

TABLE 12-3. THE ENTROPIES OF SOME COMMON SUBSTANCES AT 298.15°K, CAL/DEG MOLE†

Solids:		Liquids:	
Ag.....	10.20	Br ₂	36.4
AgCl.....	23.00	HNO ₃	37.19
AgBr.....	25.60	• H ₂ O.....	16.73 •
AgI.....	27.6	Hg.....	18.17
Al.....	6.77	Gases:	
As.....	8.4	CH ₄	44.47
C(gr).....	1.37	CO.....	47.20
Ca.....	9.95	• CO ₂	51.08 •
CaO.....	9.5	Cl ₂	53.29
Cd.....	12.37	F ₂	48.49
Cu.....	7.97	H ₂	31.21
Fe.....	6.49	HCl.....	44.64
I ₂	27.76	H ₂ S.....	49.13
S(rh).....	7.62	• N ₂	45.77 •
Si.....	4.51	NO.....	50.34
SiO ₂ (q).....	10.00	• O ₂	49.01 •

† See K. K. Kelley, *U.S. Bur. Mines Bull.* 477, 1950, and revision by K. K. Kelley and E. G. King, *U.S. Bur. Mines Bull.* 592, in press, for a critical summary of entropy data and references to original sources.

(Lewis and Randall, 1961, p.137)

TABLE 27-1. ENTROPIES OF MONATOMIC GASES AT 298.15°K†

	$\int C_P d \ln T$	Eq. (27-2)
Ne.....	35.01 ± 0.10	34.95 ± 0.01
• • Ar.....	36.95 ± 0.2	36.99 ± 0.01
Kr.....	39.17 ± 0.1	39.20 ± 0.01
Xe.....	40.7 ± 0.3	40.54 ± 0.01

† K. K. Kelly, *U.S. Bur. Mines Bull.* 477, 1950, reviews critically the available data and gives original references.

(Lewis and Randall, 1961, p.421)

Figure 15: The molar entropies \bar{S}^o at 25°C for liquid water (H_2O) and the main atmospheric gases (N_2 , O_2 , CO_2 , Ar) published by Lewis and Randall (1961). **Top:** the Table 12-3 of (p.137) for the molar entropy of liquid water H_2O ($16.73 \times 4.184 \approx 70.00 \text{ J K}^{-1} \text{ mol}^{-1}$), together with the molar entropy for three of the main dry-air atmospheric gases (N_2 , O_2 , CO_2). **Bottom:** the Table 27-1 (p.421) for the molar entropy of the Argon noble gaz ($36.99 \times 4.184 \approx 154.77 \pm 0.8 \text{ J K}^{-1} \text{ mol}^{-1}$).

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

Ion	\bar{C}_p°	S°	ΔH_f°	ΔF_f°
H ⁺	0	0	0	0
OH ⁻	-32.0	-2.52	-54.96	-37.59
F ⁻	-29.5	-2.3	-78.66	-66.08
Cl ⁻	-30.0	13.2	-40.02	-31.35
ClO ₂ ⁻		24.1	-17.18	2.74
ClO ₃ ⁻	-18	39	-23.5	-0.6
ClO ₄ ⁻		43.2	-31.41	-2.47
Br ⁻	-31	19.29	-28.90	-24.57
I ⁻	-31	26.14	-13.37	-12.35
I ₃ ⁻		57.1	-12.4	-12.31
S ⁻²		-4	7.8	20.6
HS ⁻		15.0	-4.10	3.00
SO ₃ ⁻²	-66	4.1	-216.90	-177.34
HSO ₄ ⁻		30.52	-211.70	-179.94
SeO ₃ ⁻²		3.9	-122.39	-89.33
SeO ₄ ⁻²		5.7	-145.3	-105.42
HSeO ₄ ⁻		22.0	-143.1	-108.2
NH ₄ ⁺	16.9	26.97	-31.74	-19.00
N ₂ H ₅ ⁺		19	4	22.5
N ₂ H ₅ ⁺		31	-1.7	21.0
NH ₂ OH ₂ ⁺		37	-30.7	-13.54
NO ₂ ⁻		29.9	-25.4	-8.25
NO ₃ ⁻	-18	35.0	-49.37	-26.43
PO ₄ ⁻³		-52	-306.9	-245.1
HPO ₄ ⁻²		-8.6	-310.4	-261.5
H ₂ PO ₄ ⁻		21.3	-311.3	-271.3
HAsO ₄ ⁻²		0.9	-214.8	-169
H ₂ AsO ₄ ⁻		28	-216.2	-178.9
HCOO ⁻		21.9	-98.0	-80.0
HCO ₃ ⁻		22.7	-165.18	-140.31
CO ₃ ⁻²		-12.7	-161.63	-126.22
CH ₃ COO ⁻				

(Lewis and Randall, 1961, p.400)

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

Ion	\bar{C}_p°	S°	ΔH_f°	ΔF_f°
PtCl ₄ ⁻		42	-123.4	-91.9
PtCl ₆ ⁻²		52.6	-167.4	-123.1
Fe ²⁺		-27.1	-21.0	-20.30
Fe ³⁺		-70.1	-11.4	-2.53
Fe(OH) ⁺		-23.2	-67.4	-55.91
FeNO ²⁺		-10.6	-9.7	1.5
Mn ²⁺		-20	-53.3	-54.4
MnO ₄ ⁻		45.4	-129.7	-107.4
H ₂ BO ₃ ⁻		7.3	-251.8	-217.6
BF ₄ ⁻		40	-365	-343
Al ³⁺		-74.9	-125.4	-115
Gd ³⁺		-43	-168.8	-165.8
Mg ²⁺	4	-28.2	-110.41	-108.99
Ca ²⁺	-9	-13.2	-129.77	-132.18
Sr ²⁺		-9.4	-130.38	-133.2
Ba ²⁺	-11	3	-128.67	-134.0
Li ⁺	14.2	3.4	-66.55	-70.22
Na ⁺	7.9	14.4	-57.28	-62.59
K ⁺	2.3	24.5	-60.04	-67.46
Rb ⁺	-8.7	28.7	-59.4	-67.65
Cs ⁺	-18.7	31.8	-62.6	-70.8
UO ₂ ²⁺		-17	-250.4	-236.4

(Lewis and Randall, 1961, p.401)

TABLE X

Calculation of the Partial Molal Entropy of Sea Salt at 25°C

Species	\bar{S}_i°	N_i	$N_i \bar{S}_i^\circ$
Na ⁺	60.2	0.83619	50.34
Mg ²⁺	-118.0	0.09509	-11.22
Ca ²⁺	-55.2	0.01834	-1.01
K ⁺	102.5	0.01822	1.87
Sr ²⁺	-39.3	0.00016	-0.01
Cl ⁻	55.2	0.97481	53.81
SO ₄ ²⁻	17.2	0.05042	0.87
HCO ₃ ⁻	95.0	0.00345	0.33
Br ⁻	80.8	0.00151	0.01
B(OH) ₃	~50	0.0006	0.03
CO ₃ ²⁻	-53.1	0.0004	-0.02
B(OH) ₄ ⁻	~100	0.00015	0.01
F ⁻	-9.6	0.0001	-0.001
			95.01

(a) Based on $\bar{S}^\circ(\text{H}^+) = 0$ and taken from Lewis and Randall (1961). The values of B(OH)₃ and B(OH)₄⁻ have been estimated by comparison with solutes of similar size and charge.

