:

- $r_v = m_v / m_d = q_v / q_d$  for the water vapour;
- $r_l = m_l / m_d = q_l / q_d$  for the liquid water; and
- $r_t = (m_v + m_l) / m_d = q_t / q_d$  for the total water,

and with the obvious relationships:

$$q_d = \frac{1}{1 + r_t}, \quad q_v = \frac{r_v}{1 + r_t}, \quad q_l = \frac{r_l}{1 + r_t}, \quad q_t = \frac{r_t}{1 + r_t},$$

$$r_v = \frac{q_v}{1 - q_t}, \quad r_l = \frac{q_l}{1 - q_t}, \quad r_t = \frac{q_t}{1 - q_t}.$$


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- Starting from the moist-air enthalpy (326), with the latent heat of vaporisation equal to

$$L_v(T) = h_v(T) - h_l(T)$$



and with the properties  $q_d = 1 - q_t$  and  $q_l = q_t - q_v$ , we can derive the same equation as in Iribarne and Godson (1973, Eq.92, p.72) or Iribarne and Godson (1981, Eq.98, p.79):

$$\begin{aligned} h &= q_d h_d(T) + q_v [h_v(T) - h_l(T)] + q_t h_l(T), \\ h &= q_d h_d(T) + q_t h_l(T) + q_v L_v(T), \end{aligned} \quad (328)$$

with (328) corresponding, after a division by  $q_0$ , to the relationship written by Emanuel (1994, p.4.5.3, p.118):

$$h^* = h_d(T) + r_t h_l(T) + r_v L_v(T). \quad (329)$$

- 
- Similarly, the specific moist-air entropy (327) can be written as

$$\begin{aligned} s &= q_d s_d(T, p_d) + q_t s_l(T) + q_v [s_v(T, p_v) - s_l(T)], \\ s &= q_d s_d(T, p_d) + q_t s_l(T) + q_v [s_v(T, p_{sat}) - s_l(T)] + q_v [s_v(T, p_v) - s_v(T, p_{sat})], \\ s &= q_d s_d(T, p_d) + q_t s_l(T) + \frac{q_v L_v(T)}{T} - q_v R_v \ln(H_l), \end{aligned} \quad (330)$$

with after a division by  $q_0$  the relationship written by Emanuel (1994, p.4.5.7, p.119):

$$s^* = s_d(T, p_d) + r_t s_l(T) + \frac{r_v L_v(T)}{T} - r_v R_v \ln(H_l). \quad (331)$$

The two relationships

$$s_v(T, p_{sat}) - s_l(T) = \frac{L_v(T)}{T} \quad \text{and} \quad s_v(T, p_v) - s_v(T, p_{sat}) = -R_v \ln(H_l)$$

has been used. They show two links between the difference in entropy and the latent heat of vaporisation  $L_v(T)$ , on the one hand, the relative humidity  $H_l = p_v/p_{sat}(T)$  with respect to liquid water with a saturation pressure  $p_{sat}(T)$ , on the other hand.

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- Normally, a normal scientific attitude should lead us to consider the reference values of enthalpies ( $h_d(T_0)$ ,  $h_v(T_0)$ ,  $h_l(T_0)$ ) and entropies ( $s_d(T_0, p_0)$ ,  $s_v(T_0, p_0)$ ,  $s_l(T_0)$ ) for dry air, water vapour and liquid water in all generality, before being able, possibly, in a second step, to fix them at such or such values, arbitrary or in accordance with the third law of thermodynamics.

A general way to take into account of these reference values (for instance at  $T_0 = 273.15$  K and  $p_0 = 1000$  hPa) is to consider the enthalpies:

$$\begin{aligned} h_d(T) &= c_{pd} (T - T_0) + h_d(T_0), \\ h_v(T) &= c_{pv} (T - T_0) + h_v(T_0), \\ h_l(T) &= c_l (T - T_0) + h_l(T_0), \end{aligned}$$

and the entropies:

$$\begin{aligned} s_d(T, p_d) &= c_{pd} \ln\left(\frac{T}{T_0}\right) - R_d \ln\left(\frac{p_d}{p_0}\right) + s_d(T_0, p_0), \\ s_v(T, p_d) &= c_{pv} \ln\left(\frac{T}{T_0}\right) - R_v \ln\left(\frac{p_v}{p_0}\right) + s_v(T_0, p_0), \\ s_l(T, p_d) &= c_l \ln\left(\frac{T}{T_0}\right) + s_l(T_0). \end{aligned}$$

