A Third-Law Isentropic Analysis of a Simulated Hurricane

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ABSTRACT

The moist-air entropy can be used to analyze and better understand the general circulation of the atmosphere or convective motions. Isentropic analyses are commonly based on studies of different equivalent potential temperatures, all of which are assumed to fully represent the entropy of moist air. It is, however, possible to rely either on statistical physics or the third law of thermodynamics when defining and computing the absolute entropy of moist air and to study the corresponding third-law potential temperature, which is different from the previous ones. The third law assumes that the entropy for the most stable crystalline state of all substances is zero when approaching absolute zero temperature.

This paper shows that the way all these moist-air potential temperatures are defined has a large impact on (i) the plotting of the isentropes for a simulation of Hurricane Dumile, (ii) the changes in moist-air entropy computed for a steam cycle defined for this hurricane, (iii) the analyses of isentropic streamfunctions computed for this hurricane, and (iv) the computations of the heat input, the work function, and the efficiency defined for this steam cycle.

The moist-air entropy is a state function and the isentropic analyses must be completely determined by the local moist-air conditions. The large differences observed between the different formulations of moist-air entropy are interpreted as proof that the isentropic analyses of moist-air atmospheric motions must be achieved by using the third-law potential temperature defined from general thermodynamics.

1. Introduction

In a recent paper, Mrowiec et al. (2016, hereafter MPZ) investigated the thermodynamic properties of a three-dimensional hurricane simulation. The MPZ paper focuses on isentropic analysis based on the conditional averaging of the mass transport with respect to the equivalent potential temperature \( \theta_e \).

The methodology employed in MPZ originated in the concept of a thermal or Carnot heat engine applied to hurricanes by Riehl (1950), Kleinschmidt (1951), Emanuel (1986, 1988, 1991, hereafter E86, E88, E91), and Gray (1994) and to a study of steam cycle and entropy budgets described in Pauluis (2011, hereafter P11). In these papers, it is assumed that the equivalent potential temperature \( \theta_e \) or the saturation value \( \theta_{es} \) are logarithmic measurements of the moist-air entropy, according to
\[
s \approx S_{0m} + C_{pm} \ln(\theta_e) \quad \text{or} \quad s^* \approx S_{0m} + C_{pm} \ln(\theta_{es}),
\]
which are valid for unsaturated or saturated moist air, respectively. It is thus assumed that isentropic surfaces are represented by constant values of \( \theta_e \) or \( \theta_{es} \) despite the terms \( S_{0m} \) and \( C_{pm} \), which may depend on the water content and may thus vary with space or time, making the link between \( s \) and \( \theta_e \) or \( \theta_{es} \) unclear, at the very least.

The equivalent potential temperatures are sometimes replaced by the moist static energy counterparts \( C_{pm} T + L_{v} q_{v} + g z \) or \( C_{pm} T + L_{o} q_{sw} + g z \), where \( C_{pm} \) may depend on water vapor or condensed water contents, \( L_{v} \) is the latent heat of vaporization, and \( q_{v} \) or \( q_{sw} \) is the unsaturated or saturated specific content of water vapor, respectively.

The use of static energies or equivalent potential temperatures as a proxy for the moist-air entropy has been described and discussed at some length in other studies over the years: Malkus (1958), Miller (1958), Green et al. (1966), Darkow (1968), Madden and Robitaille (1970, 1972), Levine (1972), Betts and Dugan (1973), Betts (1973, 1974, 1975), Rotunno and Emanuel (1987), Emanuel et al. (1987), E88, Emanuel (1989),

In the present paper, it is shown that the way in which the moist entropy and the equivalent potential temperatures are defined may lead to opposite results in studies of isentropic processes in hurricanes. It is shown that, the more the total water varies with space, the more the isentropes differ, leading to large discrepancies in computations and plots of 1) the isentropes themselves; 2) the changes with space of the equivalent potential temperatures and the moist-air entropies for a thermodynamic heat cycle; 3) the isentropic streamfunction $\Psi$ defined in Pauluis and Mrowiec (2013) and studied in MPZ; 4) the heat input and work function studied in E88, E91, Emanuel (1995), Rennó and Ingersoll (1996), Pauluis and Held (2002a), and P11; and 5) the efficiency of a (moist) steam cycle defined in P11.

The definitions and the values of the heat input and work functions, the streamfunction, the efficiency, and the moist-air entropy itself cannot be subject to arbitrariness. This paper thus advocates using the absolute value of the moist-air entropy to study the thermodynamic properties of atmospheric processes or to perform isentropic analyses.

It is explained in appendix A that the third law of thermodynamics leads to such a physically founded definition of the absolute entropy, which can be computed for all substances. The third-law values are determined by using experimental calorimetric values of the specific heat and with the hypothesis that the same (zero) value of entropy is reached for the most stable crystalline state of all substances when approaching absolute zero temperature. Appendix A also explains that the third-law values are very close to values of entropies determined from theoretical methods based on statistical and quantum physics, for both mono- and polyatomic molecules. Accordingly, the term “third law” entropy will herein denote either the theoretical or the experimental absolute value of the entropy.

Appendix B recalls that several applications of the third law of thermodynamics to atmospheric studies already exist: Hauf and Höller (1987), Bannon (2005), and Marquet (2011, hereafter M11), a process recently improved by Marquet and Geleyn (2015) and Marquet (2015b, 2016b,c). It is thus possible to study the absolute moist-air entropy defined by $s(\theta_e) = s_{\text{ref}} + c_{pd} \ln(\theta_e)$, where both $s_{\text{ref}}$ and $c_{pd}$ are constant and where the third-law potential temperature $\theta_e$ is synonymous with the absolute moist-air entropy.