(Millero, 1983, p.35)

Table 3.3

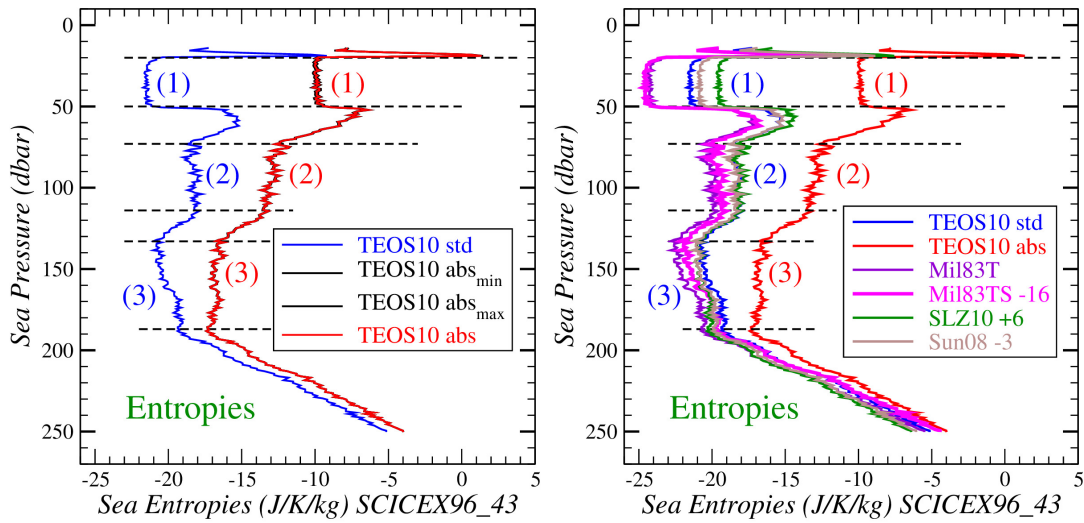
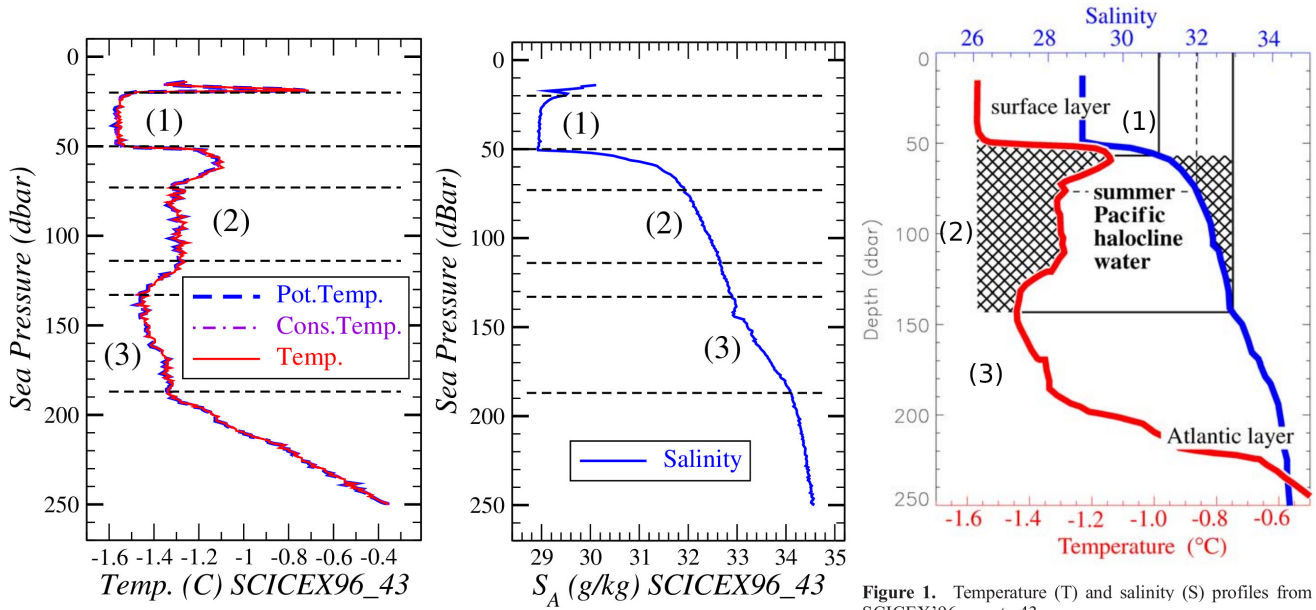
Conventional Ionic Entropies at 25°C (298.16°K), computed relative to $\bar{S}_{\text{H}^+}^\circ = 0$ in the hypothetical standard state of one gram-ion per kg of water.

Ion	\bar{S}_i° cal deg ⁻¹ mole ⁻¹	Ion	\bar{S}_i° cal deg ⁻¹ mole ⁻¹	Ion	\bar{S}_i° cal deg ⁻¹ mole ⁻¹
H ⁺	(0.00)	Mg ²⁺	-28.2	Al ³⁺	-74.9
Li ⁺	3.4	Ca ²⁺	-13.2	Cr ³⁺	-73.5
Na ⁺	14.4	Sr ²⁺	-9.4	Fe ³⁺	-70.1
K ⁺	24.5	Ba ²⁺	3.0	Ga ³⁺	-83
Rb ⁺	29.7	Mn ²⁺	-20	In ³⁺	-62
Cs ⁺	31.8	Fe ²⁺	-27.1	Gd ³⁺	-43
Tl ⁺	30.4	Cu ²⁺	-23.6	U ³⁺	-36
Ag ⁺	17.67	Zn ²⁺	-25.45	Pu ³⁺	-39
F ⁻	-2.3	Cd ²⁺	-14.6	U ⁴⁺	-78
Cl ⁻	13.17	Sn ²⁺	-5.9	Pu ⁴⁺	-87
Br ⁻	19.25	Hg ²⁺	-5.4		
I ⁻	26.14	Pb ²⁺	5.1		
OH ⁻	-2.5	S ⁻²	-6.4		
SH ⁻	14.9				

Data from POWELL, R. E. and LATIMER, W. M., *J. chem. Phys.*, 19 (1951) 1139.