The visions “*per unit mass of moist air*” (328) and (330), or “*per unit mass of dry air*” (329) and (331), can all be generally written in the form:

$$h = (q_d c_{pd} + q_t c_l) (T - T_0) + q_v L_v(T) + \boxed{q_t [h_l(T_0) - h_d(T_0)] + h_d(T_0)} \quad (332)$$

$$\text{or } h^* = (c_{pd} + r_t c_l) (T - T_0) + r_v L_v(T) + \boxed{r_t [h_l(T_0)] + h_d(T_0)} \quad (333)$$

for the moist-air enthalpy, and for the moist-air entropy:

$$s = (q_d c_{pd} + q_t c_l) \ln(T) - q_d R_d \ln(p_d) + \frac{q_v L_v(T)}{T} - q_v R_v \ln(H_l) \\ - \boxed{(q_d c_{pd} + q_t c_l) \ln(T_0) + q_d R_d \ln(p_0)} + \boxed{q_t [s_l(T_0) - s_d(T_0, p_0)] + s_d(T_0, p_0)} \quad (334)$$

$$\text{or } s^* = (c_{pd} + r_t c_l) \ln(T) - R_d \ln(p_d) + \frac{r_v L_v(T)}{T} - r_v R_v \ln(H_l) \\ - \boxed{(c_{pd} + r_t c_l) \ln(T_0) + R_d \ln(p_0)} + \boxed{r_t [s_l(T_0)] + s_d(T_0, p_0)}. \quad (335)$$

Iribarne and Godson (1973, Eqs. 97 and 111, p.74 and 77) and Iribarne and Godson (1981, Eqs. 104 and 119, p.81 and 84) wrote equivalent of the moist-air enthalpy and entropy functions expressed “*per unit mass of moist air*” given by (332) and (334), but without the boxed terms noted “const.” instead, although with several of these boxed terms depending on the variable total-water content  $q_t$ .

Similarly, Iribarne and Godson (1981, Eqs. 105 and 120, p.81 and 84) wrote equivalent of the moist-air enthalpy and entropy functions expressed “*per unit mass of dry air*” given by (333) and (335), still without the boxed terms, still noted “const.” instead, and still with several of these boxed terms depending on the variable total-water content  $r_t$ .

The same moist-air enthalpy and entropy functions expressed “*per unit mass of dry air*” given by (333) and (335) also appeared in Emanuel (1994, Eqs. 4.5.4 and 4.5.9, p.118 and 120), but with the whole second line removed (although with several of the boxed terms depending on the variable total water mixing ratio  $r_t$ ).

- Even if the vision “*per unit mass of dry air*” has long been used to derive several atmospheric thermodynamic variables defined in terms of mixing ratios, and to remove the reference values in the definition of the moist-air internal energy, enthalpy and entropy (in particular by Guldberg and Mohn, 1876; von Bezold, 1888, 1891a,b; Neuhoff, 1900; Guldberg and Mohn, 1910; Humphreys, 1920; Normand, 1921; Rossby, 1932; Saunders, 1957, among others), we can likely recognize in the more recent books by Iribarne and Godson (1973, 1981) and Emanuel (1994) the origin of the habit to remove the reference enthalpies and entropies involved in most of the modern moist-air specific functions  $h$  and  $s$  derived “*per unit mass of moist air*” and the moist-air functions  $h^*$  and  $s^*$  derived “*per unit mass of dry air*.”

- For an example, the same habit to remove (cancels out) the reference enthalpy and entropy values is found in all of Olivier Pauluis’ articles (in particular: Pauluis and Held, 2002a,b; Pauluis and Schumacher, 2010; Pauluis et al., 2010; Pauluis, 2011, 2016; Pauluis and Zhang, 2017; Fang et al., 2019, ...).