The paper is organized as follows. The definitions of most existing equivalent potential temperatures $\theta_c$ or $\theta_{es}$ are recalled in section 2a, together with the third-law value $\theta_e$. Several of the existing moist-air entropies are listed in section 2b, including the third-law value $s(\theta_e)$. A dataset derived from a simulation of Hurricane Dume in is presented in section 2c and isentropic surfaces corresponding to $\theta_c$ and $\theta_e$ are computed, plotted, and compared in sections 3a and 3b for a cross section of this hurricane. Differences in the associated moist-air entropies are described in section 3c and it is shown that the two isentropic streamfunctions computed in section 3d for both $\theta_c$ and $\theta_e$ exhibit large differences. The heat input and work function are computed in section 3e for a steam cycle in the so-called temperature–entropy diagram. The efficiencies of such steam cycles are computed and compared in section 3f for both $\theta_c$ and $\theta_e$.

Finally, conclusions are presented in section 4.

2. Data and method

a. Moist-air potential temperatures

The equivalent potential temperature $\theta_e$ defined by Eq. (4.5.11) in Emanuel (1994, hereafter E94) can be written as

$$\theta_{e/E94} = \theta^* \exp \left( \frac{L_u}{c_{pd} R_a T} \right) (H_l)^{-R_e r_e/c_{pl}},$$

where $\theta^* = T(p_0/p_d)^{R_d/c_{pl}}$, $T$ is the temperature, $p_0$ is the standard pressure, $p_d$ is the dry-air pressure, and $R_d$ and $R_e$ are the gas constant of water vapor and dry air, respectively. The specific heat $c_{st}^* = c_{pd} + r_c c_l$ depends on the values for dry air ($c_{pd}$) and liquid water ($c_l$). The mixing ratios $r_e$ and $r_c$ represent water vapor and total water, respectively. The quantity $L_u$ is the latent heat of vaporization. The relative humidity with respect to liquid water $H_l = e/e_{sw}$ is the ratio of the water vapor pressure ($e$) to the saturated value ($e_{sw}$).

The saturated equivalent potential temperatures studied in E86 and E94 will be written as

$$\theta_{es/E86} = \theta^* \exp \left( \frac{L_u r_{es}}{c_{pd} T} \right)$$

and

$$\theta_{es/E94} = \theta^* \exp \left( \frac{L_u r_{es}}{c_{pd} T} \right) (H_l)^{-R_e r_{sw}/c_{pl}},$$

where $p$ is the total pressure and $r_{sw}(T, p)$ is the saturation mixing ratio at temperature $T$ and pressure $p$. 

The equivalent potential temperature studied in Betts (1973, hereafter B73) can be written as
\[
\theta_{e/B73} = \theta_e \exp \left( \frac{L_v q_v}{c_p T} \right),
\]
where the dry-air potential temperature is \( \theta = T(p_d/p)^{\kappa} \) with \( \kappa = R_d/c_{pd} \approx 0.286 \).

The equivalent potential temperature \( \theta_e \) on page 1860 of MPZ can be written as
\[
\theta_{e/MPZ} = \theta_e \exp \left( \frac{L_v r_d}{c_p T} (H_r)^{-1} R_r / c_p \right).
\]

The difference between \( \theta_{e/MPZ} \) and \( \theta_{e/E94} \) is that \( p_d \) is replaced by \( p \) in the Exner function. The differences between \( \theta_{e/MPZ} \) and \( \theta_{e/E94} \) are that \( r_w \) is replaced by \( r \), and the additional term depending on \( H \) is included. The differences between \( \theta_{e/MPZ} \) and \( \theta_{e/B73} \) are that \( c_{pd} \) is replaced by \( c_p^* \), \( q_v \) is replaced by \( r_v \), and the additional term depending on \( H \) is included.

Even though the potential temperatures truly considered in MPZ are \( \theta_{e/E94} \), it is interesting to consider \( \theta_{e/MPZ} \) given by Eq. (5) in order to demonstrate that the a priori small change of \( p_d \) into \( p \) may have a large impact on the definition of isentropic processes.

The third-law based potential temperature defined in M11, Marquet and Geleyn (2015), and Marquet (2015b, 2016b,c) can be written as
\[
\theta_{s/M11} = \theta_e \exp \left( -\frac{L_v q_v + L_q q_i}{c_p T} \right) \exp(\Lambda q_v)
\times \left( \frac{T}{T_r} \right)^{\lambda q_v} \left( \frac{\eta}{\eta_r} \right)^{-\delta q_v} \frac{(1 + \eta_r)^{1+\delta q_v}}{(1 + \eta_r)_{\text{dry}}}
\times (H_r)^{\gamma q_v} (H_i)^{\gamma i} \left( \frac{c_q / c_{pd}}{T / T_r} \right) \left( \frac{c_q / c_{pd}}{T / T_r} \right),
\]
where \( \lambda = c_{pd}/c_p - 1 \approx 0.837, \eta = R_d/R_d \approx 1.608, \varepsilon = R_d/R_r \approx 0.622, \delta = \eta - 1 \approx 0.608, \) and \( \gamma = R_d/c_{pd} \approx 0.46 \). The term \( \Lambda_r \) is \( [(s_v)_r - (s_d)_r]/c_{pd} \approx 5.87 \) depends on the third-law values of the reference entropies for water vapor and dry air, and \( L_r \) is the latent heat of sublimation. The water vapor, liquid, ice, and total specific contents \( q_v, q_i, q_d \), and \( q_{pd} = q_v + q_i + q_d \) replace the mixing ratios involved in most of the previous formulations.

The water vapor and dry-air reference entropies \( (s_v)_r = s_v(T_r, e_r) \) and \( (s_d)_r = s_d(T_r, p_r - e_r) \) depend on the reference temperature \( T_r = 273.15 \) K, the total reference pressure \( p_r = 1000 \) hPa, and the water vapor partial pressure \( e_r \). However, it is shown in M11 that \( \theta_{s/M11} \) defined in Eq. (6) is independent of \( T_r \) and \( p_r \) if the reference mixing ratio \( r_r = e_r/(p_r - e_r) \approx 3.82 \) kg kg\(^{-1}\) corresponds to the saturating pressure value at \( T_r \); \( e_r = e_{sw}(T_r) = 6.11 \) hPa.

The first two lines of Eq. (6) are derived in (40) in M11. The four terms in the last line of Eq. (6) derived in Marquet (2016c) are improvements with respect to M11. They take possible nonequilibrium processes into account, such as under- or supersaturation with respect to liquid water (\( H_l \neq 1 \)) or ice (\( H_i \neq 1 \)) and possible temperatures of rain \( T_r \), or snow, \( T_s \), which may differ from the T for dry air and water vapor.