(Robinson and Stokes, 1970, 1955, p.67)

Figure 16: **Top:** The molar entropy \bar{S}° and specific heat at constant pressure \bar{C}_p° listed in the Tables 25-7 of Lewis and Randall (1961, p.400-401) for most of the sea-salt anions and cations (at 298.15 K and relative to $\bar{S}_{\text{H}^+}^\circ = 0$). **Bottom-left:** The same sea-salts entropies as in Lewis and Randall (1961, p.400-401), but used in Millero (1983, p.35) with 1 cal = 4.184 J; **Bottom-right:** values of the "Conventional Ionic Entropies" (at 298.16 K and relative to $\bar{S}_{\text{H}^+}^\circ = 0$) given in the Table 3.3 of Robinson and Stokes (1970, 1955, p.67) and given for most of the sea-salt ions (in particular Na⁺, K⁺, Cl⁻, Br⁻, Mg²⁺) from Powell and Latimer (1951).



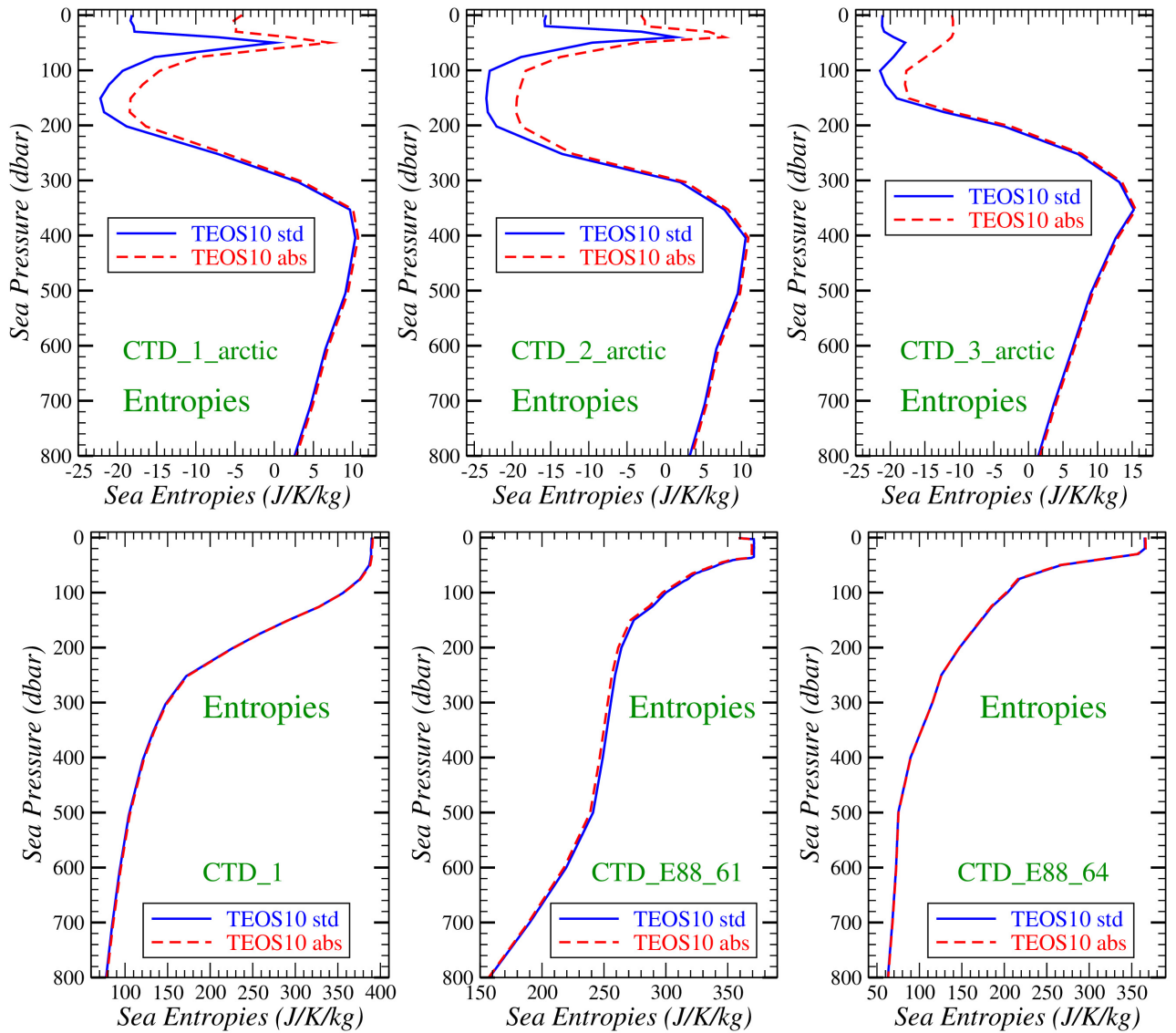


Figure 18: A study of the (std and abs) seawater entropies for 6 CTD profiles available: 1) for "CTD-1-arctic" "CTD-2-arctic" "CTD-3-arctic" and "CTD-1" profiles in the subroutine `gsw_mod_check_data.f90` in Feistel and TEOS10 (2010) software; 2) for "CTD-E88-61" and "CTD-E88-64" in the document UNESCO-JPOTS (1991, August 1982 tropical profiles, Endeavour cruise 88, stations 61 and 64, Tables 2.1, 2.2, 2.3, p.49, 51, 53).