- However, the vision “*per unit mass of dry air*” adds almost nothing regarding the impact of reference values. Indeed, both  $h^*$  and  $s^*$  defined above in (333) and (335) depend on  $r_t h_l(T_0)$  and  $r_t s_l(T_0)$ , respectively, and there is no physical justification for cancelling these two terms depending on the varying total water content  $r_t = r_v + r_l$ . Indeed, the cancellation of these two terms would impact the gradients and derivative of the moist-air enthalpy and entropy, via the non-zero terms  $\vec{\nabla}(r_t) \neq 0$  and  $dr_t/dt \neq 0$ .

---

- The apparent small advantage of the “*per unit mass of dry air*” versions (333) and (335) is that the true constant dry-air reference values  $h_d(T_0)$  and  $s_d(T_0, p_0)$  are independent on  $r_t$  and have no impact in both (333) and (335).

However, this is only an apparent small advantage, as shown by a clear example published in the book by Emanuel (1994) that ruins the physical meaning of this “*per unit mass of dry air*” vision for defining the internal energy, enthalpy and entropy specific functions.

Indeed, for instance Emanuel (1994, p.122-123) defined the “*moist-static energy*” that is expected to be “*conserved in adiabatic and hydrostatic displacements*” with the differential equation:

$$(Eq. 4.5.22, p.123) \quad 0 = (c_{pd} + r_t c_l) dT + d(L_v r_v) + (1 + r_t) g dz ,$$

where the term  $(1 + r_t)$  in factor of the differential of the geopotential  $d[g(z - z_0)] = g dz$  is a direct consequence of the division by  $q_d = 1/(1 + r_t)$ .

For the case of a closed parcel for which  $r_t$  is conserved, the previous equation can be integrated into the so-called “*moist-air static energy*” function, written by Emanuel (1994, but noted  $h$ ) as:

$$(Eq. 4.5.23, p.123) \quad MSE^* = (c_{pd} + r_t c_l) T + L_v r_v + (1 + r_t) g z + F^*(r_t) .$$

This “*per unit mass of dry air*” function  $MSE^*$  is often interpreted as possible exchanges between the three forms of energy:

- the thermal energy term  $(c_{pd} + r_t c_l) T$  ;
- the latent heat term  $L_v(T) r_v$  ;
- the geopotential term  $(1 + r_t) g z = (g z)/q_d$  .

However, since this Eq. 4.5.23 is obtained by integrating Eq. 4.5.22 with a constant value of  $r_t$ , this Eq. 4.5.23 is defined up to an arbitrary function of  $r_t$  not mentioned by Emanuel (1994), but noted  $F^*(r_t)$  here. As an example, this Eq. 4.5.23 could have been equally written as

$$MSE^{**} = (c_{pd} + r_t c_l) (T - T_0) + L_v r_v + (1 + r_t) g (z - z_0) + F^{**}(r_t) , \quad (336)$$

where  $T_0$  and  $z_0$  are two constant reference values for the temperatures and the height and with  $F^{**}(r_t)$  another arbitrary function of  $r_t$ . Moreover, the boxed terms  $r_t [h_l(T_0)] + h_d(T_0)$  in the “*per unit mass of dry air*” function  $k^*$  in (333) should also be included into  $F^*(r_t)$  or  $F^{**}(r_t)$ , with the term  $r_t [h_l(T_0)]$  depending on  $r_t$ .

Emanuel (1994, p.123) defined other  $MSE$ -like functions, such as the “*dry-air static energy*”  $MSE_d^*$  (noted  $h_d$  by Emanuel) and the “*liquid-water static energy*”  $MSE_l^*$  (noted  $h_w$  by Emanuel p.123, and then  $h_l$  p.434):

$$(Eq. 4.5.24, p.123) \quad MSE_d^* = (c_{pd} + r_v c_{pv}) T + (1 + r_v) g z + F_d^*(r_t) ,$$

$$(Eq. 4.5.25, p.123) \quad MSE_l^* = (c_{pd} + r_t c_{pv}) T - L_v r_l + (1 + r_t) g z + F_l^*(r_t) .$$

The quantity  $MSE_d^*$  is intended to be used for unsaturated conditions ( $r_t = r_v$ ), although without the term  $L_v r_v$ . Moreover,  $MSE_d^*$  is not a true “*dry-air*” value, for which we should have  $r_v = 0$ .