The advantage of the term \( (H_i)^{\gamma i} \) in Eq. (6) compared with \( (H_i)^{-1} \) in Eq. (1) or (5) is that \( q_i \) replaces \( r_i \) in the exponent, making no impact in clear air, or under- or supersaturated moist regions (where \( H_l \neq 1 \) and \( r_l \) may be large, but where \( q_i = 0 \) and having less impact in cloud in under or supersaturated regions (where \( H_l \neq 1 \) but where, typically, \( q_i < r_i \)).

The first- and second-order approximations of \( \theta_s \) are derived in Marquet (2015b, 2016b,c) and lead to
\[
(\theta_s)_1 \approx \theta_e \exp \left( -\frac{L_v q_v + L_q q_i}{c_p T} \right) \exp(\Lambda q_v),
\]
\[
(\theta_s)_2 \approx (\theta_s)_1 \exp \left[ -\gamma q_v \ln \frac{r_v}{r_e} \right] - \gamma q_v, \quad \text{and}
\]
\[
(\theta_s)_2 \approx (\theta_s)_1 \exp \left[ -\gamma q_v \ln \frac{r_v}{r_e} - \gamma(q_i + q_l) \right],
\]
where \( r_e \approx 0.0124 \) kg kg\(^{-1}\). Both \( (\theta_s)_1 \) and \( (\theta_s)_2 \) must be multiplied by the last line of Eq. (6) if nonequilibrium processes are to be described.

b. The moist-air entropies

The moist-air entropy is computed in M11 from the third law of thermodynamics. It can be written as
\[
s(\theta_{s/M11}) = s_{ref} + c_{pd} \ln(\theta_s) \quad \text{and}
\]
\[
s(\theta_{s/M11})/q_d = (s_{ref}/q_d) + (c_{pd}/q_d) \ln(\theta_s),
\]
where both \( s_{ref} \approx 1139 \) J K\(^{-1}\) kg\(^{-1}\) and \( c_{pd} \approx 1004 \) J K\(^{-1}\) kg\(^{-1}\) are constant, making \( \theta_s \) a true equivalent of the specific moist-air entropy. The formulation (11) is expressed “per unit of dry air,” in order to be better compared with the entropies computed in other studies such as E94 or MPZ.

Other definitions of “moist-air entropy” are derived with either \( s_{ref} \) or \( c_{pd} \) (often both of them) replaced by quantities that depend on the total-water mixing ratio \( r_w \). This is true in Eq. (4.5.10) in E94, which can be written as
Employing the French model Aire Limitée Adaptation (ALADIN–Réunion International (ALADIN), with a resolution of about 8 km. The ALADIN–Réunion model is as described in Montrotty et al. (2008) but with two main changes: (i) the diagnostic turbulence scheme (Cuxart et al. 2000) is based on a 1.5-order prognostic TKE equation and (ii) the shallow convection is based on Bechtold et al. (2001).

The ALADIN model is not perfect, owing to the uncertainties concerning the description of the dynamics (nonconservative schemes) and the thermodynamics (more or less accurate parameterizations of microphysics, turbulence, and clouds). Nonetheless, it is assumed that the quality of the ALADIN model is sufficient to describe, in broad terms, relevant spatial variations of the thermodynamic variables.

The two cross sections marked in Figs. 1 and 2 are plotted with the pseudoadiabatic potential temperature \( \theta_e^w \) and the relative humidity \( H_t \). The use of \( \theta_e^w \) gives a clear, unambiguous definition of thermal properties, differing from the uncertain and multiple definitions of \( \theta_e \) recalled in section 2a, which will be compared in later sections.

The 15 points describe a moist-air steam cycle similar to the one described in P11 and inspired by the Carnot heat engine studied by E86, E88, E91, and Emanuel (2004). The basic thermodynamic conditions \( (\rho, T, r_e, q_e = q_i = 0) \) of these points are listed in Table 1. The dry
descent follows a path of almost constant relative humidity between 60% and 70% (points 11–15).

The impacts of condensed water and of non-equilibrium terms will not be tested with these 15 points, chosen such that \( T_l = T_i = T \) everywhere and \( H_l = H_i = 1 \) and \( q_l = q_i = 0 \) for the just-saturated regions (points 5–7). However, these impacts are expected to be small in comparison with those induced by the large changes in \( q_t = q_y \), which vary from 3 to 17 g kg\(^{-1}\).

The eyewall and the core of Hurricane Dumile are similar to the Figs. 16 and 12 (top) plotted in Hawkins and Imbembo (1976) for Hurricane Inez, where \( u_e \) was likely computed as an equivalent for \( u_0 \), which is a kind of validation of the modeling of Hurricane Dumile by ALADIN. The same high values of \( u_0 \) observed in the eye of Inez are simulated in Fig. 1 for Dumile at the lower and upper levels. Figure 3 shows that the general patterns for \( \theta_e/B73 \) are similar to those for \( \theta_e \) shown in Fig. 1, but with change of labels for the potential temperature units. This confirms that the isolines defined by constant values of either \( \theta_e \) or \( \theta_e/B73 \) almost overlap.

3. Results

a. Impact on plotting isentropic surfaces

The cross section indicated in Fig. 4 for \( \theta_e \) exhibits great differences in comparison with Figs. 1 and 3 valid for \( \theta_e \) and \( \theta_e/B73 \) and with Fig. 2a for \( \theta_e/MPZ \) in MPZ. To facilitate comparisons, the isolines of \( \theta_e \) and \( \theta_e/B73 \) are plotted in Fig. 5 for the complete west–east cross section.

Generally speaking, the isentropes traced with \( \theta_e/M11 \) are smoother than the isolines plotted with \( \theta_e/B73 \). This can be interpreted as a moderate impact of the total-water content \( q_t \) on the moist-air entropy variable \( \theta_e/M11 \approx \theta_i \exp(6q_t) \), where the factor 6 is about two-thirds of that included in \( \theta_e/E94 \approx \theta_i \exp(9q_t) \). The general aspect of the isolines plotted in Fig. 5 is pretty similar to those that can be observed on polar–equator sections depicted in zonal averages (not shown).