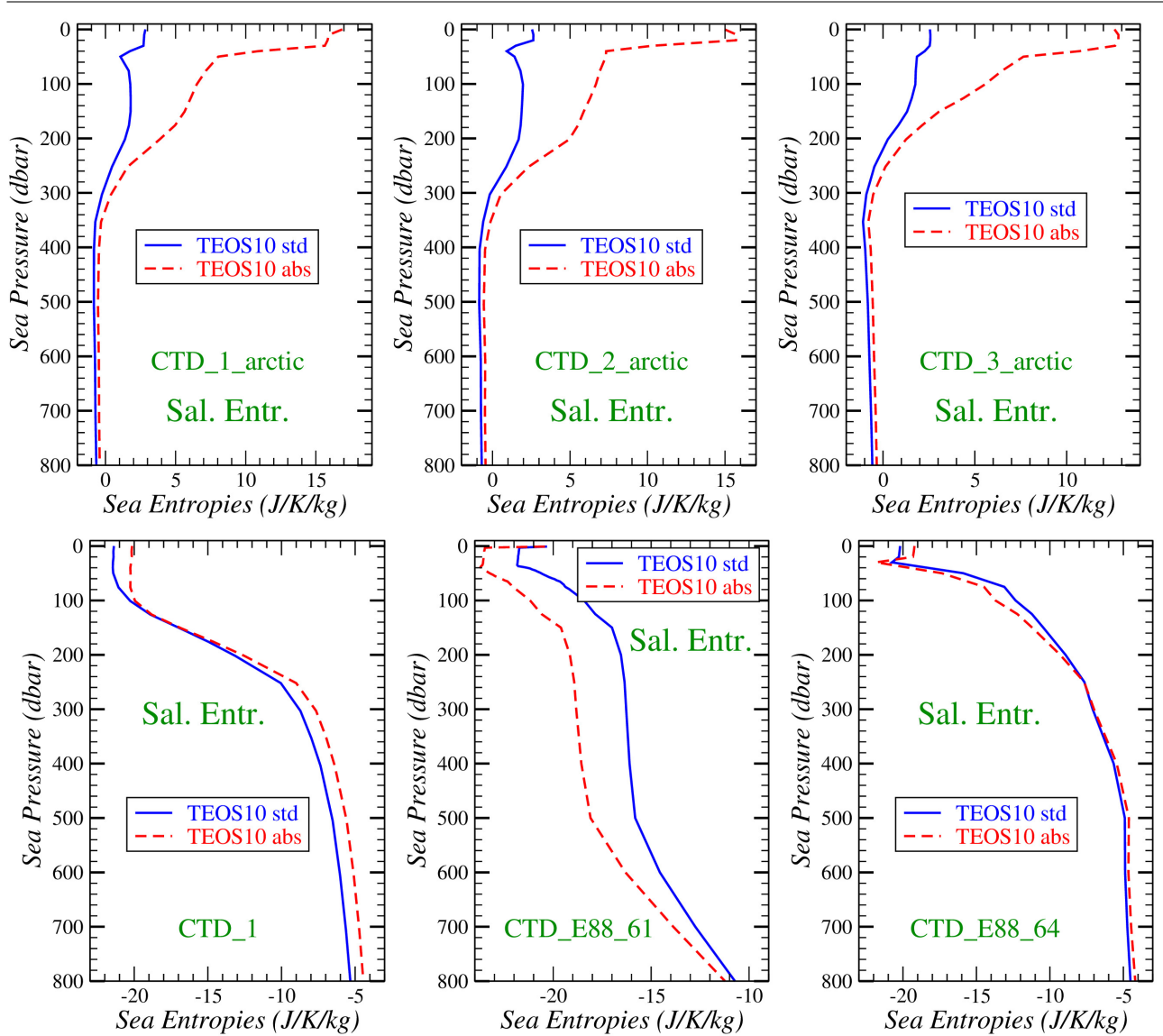


Figure 19: The “bulk salinity parts” of the seawater entropies for the same vertical profiles shown in the Figs. 5, computed by removing at each level the quantity $4217.4 \times \ln[(t + 273.15) / 273.15]$, namely $c_w \ln(T / T_0)$.

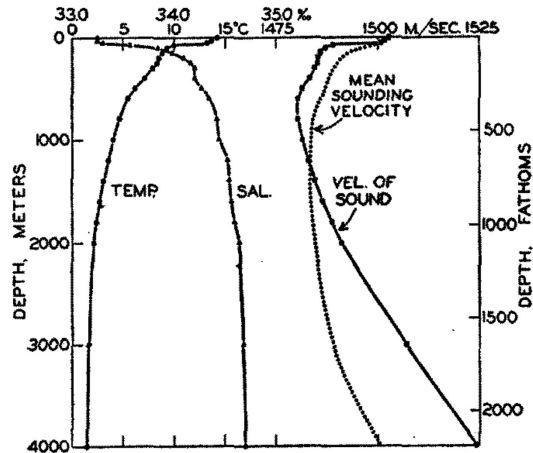
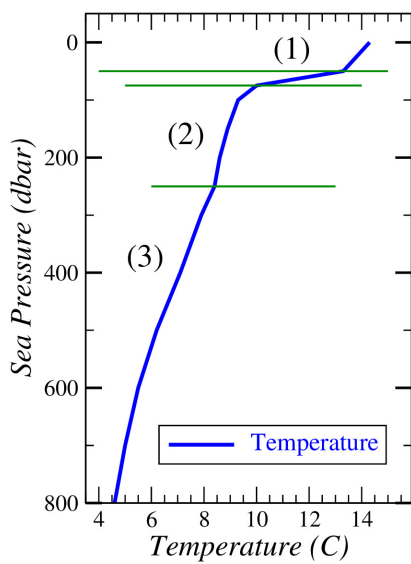


Fig. 19. Vertical distributions of temperature and salinity off southern California at $32^{\circ}57'N$ and $122^{\circ}07'W$, the computed velocity of sound, and the mean sounding velocity.

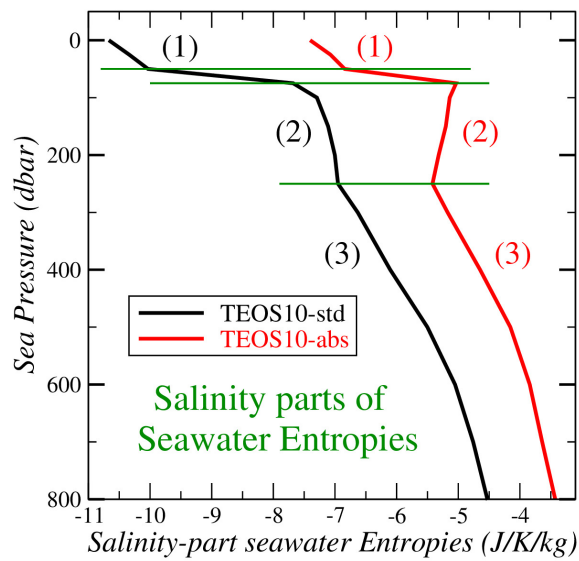
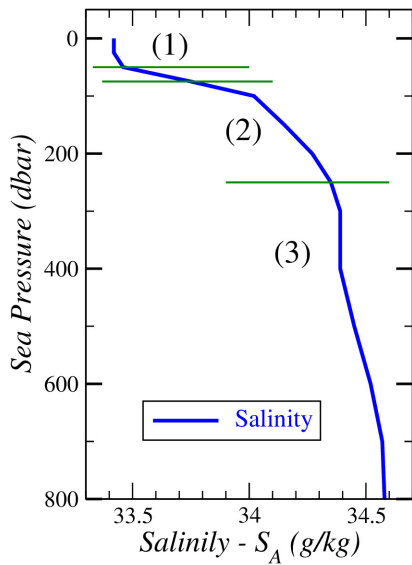


Figure 20: The vertical profiles (from 0 to 800 m depth) for the temperature (t , in $^{\circ}C$), the absolute salinity ($S_A = 1.00488 \times S_p$), and the “bulk salinity parts” of the seawater entropies for both the standard and absolute (with a threshold of -1) versions of TEOS10 computed from the Fig. 19 (p.79) of Sverdrup et al. (1942) and the dataset recalled (up to 800 m depth) in the Table 8.