The quantity  $MSE_l^*$  is obtained by Emanuel (1994) from Eq. 4.5.23 by “*subtracting the conserved variable*”

$$r_t [L_v(T_0) - (c_{pv} - c_l) T_0] = r_t [L_v(T) - (c_{pv} - c_l) T] .$$

This means that the arbitrary term  $F_l^*(r_t)$  must also include this arbitrary “*conserved variable*” that depends on  $r_t$ .

As a consequence, since all the arbitrary terms  $F^*(r_t)$ ,  $F^{**}(r_t)$ ,  $F_d^*(r_t)$  and  $F_l^*(r_t)$  depends on  $r_t$  but were derived with the hypothesis of constant values of  $r_t$ , all the corresponding  $MSE$  functions should not be plotted nor studied for real cases where  $r_t$  is not a constant.

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Emanuel (1994) also defined other *MSE*-like functions, such as the “*virtual liquid-water static energy*” (noted  $h_{lv}$  by Emanuel):

$$(Eq. 13.3.5, p.435) \quad MSE_{lv} \approx c_{pd} T_{lv} - \frac{L_v r_l}{1 + r_t} + g z + \frac{F_l^*(r_t)}{1 + r_t},$$

where  $\epsilon = R_d/R_v$  and

$$T_{lv} = \left( \frac{1 + r_t/\epsilon}{1 + r_t} \right) T$$

is a kind of “*virtual liquid-water temperature*” (called “*density temperature*” by Emanuel).

This quantity  $MSE_{lv}$  has been obtained by Emanuel (1994, p.434-435) by dividing  $MSE_l^*$  by  $1 + r_t = 1/q_d = 1/(1 - q_t)$ . with the following justification: “(...) *it is useful to define one other quantity by dividing Eq. 13.3.3 by  $(1 + r_t)$ ,*” which is equal to  $1/q_d = 1/(1 - q_t)$ , and by neglecting several terms depending on  $r_t$ ...

---

As a consequence of all the manipulations carried out by Emanuel (1994) and recalled above to calculate the enthalpies, entropies and static energies by neglecting the reference values and several other terms like the arbitrary functions  $F$  depending on  $q_t = r_t/(1 + r_t)$   $r_t = q_t/(1 - q_t)$ , even if it is possible to numerically calculate these static enthalpies, entropies and energies, it is necessary to refrain from plotting, interpreting and studying their vertical profiles if the total water contents  $q_t$  and  $r_t$  are variable.

And yet, I show in the Figures 50 that Emanuel (1994) could not resist drawing several vertical profiles of these various functions, even for several atmospheric conditions where the moist-air contents (either  $q_t$  or  $r_t$ ) are not constant.

In the Fig. 13.9 (p.437), the top of the boundary layer of the stratocumulus is associated with large increase in  $T$  (typically +10 K) and large decrease in  $q_t$  (typically −8 g/kg).

The Fig. 13.11 (p.446) showed a trade (shallow) cumulus case also associated with a continuous decrease in  $r_v$  and  $r_t$ .

The Fig. 14.6 (p.478) showed a deep-convection cumulus case, also associated with a continuous decrease in  $r_v$  and  $r_t$ .

For all these typical conditions:

- the boxed terms in the “*per unit mass of moist air*” formulations (332) and (334) depending on the moist-air reference enthalpy and entropy values  $h_l(T_0)$ ,  $h_d(T_0)$ ,  $s_l(T_0)$  and  $s_d(T_0, p_0)$  –discarded in the *MSE*’s and entropy formulations 4.5.23, 4.5.9 and 13.3.5 recalled in the Figures 50– should have an impact due to the varying term  $q_t$ ;
- the same is true for the boxed terms in the “*per unit mass of dry air*” formulations (333) and (335), where the reference enthalpy and entropy values  $h_l(T_0)$  and  $s_l(T_0)$  should have an impact due to the varying term  $r_t$ ;
- even in the more general “*per unit mass of dry air*” geopotential term  $(1 + r_t) g(z - z_0)$  in (336), which should replace Eq. 4.5.23, the impact of the varying reference part  $-r_t g z_0$  might be made as large (negative or positive) as we want, depending on the arbitrary value of  $z_0$ ;
- I have studied the impacts of these missing terms since Marquet (2011a, 2017) and Marquet and Dauhut (2018) for the moist-air entropy, and since Marquet (2015a, 2019a) for the moist-air enthalpy;
- with indeed large observed impacts for marine stratocumulus (like in the Fig. 13.9) if we use the absolute version of the water-vapour and dry-air reference entropies;