The vertical changes in potential temperatures in the core region are characterized by minimum values of \( \theta_e \) close to the surface with increasing values above, up to 100 hPa. In contrast, maximum values are observed for \( \theta_e \) at 1000 hPa, with values decreasing up to 600 hPa and increasing values above.

At some distance from the center, \( \theta_e \) exhibits mid-tropospheric minimum values in the layers from 900 to 750 hPa while the minimum values of \( \theta_e \) and \( \theta_e/B73 \) are located higher, close to 700 hPa. The mixing in \( \theta_e \) is greater in the boundary layer below 950 hPa, while the vertical gradient in \( \theta_e \) is smaller than those for \( \theta_e \) and \( \theta_e/B73 \).

The isentropes plotted with \( \theta_e \) in Fig. 5 almost coincide with the isolines of \( \theta_e/B73 \) in the dry regions where \( q_t \) is small, namely in the high troposphere above the 200-hPa level and west of the core region (longitudes < 50°).
specific humidity $q_e$ is larger east of the core region because the hurricane is not symmetric (not shown). The isentropes are thus different from the isolines of $\theta_{s/B73}$ at all levels below 300 hPa and for longitudes between 56° and 60°. Consequently, the vertical tilts of the isolines of $\theta_s$ and $\theta_{s/B73}$ can be very different locally, and especially within the eyewalls of the hurricane (close to or above the points 4–9, where largest values of $q_e$ are simulated).

The isentropes computed with $\theta_e$ are therefore not compatible with the isolines of $\theta_{w/E}$ or $\theta_{s/B73}$ and the larger the specific content $q$, and the relative humidity $H_l$ are in Fig. 2, the more the isentropes differ in Fig. 5. It can be seen in Fig. 5 that the ascending branches of the eyewalls of Hurricane Dumile cannot follow both the isentropes plotted with the third-law value $\theta_s$ and the isolines of $\theta_{s/B73}$. This demonstrates that the different ways of computing the entropy, with either one of the formulations of $\theta_e$ or with $\theta_s$, cannot be true simultaneously. Only one of them can be applied to plot moist-air isentropes and, thus, to achieve isentropic analyses for the atmosphere.

**b. Impacts on computing potential temperatures**

All moist-air potential temperatures given by Eqs. (1)–(8) are plotted in Fig. 6 and listed in Table 2 (except $\theta_{e/M11}$).

Three groups of loops are shown in Fig. 6: (i) the three definitions for $\theta_e$, $(\theta_e)_1$, and $(\theta_e)_2$, are plotted in dark on the left; (ii) the three equivalent potential temperatures $\theta_{e/MPZ}$, $\theta_{e/E94}$, and $\theta_{e/B73}$ are plotted in light gray in the center; and (iii) the two saturated equivalent potential temperatures $\theta_{es/E86}$ and $\theta_{es/E94}$ are plotted in dark on the right.

Clearly, $(\theta_e)_1$, $(\theta_e)_2$, and $\theta_e$ remain close to each other with an accuracy of $\pm 0.8$ K for $(\theta_e)_1$, and with $(\theta_e)_2$ almost overlapping $\theta_e$ (errors are smaller than 0.08 K). This is new proof that $(\theta_e)_1$ and $(\theta_e)_2$ are accurate increasing-order approximations for $\theta_e$.

The equivalent formulations $\theta_{e/MPZ}$, $\theta_{e/E94}$, and $\theta_{e/B73}$ exhibit larger discrepancies, especially in the warm and moist ascent where differences of $\pm 2.5$ K are observed between 900 and 700 hPa. Moreover, the dry descent for the saturated versions $\theta_{es/E86}$ and $\theta_{es/E94}$ are 10 K warmer than that of other definitions of $\theta_e$, making the loops for $\theta_{es/E86}$ and $\theta_{es/E94}$ (where $r_w$ is replaced by the larger saturating value $r_{sw}$) much narrower than the others.

The saturated values $\theta_{es/E86}$ and $\theta_{es/E94}$ remain close to one another. The differences of about 1 K in the dry descents can be understood by computing the factor ($H_l$)$^{-(R_{sw}/c_p)\gamma}$ with $H_l \approx 60\%$, $R_{sw}/c_p \approx R_{w}/c_{pd} \approx 0.46$ and $r_{sw} \approx 15$ g kg$^{-1}$, leading to (0.60)$^{-0.46 \times 0.015} \approx 1.0035$ and to $1.0035 \approx 341.2$ K.

Moderate differences of about $\pm 3.5$ K are observed between the five potential temperatures at elevated levels, at 450 hPa where $\approx 3$ g kg$^{-1}$ is small. The impact is much larger at low level where $r_w > 15$ g kg$^{-1}$, with the ascent values of $\theta_e$ about 15 K colder than those for $\theta_e$ and $\theta_{es}$ at 950 hPa.

“Isentropic” surfaces or regions cannot, therefore, be the same when diagnosed using values of either $\theta_e$, $\theta_e$, or $\theta_{es}$. The comparisons described in MPZ, which were based on analyses of altitude-$\theta_{e/MPZ}$ diagrams

**Table 1.** Pressure (hPa), temperature (K), water vapor mixing ratios (g kg$^{-1}$), relative humidity (relative to liquid water, %), and pseudoadiabatic potential temperature (K) for the 15 points indicated in Figs. 1–3.

<table>
<thead>
<tr>
<th>N</th>
<th>$p$</th>
<th>$T$</th>
<th>$r_w$</th>
<th>$H_l$</th>
<th>$\theta'_e$</th>
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(MPZ’s Figs. 4 and 6–9), might be invalid since changes in the vertical direction may be of sign opposite the one for \( \theta_e \).

The solid disks plotted in Fig. 6 and the corresponding values in Table 1 show that ascents between the levels 800 and 450 hPa correspond to a small increase in \( \theta_u \) of about +1 K, while they correspond to a large decrease in \( \theta_e/\text{MPZ} \) of about –6 K. These differences in signs and in magnitudes between the properties of updrafts and downdrafts are not compatible with the differences in equivalent potential temperatures of about 5 K described in MPZ (p. 1867, right).

