

Computation of moist-air surface entropy at Mauna Loa.

by *Pascal Marquet.*

CNRM, Université de Toulouse, Météo-France, CNRS, Toulouse. France. *E-mail: pascal.marquet@meteo.fr*

1) Motivations - Introduction.

Different assumptions exist for the calculation of the entropy of the atmosphere. A common practice in meteorology is to assume that the entropies of dry air and liquid water are zero at a pressure of $p_0 = 1000$ hPa and a temperature of $T_0 = 273.15$ K (0°C), leading to the “equivalent” version of the entropy defined with the reference values $s_{d0} = s_{l0} = 0$ (see for instance Pauluis *et al.*, 2010, Feistel. *et al.*, 2010).

In contrast, the usual practice in thermodynamics is to assume that “the entropies of all solids are zero for the most stable crystalline phase at 0 K” (the third law). Accordingly, the entropy for dry air at p_0 and T_0 is set to $s_{d0} \approx 6775$ J K⁻¹ kg⁻¹ in Hauf and Höller (1987) and Marquet (2011), $s_{d0} \approx 6776.1$ J K⁻¹ kg⁻¹ in Lemmon *et al.* (2000) and $s_{d0} \approx 6783$ J K⁻¹ kg⁻¹ in Stevens and Siebesma (2020). The more accurate value $s_{d0} \approx 6776.4$ J K⁻¹ kg⁻¹ is computed from the NIST-JANAF values at p_0 and T_0 (Chase, 1998).

The purpose of this note is to test some consequences of these hypotheses using CO₂ and surface atmospheric observations at the Mauna Loa observatory.

2) Dry-air values

Dry air is assumed to be composed of the four gases N₂, O₂, Ar and CO₂. The mole fractions (x) are taken from Table A2 in Feistel. *et al.* (2010) with 400 ppm (0.000400) for CO₂, 0.780848 for N₂, 0.209390 for O₂ and 0.009332 for Ar. The NIST-JANAF absolute (third-law) entropies at 1000 hPa and 273.15 K are (Chase, 1998): 6748.9 ± 0.7 J K⁻¹ kg⁻¹ for N₂, 6330.8 ± 1.1 J K⁻¹ kg⁻¹ for O₂, 3830.6 ± 0.1 J K⁻¹ kg⁻¹ for Ar and 4784.8 ± 2.7 J K⁻¹ kg⁻¹ for CO₂.

Fig. 1 (top) shows the change in CO₂ mole fraction at Mauna Loa over the period 1958 to 2020. The molar mass of dry air (M_d) increases over the period by 0.0015 g kg⁻¹, while the gas constant for dry air (R_d) decreases by 0.015 J K⁻¹ kg⁻¹. These “constants” are thus variable, and one tenth of these changes may provide an idea of the accuracy of these M_d and R_d values for a given decade. The blue dashed lines represent the values for 400 ppm retained in Feistel. *et al.* (2010).

The bottom panel in Fig. 1 shows the changes in absolute (red+black) and “equivalent” (blue+violet) dry-air entropies computed according to the formula:

$$s_{d0} = \sum_k x_k s_{k0} - \sum_k x_k \ln(x_k) R_k, \quad (1)$$

where x_k are the molar concentrations, s_{k0} the reference entropies, and $R_k = R/M_k$ the gas constants for each gases k , with $R \approx 8.314472$ J K⁻¹ kg⁻¹. The “equivalent” value is computed here with zero reference entropies $s_{k0} = 0$ but with a non-zero contribution from the second sum in (1), which depends on the partial pressures $x_k p_0$. A stricter definition that imposes a zero value of s_{d0} (Pauluis *et al.*, 2010, Feistel. *et al.*, 2010) corresponds to the constant green line. The absolute value is computed with the third-law reference values indicated above. The 2015 value ≈ 6776.38 J K⁻¹ kg⁻¹ for 400 ppm is close to the one computed with the standard NIST-JANAF values.

The absolute and equivalent formulations evolve differently over the period, one increasing while the other decreases, with a difference reaching $+0.3$ J K⁻¹ kg⁻¹ in 2020 ($+0.08$ J K⁻¹ kg⁻¹ for the stricter definition). Since time variations of opposite sign have no physical meaning, only the absolute value of the entropies should be considered, as this alone corresponds to the definition given in thermodynamics.