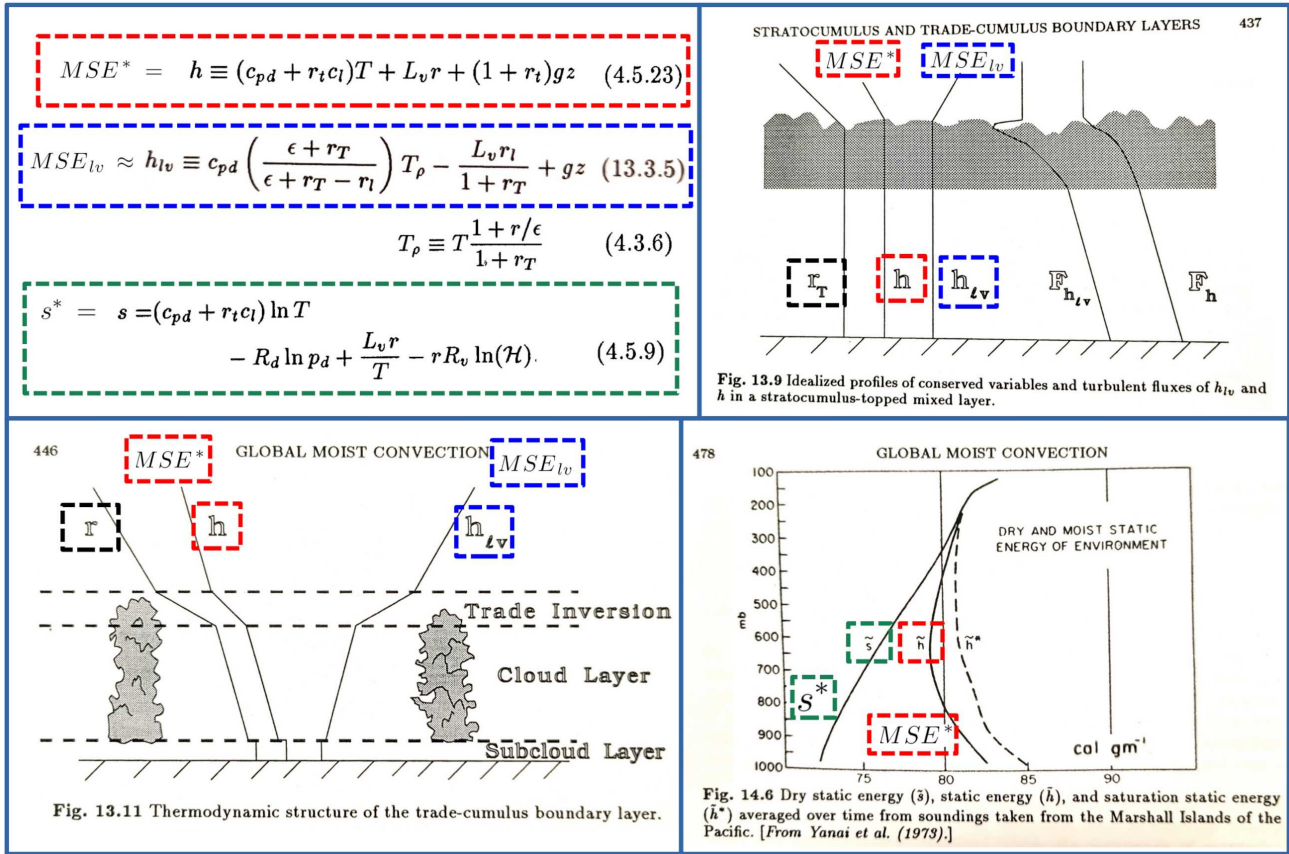


Figure 50: Several Equations for the moist-air static energies (MSE) and entropy (s) derived by Emanuel (1994), together with several Figures where Emanuel (1994) plotted the vertical profiles of these moist-air static energies and entropy for conditions where the moist-air contents (either  $q_t$  or  $r_t$ ) are not constant.