Another way to analyze the difference between \( \theta_u \) and \( \theta_e/\text{MPZ} \) or \( \theta_e/E94 \) is to consider the gap between descending and ascending values at 800 hPa: \( \Delta \theta_u \approx 17 \text{ K} \) and \( \Delta \theta_e/\text{MPZ} \approx \theta_e/E94 \approx 21 \text{ K} \). The difference is even larger for \( \Delta \theta_e/B73 \approx 24 \text{ K} \) and is much smaller for \( \Delta \theta_e/E86 \approx 12 \text{ K} \).

The important consequence of these findings is that changes in moist-air entropy represented by either \( \theta_u \) or any of the definitions of \( \theta_e \) cannot be simultaneously positive or negative, because it would then be impossible to decide whether or not turbulence, convection, or radiation processes would increase or decrease the moist-air entropy in the atmosphere. Moreover, since isentropic processes or changes in entropy must be observable facts, it is impossible to consider that all definitions given by Eqs. (1)–(8) are equivalent; at most only one them can correspond to real atmospheric processes.

\section{Impacts on computing moist-air entropies}

The issue of computing the relevant moist-air entropy is even harder than choosing one of the equivalent potential temperatures studied in the previous section, namely either \( \theta_u \) or one of the versions of \( \theta_e \) or \( \theta_{es} \). Since the aim of E86, E88, E91, Emanuel (2004), Pauluis et al. (2010), P11, or MPZ is to analyze meteorological properties in moist-air isentropic coordinates, a comparison of values of the moist-air entropy itself is needed. Let us therefore plot, in the temperature–entropy diagram of Fig. 7, the values of the six moist-air entropies considered in section 2b, with three of them listed in Table 3.

The differences between the loops (Carnot or steam cycles) are large. Some of the loops are very narrow, whereas others are wide and have a flared shape (a large gap between ascending and descending regions). Some of the loops are almost vertical (with a small change of less than \( \pm 20 \text{ J K}^{-1} \text{ kg}^{-1} \) in entropy between the surface and the upper air), whereas others exhibit a pronounced tilt (with a large decrease of \( 400 \text{ J K}^{-1} \text{ kg}^{-1} \) between the warm, moist regions and the cold, dry ones). The third-law entropy \( s(\theta_e) \) increases between points 2 and 10, whereas all the other formulations lead to a decrease between these two points.

Therefore, since the moist-air entropy is a state function, and since isentropic processes or changes in entropy must be observable facts, it is impossible to consider that all definitions given by Eqs. (10)–(15) are equivalent: at most only one of them can correspond to real atmospheric processes. Otherwise, it would be possible to modify the second law by imposing arbitrarily an increase or a decrease in entropy for an ascending parcel of moist air.

\section{Impact on isentropic streamfunctions}

An isentropic streamfunction \( \Psi(\theta_{e/E94}; z) \) is studied in Pauluis and Mrowiec (2013) and MPZ and the alternative third-law value \( \Psi(\theta_{s/M11}; z) \) is tested in this section. The isentropic streamfunction defined in MPZ can be written as...
\[
\Psi(\theta_{e}; z) = \int_{\theta_{\text{min}}}^{\theta_{\text{max}}} \int_{0}^{\infty} \langle \rho w \rangle(r, \theta, z) \, dr \, d\theta,
\]

where \( \theta_{\text{e}} \) stands either for \( \theta_{e/\text{E94}} \) or \( \theta_{e/\text{M11}} \), respectively. The isentropic mass flux \( \langle \rho w \rangle(r, \theta, z) \) is computed according to

\[
\langle \rho w \rangle = \int_{A} \rho[w - \bar{w}(z)] D(\theta) D(r) \, dx \, dy.
\]

The first rectangular function \( D(\theta) \) is different from zero and equal to \( 1/\theta_{\text{u}} \) for \( \theta = \theta_{\text{u}} \) and \( \theta_{\text{e}/\text{E94}} \) or \( \theta_{\text{e}/\text{M11}} \) varying from \( \theta_{\text{min}} = 320 \) K to \( \theta_{\text{max}} = 360 \) K in steps of \( \Delta \theta = 41 \) bin values. The second rectangular function \( D(r) \) is different from zero and equal to \( 1/15 \) km for \( r = r_{0} \) and \( r_{0} \) varying from 7.5 to 487.5 km in steps of \( \Delta r = 33 \) bin values. The radial distances \( r \) and \( r_{0} \) are computed with respect to the center of Hurricane Dumile and the average value \( \bar{w}(z) \) is computed for each vertical level for \( r < 495 \) km.

The diagram plotted in Fig. 8 for \( \Psi(\theta_{e/\text{E94}}; z) \) and for Hurricane Dumile is similar to the one plotted in Fig. 1b in Pauluis and Mrowiec (2013) and in Fig. 7a in MPZ for an idealized hurricane. The locations of the minimum values of the streamlines correspond to zero mean vertical mass flux and they are roughly aligned with the mean values of \( \bar{\theta}_{e/\text{E94}}(z) \) (solid line).

The arrows give some hints on the average anticlockwise circulations. Values of \( \theta_{e/\text{E94}} \) are conserved only for the descending branch between 4 and 2 km and for values close to 338 K. Values of \( \theta_{e/\text{E94}} \) decrease in the ascending branch below the freezing level at 5 km and they increase above this level up to the top of the troposphere.

The diagram plotted in Fig. 9 for the third-law streamfunction \( \Psi(\theta_{e/\text{M11}}; z) \) exhibits large differences with Fig. 8, in particular below the freezing level and for the larger values of \( q_{r} \).