3) Moist-air values

The entropy of moist air was calculated from hourly averages of temperature, pressure and humidity at 2m at Mauna Loa. The absolute water-vapour entropy at p_0 and T_0 if the NIST-JANAF third-law value $s_{d0} \approx 10318 \pm 2$ J K⁻¹ kg⁻¹. Figure 2 shows that if the temperature increases by more than 1 K on average over this period between 1977 and 2019, the pressure decreases by about 1 hPa and the water vapour content increases by about 0.4 g kg⁻¹. The larger monthly and annual variations can reach 2 K, 2 hPa and 2 g kg⁻¹.

The impact on the moist-air entropy (for the average trend over the period as well as for the monthly variations) is, again, of a different nature if one considers the absolute (red) or “equivalent” (blue) definitions of the moist-air entropy. The impact of water-vapour variations is clearly overestimated with the “equivalent” version, which is therefore not *equivalent* to the thermodynamic absolute definition of entropy.

4) Conclusions.

The data observed at Mauna Loa show: 1) that the quantities M_d and R_d should not be constants in weather forecasting and climate models; 2) that the entropy of both dry and moist air varies differently from what thermodynamics predicts if the “equiva-

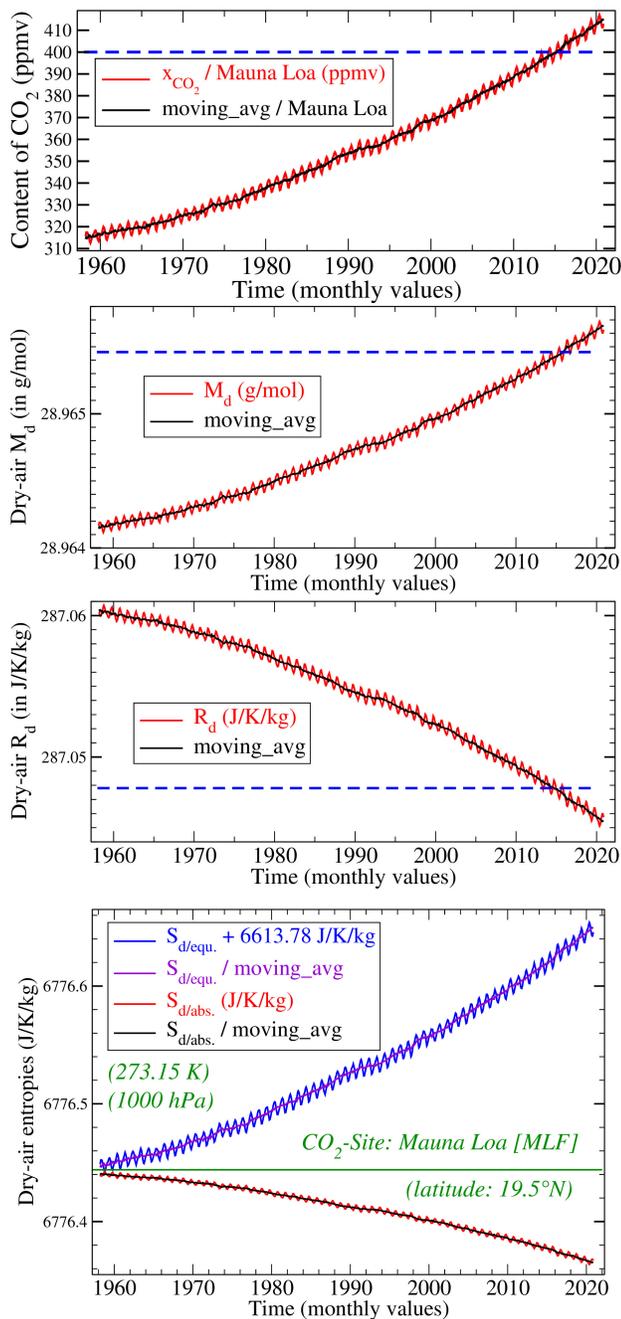


Figure 1: Change in several dry-air physical properties at Mauna Loa between 1958 and 2020 (monthly means).

lent” value is considered; 3) and therefore with the need to take into account the absolute definition of the moist-air entropy, which can be easily calculated from the third law and the NIST-JANAF dataset.

Acknowledgements

Monthly means and de-seasonalized CO₂ concentration at Mauna Loa are from Pieter Tans, NOAA/GML (www.esrl.noaa.gov/gmd/ccgg/trends/) and Dr. Ralph Keeling, Scripps Institution of Oceanography (scrippsco2.ucsd.edu/). Meteorology Measurements are from the NOAA/ESRL/GMD Baseline Observatories (Brian Vasel, Boulder, Colorado, brian.vasel@noaa.gov).