- and with indeed large large impacts observed for the EBEX-2000 campaign and the associated surface-energy budget if we use the absolute calorimetric version of the water-vapour and dry-air reference enthalpies.

In conclusion, the hope that the variables defined “*per unit mass of dry air*” may not depend on the reference values of enthalpies or entropies is illusory, with the additional unforeseen and detrimental effect on the undesirable impact of the reference value  $z_0$  for the geopotential written as  $(1 + r_t)g(z - z_0)$ .

The only way to no longer depend on these arbitrary definitions is to use the true specific values defined “*per unit mass of moist air*” (with the geopotential written as  $gz$ ) and to use the absolute reference values of entropies and enthalpies.

## 12.18 Validations and physical meaning of absolute entropies / Potential temp.?

It is often been suggested that it would be better to concentrate on calculating the entropies of moist air and seawater, without necessarily understanding the need to calculate potential temperatures.

I agree that we must first be able to calculate the thermodynamic values of these entropies, in accordance with the recommendations of the 4 laws of thermodynamics:

- the zeroth law and the existence of the absolute temperature variable  $T$  for systems in local thermal equilibrium;

- the first law and the conservation of the total energy for a close and adiabatic system;
  - the second law and the principle of increase of entropy due to irreversible processes occurring in a close and adiabatic system;
  - the third law and the principle that the entropy of the more stable solid state at 0 K tends toward a universal constant value, which can be put to zero for all substance at 0 K without loss of generality.
- A consequence of the third law is the principle of unattainability of the 0 K state.

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Accordingly, I have first computed and studied in Marquet (2010, 2011a) the absolute moist-air entropy made of a mixture of dry air, water vapour, liquid water droplets and snow crystals

$$s = q_d s_d(T, p_d) + q_v s_v(T, p_v) + q_l s_l(T) + q_i s_i(T), \quad (337)$$

leading in terms of the temperature ( $T$ ), pressure ( $p = p_d + p_v$ ) and specific contents ( $q_t = 1 - q_d = q_v + q_l + q_i$ ) variables to the absolute moist-air entropy relationship

$$\begin{aligned} s = & c_{pd} \ln(T) - c_{pd} \kappa \ln\left(\frac{p}{p_0}\right) - \frac{q_l L_v(T) + q_i L_s(T)}{T} + c_{pd} \Lambda_r q_t \\ & + c_{pd} \lambda q_t \ln\left(\frac{T}{T_r}\right) + c_{pd} \kappa \delta q_t \ln\left(\frac{p_r}{p}\right) + c_{pd} \gamma q_t \ln\left(\frac{r_r}{r_v}\right) \\ & + c_{pd} \kappa \ln(1 + \eta r_v) + c_{pd} \kappa \delta q_t \ln\left(\frac{1 + \eta r_v}{1 + \eta r_r}\right) + c_{pd} \gamma q_l \ln(H_l) + c_{pd} \gamma q_i \ln(H_i) \\ & + (1 - q_r) s_{dr} + q_r s_{vr} - c_{pd} \Lambda_r q_r - c_{pd} \ln(T_r) - c_{pd} \kappa \ln\left(\frac{p_0}{p_r}\right) - c_{pd} \kappa \ln(1 + \eta r_r) \end{aligned} \quad (338)$$

which is in full agreement with the third law of thermodynamics, and in particular via the term

$$\Lambda_r = \frac{s_{vr}(T_r, p_{vr}) - s_{dr}(T_r, p_r - p_{vr})}{c_{pd}} \approx 5.865 \pm 0.004 \quad (339)$$

which depend on the absolute (third-law) values of the reference entropies for the water-vapour ( $s_{vr}$ ) and dry-air ( $s_{dr}$ ) perfect gases.