Values of \( \theta_{e/\text{M11}} \) are conserved for the ascending branch between 1.5 and 4 km and for values close to 335 K. As in Fig. 8, the locations of the minimum

<table>
<thead>
<tr>
<th>N</th>
<th>( \theta_{e/\text{M11}} )</th>
<th>( \theta_{e/\text{E94}} )</th>
<th>( \theta_{e/\text{MPZ}} )</th>
<th>( \theta_{e/\text{BB73}} )</th>
<th>( \theta_{e/\text{E86}} )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>328.25</td>
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<td>348.10</td>
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</tr>
<tr>
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<td>339.62</td>
<td>348.34</td>
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</tr>
<tr>
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<tr>
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</tr>
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<td>321.09</td>
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</tr>
</tbody>
</table>
values of the streamlines are roughly aligned with the mean values of $\bar{u}_{\text{M11}}(z)$ (solid line). Moreover, a dashed straight line has been added on Fig. 9 to show an intriguing linear organization from 2 to 12 km, which follows the location of all minimum values of $C(u_{\text{E94}}/E_{86}; z)$. The upward and downward motions in Hurricane Dumile are located below and above this straight line and they correspond to monotonic increases and decreases in $u_{\text{E94}}/E_{86}$, respectively. This simple linear organization is not observed for $C(u_{\text{E94}}/E_{86}; z)$ in Fig. 8.

The underlying hypothesis justifying the study of the isentropic streamfunction is the fact that adiabatic and reversible processes lead to isentropic states, namely that any change in the moist-air entropy must correspond to diabatic sources or sinks. Accordingly, the diabatic processes of mixing and entrainment are considered in MPZ to explain 1) the decrease in $\theta_{\text{E94}}$ by following the streamlines of $\Psi(\theta_{\text{E94}}; z)$ from the surface up to the melting level and 2) the increase in $\theta_{\text{E94}}$ above the melting level. Clearly, if a similar increase of $\theta_{\text{M11}}$ is observed in Fig. 9 in dry regions above the freezing level, the decrease of $\theta_{\text{M11}}$ with $z$ below the freezing level does not exist, except for a small decrease close to the ground (below 0.5 km) which is likely due to the impact of surface heating.

Comparing Figs. 8 and 9 reveals that $\theta_{\text{E94}} \approx \theta_{\text{I}} \exp(9q_{\text{I}})$ overestimates the impact of humidity in comparison with the third-law value $\theta_{\text{M11}} \approx \theta_{\text{I}} \exp(6q_{\text{I}})$. The ratio 2/3 for the coefficients in factor of $q_{\text{I}}$ in the exponential functions reveals new patterns and it is thus important to use the absolute entropy $s(u_{\text{M11}})$ when computing the isentropic streamfunction given by Eqs. (16) and (17).
The differences between the potential temperatures $\theta_{E94}$ and $\theta_{S/M11}$ described by studying the outputs of the ALADIN model may depend on the various approximations that are made in all numerical models to describe moist-air processes and thermodynamic equations.

However, it is indicated in M11 that similarly large differences between $\theta_{E94}$ and $\theta_{S/M11}$ are observed for several vertical profiles of potential temperatures computed from the radial flights in stratocumulus for the First International Satellite Cloud Climatology Project (ISCCP) Regional Experiment (FIRE-I), Atlantic Stratocumulus Transition Experiment (ASTEX), Eastern Pacific Investigation of Climate Processes in the Coupled Ocean–Atmosphere System (EPIC), Second Dynamics and Chemistry of the Marine Stratocumulus field study (DYCOMS II) campaigns.

Moreover, it is possible to validate the previous results derived from numerical outputs of ALADIN for Hurricane Dumile by comparing these results with several observed soundings into Hurricane Earl (Wang et al. 2015). Figures 10a and 10b show that values of $\theta_{S/M11}$ near the ground are colder by about 11 K than those at altitude at 400 hPa or 10-km height, whereas values of $\theta_{E94}$ are warmer by about 10 K. In addition, the height of minimum value and the dispersion of the profiles are both smaller with $\theta_{S/M11}$ than with $\theta_{E94}$.

The shape of individual and average profiles in Figs. 10a and 10b are thus similar to the descending parts of the streamfunctions in Figs. 8 and 9 and of the loops of potential temperatures in Fig. 6. This confirms that the numerical outputs from the ALADIN model is a relevant laboratory to investigate isentropic processes and that large differences do exist between the potential temperatures $\theta_{E94}$ and $\theta_{S/M11}$.

e. Impacts on heat input and work functions

Many alternative definitions for the heat input or work functions have been considered in E86, E91, E94, Rennó and Ingersoll (1996), Pauluis and Held (2002a,b), and Goody (2003) and have been applied to different Carnot or steam cycles. The aim of this section is to use the outputs of Hurricane Dumile to compare the numerical values of the heat input and work functions computed for several of these definitions.

According to de Groot and Mazur (1984) and for a state of local equilibrium, the Gibbs differential equation for open systems can be written as

$$de_i + p\, dp^{-1} = dh - \rho^{-1} dp = T\, ds + \sum_k \mu_k\, dq_k,$$

where $e_i$ is the specific internal energy, $h$ the specific enthalpy, $\rho$ the density, and $\mu_k = h_k - T_s k$ the specific

FIG. 8. The isentropic streamfunction defined by Eq. (16) and by Eq. (4) in MPZ for $\theta_{E94}$ (10$^4$ kg m$^{-2}$ s$^{-1}$). The thin solid horizontal line represents the freezing level (273.15 K) at about 5 km. The solid line shows the vertical profile of the mean values of $\theta_{E94}$.

FIG. 9. As in Fig. 8, but for $\theta_{S/M11}$. The dashed straight line connecting the locations of the minima of this streamfunction have been added as in Fig. 8.
Gibbs’ function for $k = 0, 1, 2, 3$ denoting dry-air, water vapor, liquid water, and ice, respectively.

The work produced per unit mass of moist air $W = \int \rho^{-1} dp$ can then be computed by integrating Eq. (18) along a closed circuit. Since the integral of the total differential of enthalpy $\frac{1}{\rho} dh$ vanishes along such a loop, $W$ can be written as

$$W = -\int \frac{dp}{\rho(p)} = \int T(s) ds + \int (\mu_w - \mu_d) dq_t.$$  (19)

The last integral is derived from the last integral in Eq. (18) for the steam cycle considered in Figs. 1 to 4, where $q_l = q_i = 0$, $q_v = q_t$, and $q_d + q_l = 1$, leading to $dq_l = dq_i = 0$, $dq_v = -dq_w = -dq_t$, and thus to $\mu_v dq_w + \mu_v dq_v = (\mu_v - \mu_d) dq_t$. The same equation for $W$ holds true if liquid or solid water exist, provided that changes of phases are reversible, which implies $(\mu_v - \mu_l) dq_l = (\mu_v - \mu_w) dq_i = 0$.