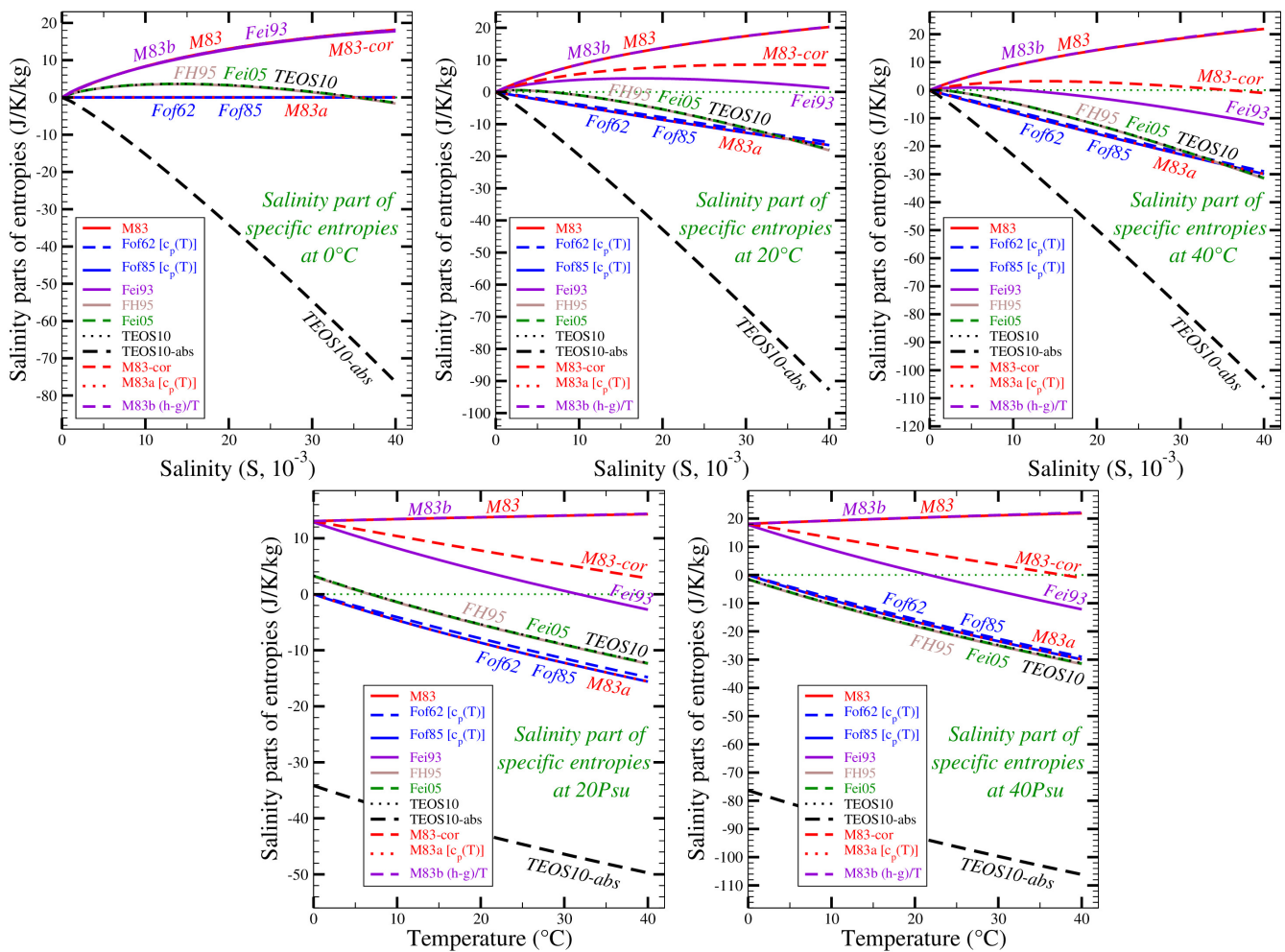


Figure 21: A study of the Salinity parts of the seawater entropies for various formulations.