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It is only in a second step that I have computed the associated potential temperature noted  $\theta_s$  via the definition :

$$s(\theta_s) = c_{pd} \ln\left(\frac{\theta_s}{T_0}\right) + s_{d0}(T_0, p_0) = c_{pd} \ln(\theta_s) + [s_{d0}(T_0, p_0) - c_{pd} \ln(T_0)], \quad (340)$$

where

$$\begin{aligned} \theta_s = & \theta \exp\left[-\frac{L_v q_l + L_s q_i}{c_{pd} T}\right] \exp(\Lambda_r q_t) \\ & \times \left(\frac{T}{T_r}\right)^{\lambda q_t} \left(\frac{p_r}{p}\right)^{\kappa \delta q_t} \left(\frac{r_r}{r_v}\right)^{\gamma q_t} (1 + \eta r_v)^{\kappa} \left(\frac{1 + \eta r_v}{1 + \eta r_r}\right)^{\kappa \delta q_t} (H_l)^{\gamma q_l} (H_i)^{\gamma q_i} \end{aligned} \quad (341)$$

is the absolute-entropy potential temperature which generalizes the dry-air value

$$\theta = T \left(\frac{p_0}{p}\right)^{\kappa} \quad (342)$$

obtained from (341) for the dry-air limit conditions:  $q_v = q_l = q_i = 0$ ,  $r_v = 0$  and  $q_t = 0$ .

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The main interest of defining the variables  $\theta_s$  via the relationship (340) is that all other terms  $s_{d0}(T_0, p_0)$ ,  $c_{pd}$  and  $T_0$  are true constant, and therefore  $\theta_s$  has exactly the same physical properties as the moist-air entropy that can indeed be noted  $s(\theta_s)$ , with for instance the moist-air entropy equation and the second law that can be expressed with any of the two variables  $s = c_{pd} \ln(\theta_s) + cste$  or  $\theta_s$ , via the relationship:

$$\frac{ds}{dt} = \frac{c_{pd}}{\theta_s} \frac{d\theta_s}{dt} = (\dots) \quad (343)$$

This means that if the moist-air entropy  $s$  is a constant, then  $ds/dt = 0$ , and then  $d\theta_s/dt = 0$ , and then the potential temperature  $\theta_s$  is a constant, and vice versa. Similarly, since  $\theta_s$  is a positive quantity, an increase (decrease) in  $s$  corresponds to an increase (decrease) in  $\theta_s$ .

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The true historical story that explains the use of potential temperatures in atmospheric science start with the reverse discovery first of the dry-air potential temperature  $\theta$ , and then the link with the dry-air entropy.

Indeed, the Greek letter “ $\theta$ ” has first been used by von Helmholtz (1888) to represent the absolute temperature (p.650), before to denote (p.652) more specifically the temperature than a mass of air would acquire if it were adiabatically moved to a given standard pressure  $p_0$  following the Thomson’s law noted  $\theta p_0^{(1-\gamma)/\gamma} = T p^{(1-\gamma)/\gamma}$  the law deduced from the Poisson equations and leading to what is nowadays called the (dry-air) “potential temperature” recalled by (342), where  $p_0 = 1000$  hPa is a constant pressure and  $\kappa = (\gamma - 1)/\gamma \approx 0.2857$ .

Helmholtz first called this quantity “*Wärmegehalt*” (total content in heat), before von Bezold (1891b, p.1189, in German) proposed, with the explicit agreement of Helmholtz, the name of “*potential temperature*”, the name that has lasted until today.

It must be emphasized that the link between the potential temperature of the dry air and entropy was not made by von Helmholtz nor by von Bezold, except through a small remark from von Bezold (1891b, p.1193 in German) where it is said that the properties of  $\theta$  “*resemble those due to Clausius’ theorem, while being different from this theorem.*” Here, reference is made to the second principle of thermodynamics and to the fact that entropy “*tends to a maximum*” in the same way as von Bezold showed that  $\theta$  is “*preserved by adiabatic movements of moist air in the free atmosphere (adiabatic and isentropic transformations), or can only increase in the presence of condensations removed by precipitations*” (pseudo-adiabatic transformations).