With the help of $h = \sum_k q_k h_k$, $s = \sum_k q_k s_k$, and $\mu_k = h_k - Ts_k$, the Gibbs Eq. (18) can be rewritten as

$$-\rho^{-1} dp = T \sum_k q_k ds_k - \sum_k q_k dh_k.$$  (20)

This relation clearly shows that, since $dh_k = c_{pk} dT$ (for all species), $ds_k = c_{pk} dT/T - R_k dp_k/p_k$ (for gases) and $ds_k = c_{pk} dT/T$ (for liquids or solids), the reference values of enthalpies and entropies have no impact and may remain undetermined if the aim is to compute $-dp/\rho$.

Accordingly, the reference enthalpies $h_{v0}$ and $h_{d0}$ can be discarded in the computations of the enthalpies of water vapor and dry air contained in the last integral of Eq. (19), which depends on $(\mu_v - \mu_d) = (h_v - h_d) - T(s_v - s_d)$. This property holds true because $\int (h_v - h_d) dq_t = (h_{v0} - h_{d0}) dq_t = 0$ since $dq_t = 0$ for a closed loop.

In contrast, the reference entropies must be taken into account in the computations of $\int T(s_{d0} - s_{v0}) dq_t = (s_{d0} - s_{v0}) \int T dq_t$, because $\int T(q_j) dq_t \neq 0$ if the area of the loop is different from zero in a $T$-$q_j$ diagram. However, the impact of the reference entropies $s_{d0}$ and $s_{v0}$ on the last integral in Eq. (19) must cancel out with the impact on the integral $\int T(s) ds$. This means that a change in the reference entropies must modify the values of the two integrals on the right-hand side of Eq. (19), although their sum, which is equal to $W = -\frac{1}{\rho} dp$, must not depend on $s_{d0}$ or $s_{v0}$.

The integrals in Eq. (19) are computed in E94, Goody (2003), and P11 with all extensive quantities expressed per unit of dry air, and thus with the specific values of $h$ and $s$ replaced by $h/q_d$ and $s/q_d$. Furthermore, the
reference entropies for dry air and liquid water are assumed to vanish at $T_0 = 0^\circ C$ in $P11$, leading to

$$W_{d} = -\int \frac{dp}{\rho_d(p)} = \int Td\left(\frac{s}{q_d}\right) + \int g_v dr_v \quad \text{and} \quad (21)$$

$$g_v = c_v[T - T_0 - T \ln(T/T_0)] + R_v T \ln(H_v). \quad (22)$$

The work functions $W$ or $W_{d}$ are approximated in the older studies on Carnot cycles by considering only the first integral on the right-hand sides of Eqs. (19) or (21)—see $E91$ (Eqs. 4 and 10) and $Renn\hat{o}$ and $Ingersoll$ [1996, Eq. (3)]—yielding

$$W = W_H = \int T(s) ds \quad \text{and} \quad (23)$$

$$W_d \approx W_{H(d)} = \int T \left(\frac{s}{q_d}\right) d \left(\frac{s}{q_d}\right). \quad (24)$$

In Eqs. (23) and (24) $W_H$ and $W_{H(d)}$ are commonly called “heat input.” They are equal to the areas enclosed by the loops in the temperature–entropy diagram of Fig. 7 and they are independent of the global offset chosen for each loop. Values of the heat input $W_H$ and $W_{H(d)}$ listed in Table 4 are calculated using the simple but robust first-order Riemann method.

Large factors, of 0.5 and 4, are observed between $W_H \approx 870 \text{ J kg}^{-1}$, computed with the third-law value $s(\theta_r)$, and $W_{H(d)} \approx 442 \text{ J kg}^{-1}$ or $W_{H(d)} \approx 3405 \text{ J kg}^{-1}$, computed with $s(\theta_{c/E86})/q_d$ or $s(\theta_{c/E86})/q_d$, respectively. Furthermore, the impact of $c_v$ is very large compared to that of $c_{pd}$, leading to a factor of more than 6 for $W_{H(d)}$ computed with the same potential temperature $\theta_{c/E86}$ (442 vs 2758 J kg$^{-1}$).

The impact on $W_H$ of the definition per unit of dry air versus the definition per unit of moist air (specific value) can be evaluated by comparing $s$ and $s/q_d$ for the same third-law value $\theta_{c/M11}$. The impact $1528 - 870 = 658 \text{ J kg}^{-1}$ is large, leading to an increase of more than 75% for the definition per unit of dry air.

The impact of the choice of the different formulations for the moist-air entropy can be evaluated differently, by computing the wind scale $W_H = V^2/2$, with $V$ becoming a crude proxy for the surface wind that a perfect Carnot engine might produce. The last line in Table 4 shows that $V$ would vary from about 30 to more than 80 m s$^{-1}$.

Since temperatures can vary by 30 K along the Carnot cycle, and for an accuracy of about 1 J K$^{-1}$ kg$^{-1}$ for entropies, errors in computations of $W_H$ and $W_{H(d)}$ are on the order of 30 J kg$^{-1}$. This means that the observed differences, of the order of hundreds or thousands of joules per kilogram, are significant and, since the moist-air entropy is a state variable, the third-law formulation computed with $\theta_{c/M11}$ must be used to compute both $W_H$ and $W_{H(d)}$.

Independent computation of the integrals on the right-hand sides of Eqs. (19) and (21) is thus impossible without knowledge of the third-law reference entropies, because only the sum of these integrals is independent of these reference values. It is thus necessary to compute the full work function and to switch from a Carnot cycle to a steam cycle, for which changes in water vapor have a large impact via the last integrals of Eqs. (19) and (21).