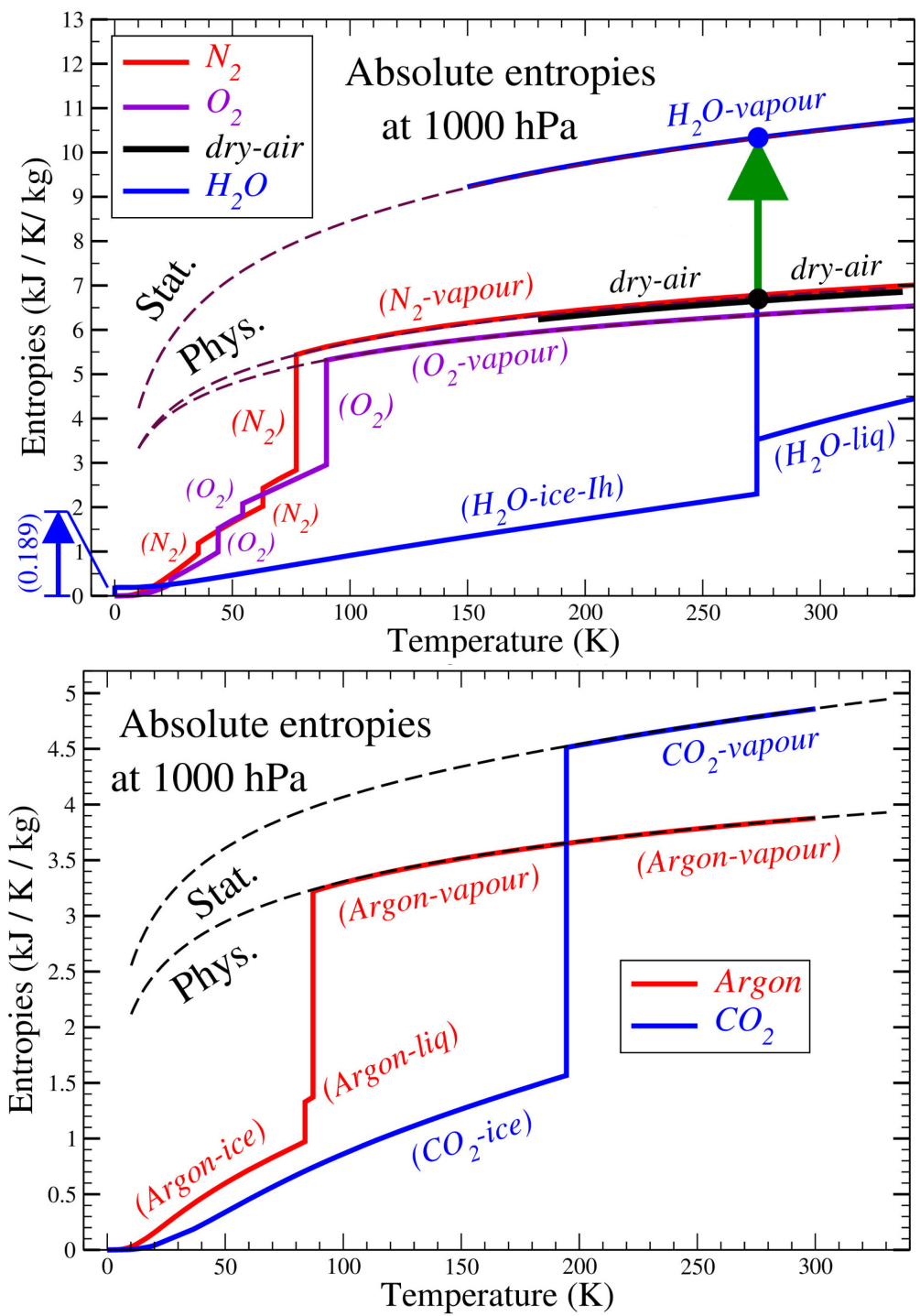


Figure 22: Entropies for dry-air (N_2 , O_2 , Ar, CO_2 and water H_2O) species plotted against the absolute temperature and computed at 1000 hPa. The calorimetric method $\left(\int_0^T c_p(T') d\ln(T') + \sum_j L(T_j)/T_j\right)$ corresponds to the coloured solid lines. The third-law hypothesis is applied at 0 K with zero entropies for all the solid phases, but with the residual entropy of $189 \text{ J kg}^{-1} \text{ K}^{-1}$ for ice-Ih. The vertical jumps correspond to phase changes at T_j with the phase-change enthalpies $L(T_j)$ between solids phases (for N_2 and O_2), then from solid to liquid phases, then from liquid to vapour phases. The statistical-physic values (black dashed lines) are computed from $S = k \ln(W)$ and $F = -kT \ln(Z)$ for the vapour phases according to the method described in Chase (1998) for translational, rotational, vibrational and electronic partition functions (Z).

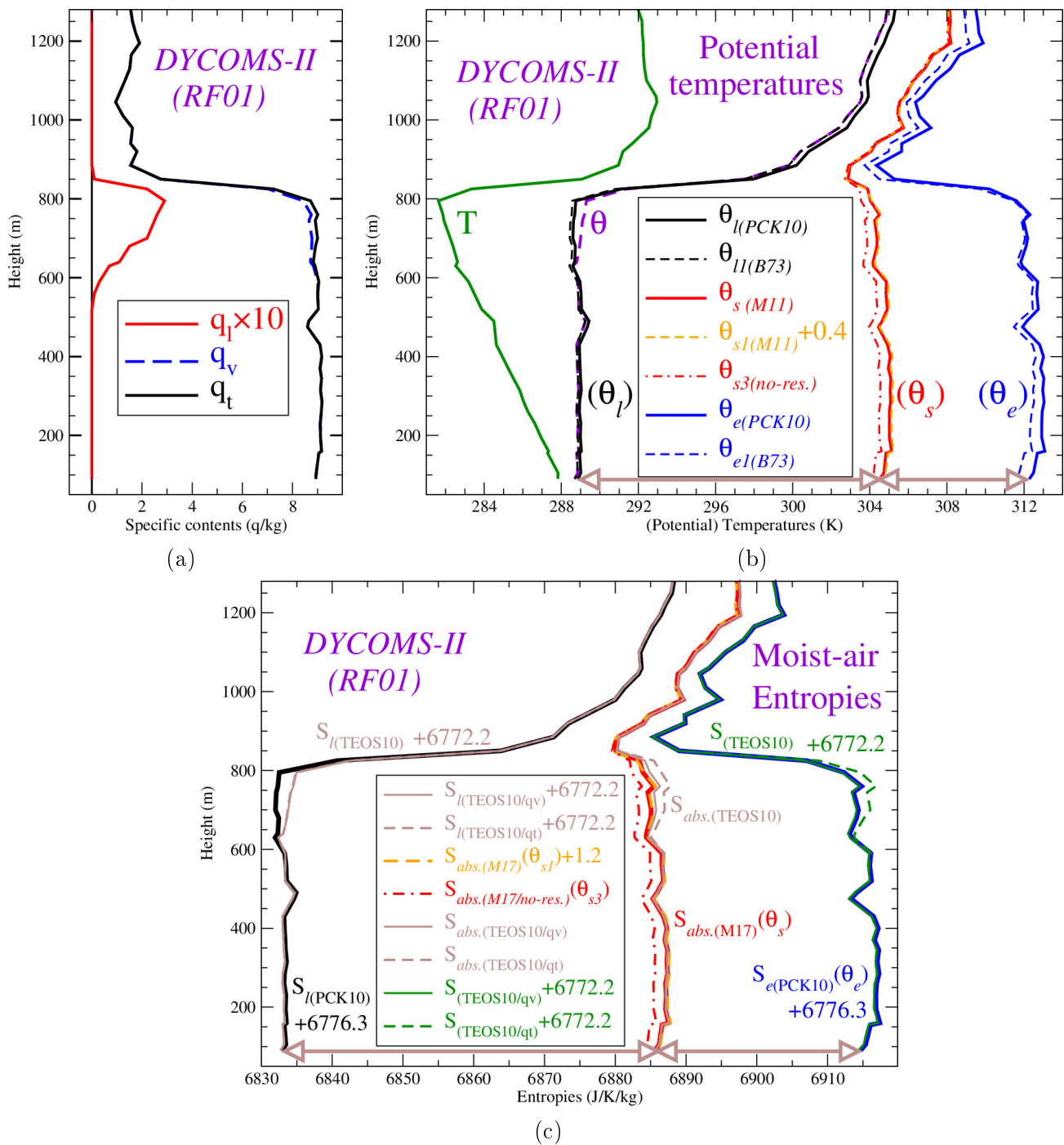


Figure 23: A study of thermodynamic vertical profiles computed from observations collected during the DYCOMS-II (RF01) Stratocumulus (from the Figs. 1 of Zhu et al., 2005, p.2742, see the dataset in the Table 10). (a): for the specific water contents in $g\ kg^{-1}$ ($q_t = q_v + q_l$, q_v and $10 \times q_l$); (b): for the absolute temperature in K (T , in green), the dry-air potential temperature in K (θ , in violet) and other moist-air potential temperatures in K (absolute in red and orange, “liquid-water” in black, “equivalent” in blue); (c): for several moist-air entropies in $J\ K^{-1}\ kg^{-1}$ (absolute in red and orange, “liquid-water” in black, “equivalent” in blue, with the corresponding TEOS10 values in grey and green).