Based on this remark made by von Bezold in 1888, it was not until Bauer (1908, 1910) that the link between the entropy of dry air ( $s$ ) and the dry-air potential temperature ( $\theta$ ) was clearly established, in the form:

$$s_d = c_{pd} \log(\theta) + \text{Const} . \quad (344)$$

We can then obtain the right law of variation of the entropy of a perfect gas according to logarithms of its temperature and its pressure:

$$s_d(T, p) = c_{pd} \log(T) - R_d \log(p) + \text{Const} . \quad (345)$$

Clearly, the definition  $s = c_{pd} \ln(\theta_s) + cste$  that I retained in (340) for the moist-air entropy is completely similar to the one (344) of Bauer, except with  $\theta_s$  replacing  $\theta$ , and the moist-air entropy relationship (338) is the moist-air generalisation of (345), because  $c_{pd} \kappa = R_d$ .

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This complete synonymy between the entropy  $s$  and the potential temperature  $\theta_s$  justifies the study of one or the other of the properties of these variables. This is the reason why I have mainly used the potential temperature  $\theta_s$  in all my papers (Marquet and Geleyn, 2013; Marquet, 2014; Marquet and Geleyn, 2015; Marquet, 2015b, 2016; Marquet and Belamari, 2017; Marquet, 2017; Marquet and Dauhut, 2018; Marquet, 2019b,c,d; Marquet and Bechtold, 2020; Marquet and Bailey, 2021; Marquet, 2021; Marquet and Stevens, 2022; Marquet, 2022).

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In a way similar to the one described above for the moist-air atmosphere, I have defined first the seawater absolute entropy from the TEOS10-GSW value, by adding the third-law increment

$$\Delta\eta = \eta - \eta_{std/TEOS10} - \eta_{w0}(T_0) = (\eta_{s0} - \eta_{w0}) \times \frac{(S_A - S_{S0})}{1000} \approx (-1880 \pm 17) \times \frac{(S_A - S_{S0})}{1000} \text{ J/K/kg},$$

where  $\eta_{s0}$  and  $\eta_{w0}$  are the absolute reference entropies for sea salts and pure-liquid water, respectively. The reference entropy of pure water  $\eta_{w0}(T_0)$  is removed in the left part of this relationship in order to agree with the TEOS10-GSW assumption that  $\eta \approx 0$  for  $T = T_0$  and  $S_A = S_{S0}$  (in g/kg), with the constant value  $\eta_{w0}(T_0)$  removed in the standard TEOS10-GSW relationship.

It is then only in a second step that I have defined the optional definition of a kind of seawater potential temperature, like in (340) written as  $s(\theta_s) - s_{d0}(T_0, p_0) = c_{pd} \ln(\theta_s/T_0)$  and leading to:

$$\eta(\theta_\eta) = \eta_{std/TEOS10} + \Delta\eta = C_w \ln\left(\frac{\theta_\eta}{T_0}\right), \quad (346)$$

$$\theta_\eta = T_0 \times \exp\left(\frac{\eta_{std/TEOS10}}{C_w}\right) \times \exp\left[\left(\frac{\eta_{s0} - \eta_{w0}}{C_w}\right) \left(\frac{S_A - S_{S0}}{1000}\right)\right], \quad (347)$$

$$\theta_\eta \approx 273.15 \times \exp\left(\frac{\eta_{std/TEOS10}}{4218}\right) \times \exp\left[(-0.446 \pm 0.004) \left(\frac{S_A - S_{S0}}{1000}\right)\right], \quad (348)$$

where  $T_0 = 273.15$  K is the 0°C standard temperature,  $C_w = 4218$  J/K/kg is the specific heat of pure liquid water.

Note that the additive true constant term  $\eta_{w0}$  is discarded in the above definition of  $\eta_{abs}$  that should be  $\eta(\theta_\eta) - \eta_{w0} = C_w \ln(\theta_\eta/T_0)$  instead, simply because  $\eta_{w0}$  has already been discarded (as a true constant) in the TEOS10-GSW conventional (standard) definition of the entropy.

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