References

- Chase, M. W., (1998). *Journal of physical and chemical reference data. Monograph No9.*, NIST-JANAF thermochemical tables. Fourth Edition. American Chemical Society and American Institute of Physics.
- Feistel R., Wright D.G., Kretzschmar H.-J., Hagen E., Herrmann S.,

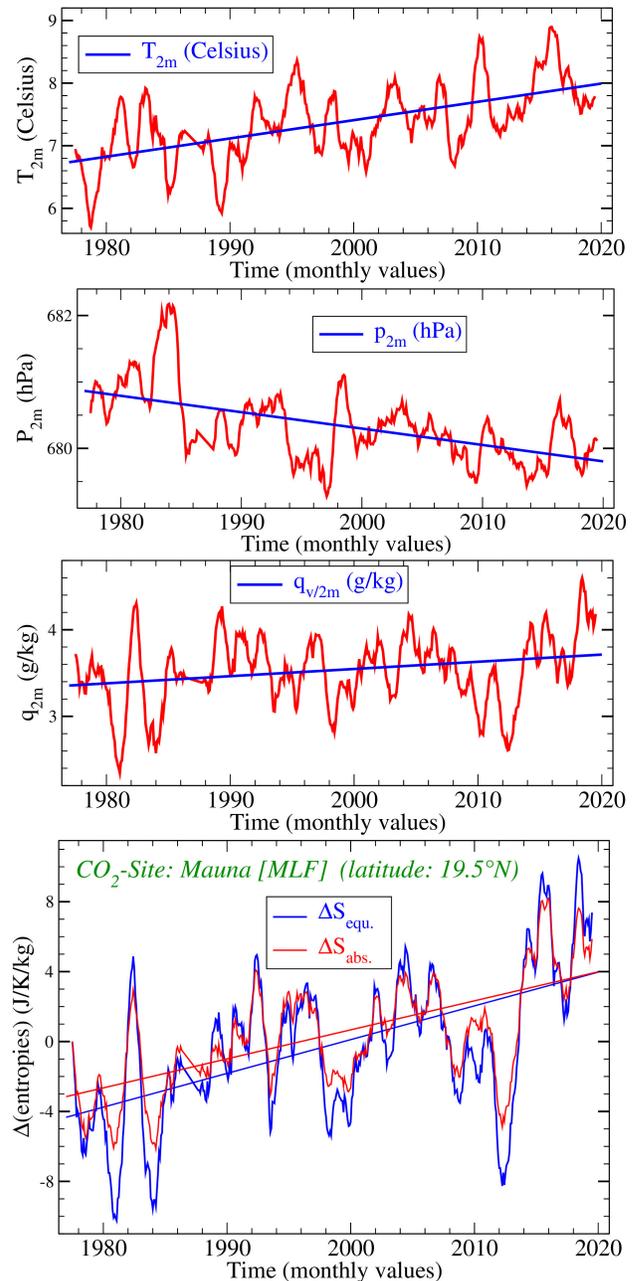


Figure 2: Change in several moist-air physical properties at Mauna Loa between 1977 and 2019 (hourly means).

Span R. (2010). Thermodynamic properties of sea air. *Ocean Sci.*, **6**: 91-141.

- Hauf T. and Höller H. (1987). Entropy and potential temperature. *J. Atmos. Sci.*, **44**: 2887-2901.
- Lemmon W.E., Jacobsen R.T., Penoncello S.G., Friend D.G. (2000). Thermodynamic Properties of Air and Mixtures of Nitrogen, Argon, and Oxygen From 60 to 2000 K at Pressures to 2000 MPa. *J. Phys. Chem. Ref. Data*, **29**: 331-385.
- Marquet P. (2011). Definition of a moist entropic potential temperature. Application to FIRE-I data flights. *Q. J. R. Meteorol. Soc.*, **137**: 768-791. <https://arxiv.org/abs/1401.1097>
- Pauluis O., Czaja A., Korty, R. (2010). The Global Atmospheric Circulation in Moist Isentropic Coordinates. *J. Clim.*, **23**: 3077-3093.
- Stevens B. and Siebesma A.P. (2020). *Clouds as Fluids*. In A. Siebesma, S. Bony, C. Jakob, & B. Stevens (Eds.), *Clouds and Climate: Climate Science’s Greatest Challenge* (pp. 35-73). Cambridge: Cambridge University Press.