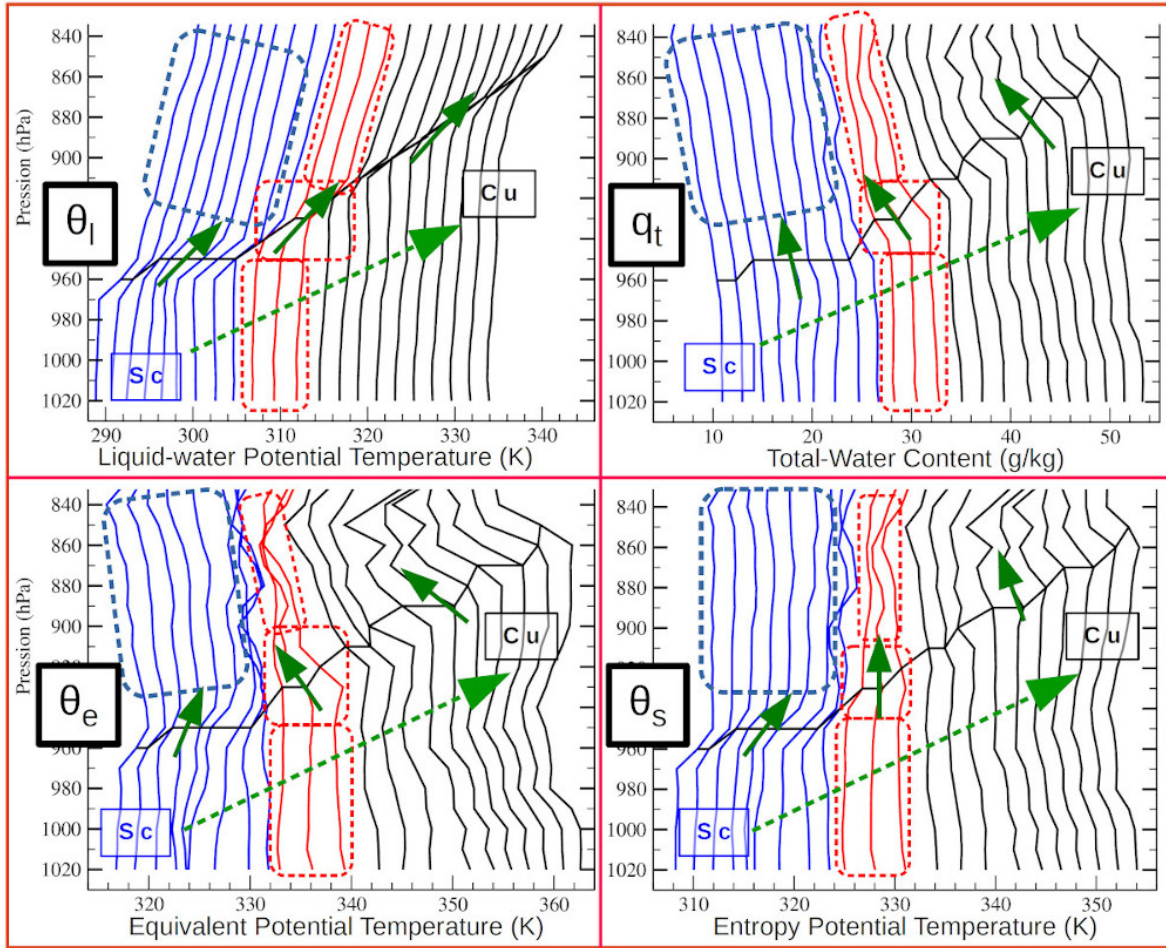


Figure 24: *The Fig. 5 of Marquet and Stevens (2022, p.1099). Vertical profiles of θ_e , θ_l , and θ_s plotted for half of the observed sounding of the first ASTEX Lagrangian experiment (with a shift of 2 K or 2 g/kg between each profiles). Stratocumulus (Sc) profiles are colored blue, whereas cumulus (Cu) profiles are colored black. Transition profiles between the two regimes are colored red, with the purple arrow indicating the deepening of the PBL associated with the transition. The green arrows show the sign of the top-PBL jump for each variable and for each regime: positive if tilted to the right, null if vertical, negative otherwise. The blue and red dashed boxes have been added to highlight the isentropic regions where θ_s (and not θ_e) is constant despite the opposite vertical gradients in θ_l and q_t which compensate with the special value of λ_r given by the third law.*

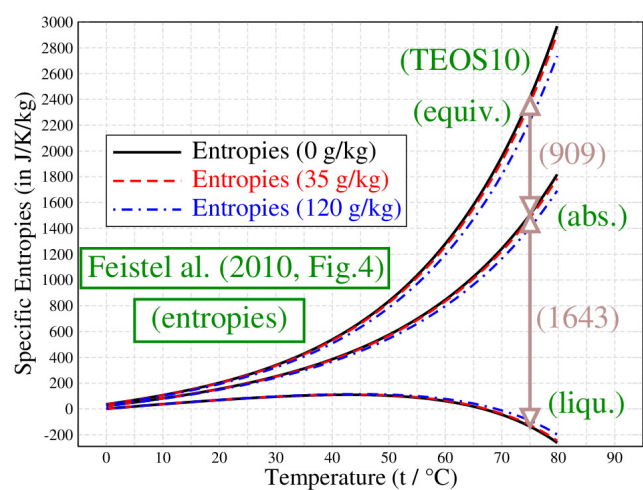
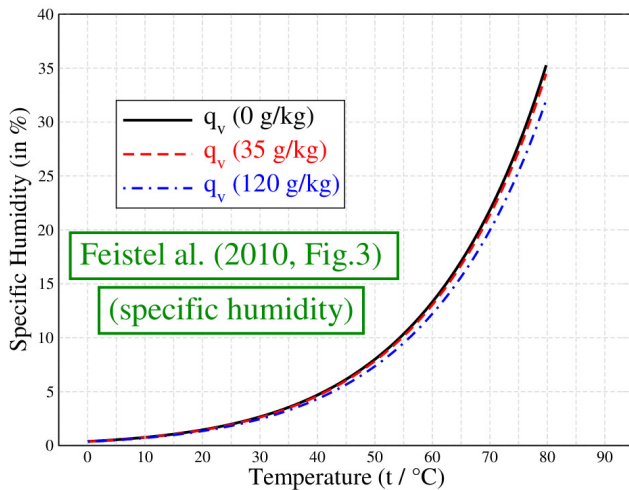
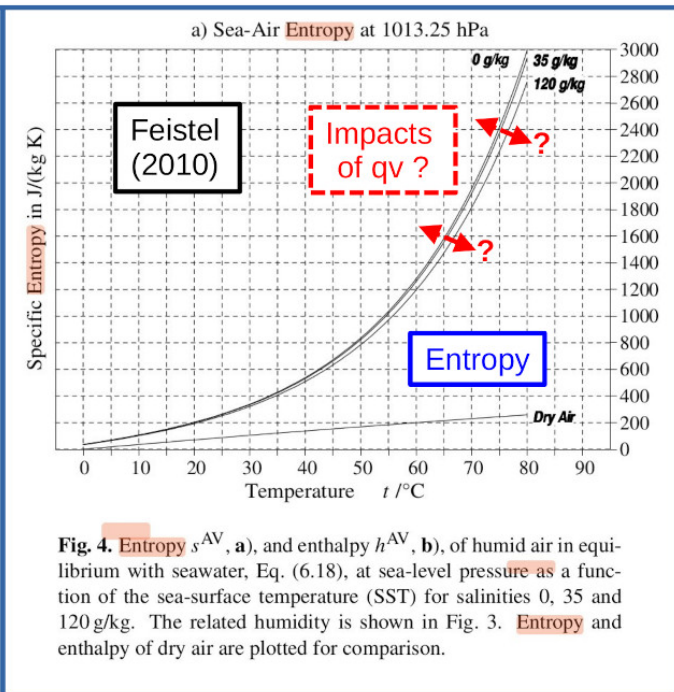
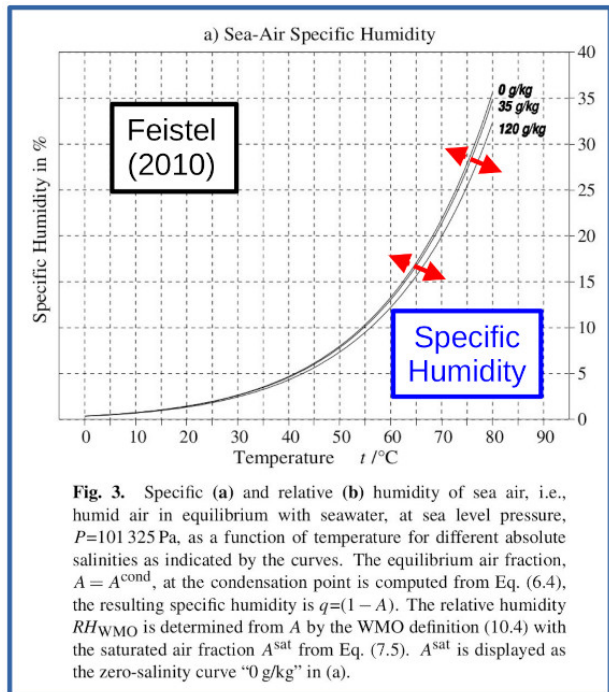


Figure 25: A study of the Figs. 3 and 4 of Feistel et al. (2010a, p.101-103)...

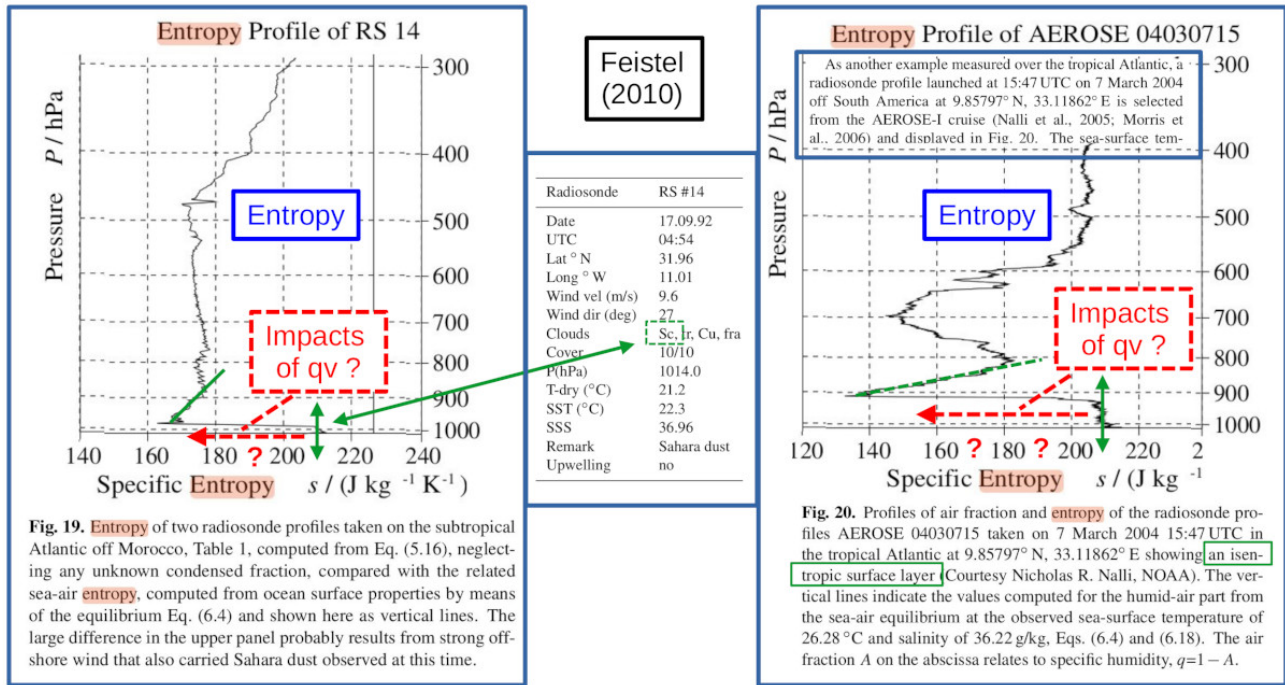


Figure 26: A study of the Figs. 19 and 20 of Feistel et al. (2010a, p.117-118)...