It is assumed in $E88$ that part of the energy available from the steam cycle is actually used to lift water and is not available for the generation of kinetic energy. However, insofar as Eqs. (19) and (21) are considered without including these possible effects, the values of all integrals appearing for $W$ and $W_{d}$ are listed in Table 5. The left- and right-hand sides of either $W$ or $W_{d}$ are equal within an accuracy of about 40 J kg$^{-1}$, which is better than 10% for $W$ and 6% for $W_{d}$. This accuracy can be improved by using a Simpson second-order method, leading to 2.5% for $W$ and 0.5% for $W_{d}$ (not shown). This confirms the theoretical methods for establishing both Eqs. (19) and (21). In particular, it proves that the reference enthalpies and entropies of dry air and water vapor do not have an impact on $W$ and $W_{d}$.

It seems somewhat surprising that $W_{d}$ can be $(703 - 455)/455 = 55\%$ higher than $W$. However, this large difference is not a numerical artifact; it merely comes from the replacement of $\rho$ by $\rho_d$ in the computation of $W_{d}$. To demonstrate this result, values of $\rho$ and $\rho_d$ are shown in Fig. 11 for the 15 points of the steam cycle of Hurricane Dumile. To facilitate visual comparisons, the terms $F(p) = 0.7(p - 950)/450$ and $F(p) - 0.014$ have been added to $1/\rho$ and $1/\rho_d$, respectively. These terms are the same for a given pressure and they do not affect the computation of the differences between upward and downward values.

Although the replacement of $1/\rho$ by $1/\rho_d$ leads to a relative change of less than 2% if $q_v < 20 \text{ g kg}^{-1}$, the
of kinetic energy.

The aim of the present paper is not to provide the most general formulation for the work functions \( W \) given by Eq. (19) or (21). Indeed, \( W \) may be subject to some uncertainty with, for example, some additional terms that are added to Eq. (21) in E88. These additional terms are intended to take into account possible irreversible entropy sources ranging from the fallout of condensed phase water to irreversible mixing across water concentration gradients to freezing of supercooled water. Moreover, it is assumed in E88 that part of the energy available from the steam cycle is actually used to lift water and is not available for the generation of kinetic energy.

Differently, it is shown in the present paper that once a formulation for \( W \) is chosen, with or without the additional terms of E88, and provided that it is indeed derived from the Gibbs equation, the value of the work function may depend on the reference entropies of dry air and water vapor. And in this case, it is essential to use the values derived from the third law of thermodynamics.

f. Impacts on the efficiency of steam cycles

It was shown in the previous section that it is impossible to compute the integrals on the right-hand sides of Eqs. (19) and (21) independently. Nevertheless, calculations of this kind are often used in atmospheric science to evaluate the efficiency factor of a thermal engine.

The efficiency \( E \) of a tropical cyclone considered as a thermal engine was defined in Palmén and Riehl (1957) as the ratio of the mechanical energy produced to the heat released” and \( E \) was evaluated to be about 2%–3%.

The efficiency of a hurricane considered as a steam cycle is defined in P11 by taking account of the last integrals in Eqs. (19) and (21), which are intended to model the effects due to the open cycle in which mass is added and removed. These Eqs. (19) and (21) can be rewritten as

\[
Q_1 = \int \delta Q_1 = \int \left[ dh - \frac{dp}{\rho} \right] \quad \text{and} \quad (25)
\]

\[
Q_2 = \int \delta Q_2 = \int \left[ T ds + (\mu_v - \mu_d) dq_v \right], \quad (26)
\]

and

\[
Q_{1(d)} = \int \delta Q_{1(d)} = \int \left[ d \left( \frac{h}{q_d} \right) - \frac{dp}{\rho_d} \right] \quad \text{and} \quad (27)
\]

\[
Q_{2(d)} = \int \delta Q_{2(d)} = \int \left[ T d \left( \frac{s}{q_d} \right) + g_v dq_v \right]. \quad (28)
\]

The “energy input” \( Q_{in} \) is defined in P11 as \( Q_{in} = \int \delta Q^+ \), where \( \delta Q^+ = \max(0, \delta Q) \) is different from zero only for positive values of \( \delta Q \). The mechanical efficiency is then defined and computed in P11 by the ratio

### Table 5. Values of \( W \) and \( W_{(d)} \) computed by Eqs. (19) and (21) with Riemann integrals.

<table>
<thead>
<tr>
<th>( W/M11 )</th>
<th>( T ds )</th>
<th>( (\mu_v - \mu_d) dq_v )</th>
<th>( \Delta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>455</td>
<td>870</td>
<td>-371</td>
<td>-44 (-9.7%)</td>
</tr>
<tr>
<td>( W_{(d)/P11} )</td>
<td>( T d(s(q_d)) )</td>
<td>( g_v dr_v )</td>
<td>( \Delta )</td>
</tr>
<tr>
<td>703</td>
<td>1201</td>
<td>-458</td>
<td>-40 (-5.7%)</td>
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</table>
where all quantities are expressed per unit mass of dry air. From Eq. (22) in P11, this ratio can be approximated by \( X_S ≈ (T_{in} - T_{out})/1540 \) K, where \( T_{in} \) is the highest and \( T_{out} \) the lowest temperature of the cycle and where \((R_L L_d) / (R_C p_d) \approx 1540 \) K. The steam cycle considered for Hurricane Dumile corresponds to \( T_{in} \approx 296 \) K and \( T_{out} \approx 265 \) K, leading to \( X_S \approx 0.020 \).

Table 6 shows that \( W = Q_1 \approx Q_2 \) and \( W_{(d)} = Q_{1(d)} \approx Q_{2(d)} \) with the same accuracy of about 40 J kg\(^{-1}\) previously noted for the Riemann method. The differences \( Q_1 \neq Q_{1(d)} \) and \( Q_2 \neq Q_{2(d)} \) are due to the use of mixing ratios and of quantities expressed per unit mass of dry air in P11. This means that the way the work function is defined and computed may largely impact the diagnosis of the external heating required with any transformation of moist air and may modify the numerator of the efficiency factor given by Eq. (29).

Similarly, the way \( δ Q^+ \) and \( Q_{in} \) are computed may impact the denominator of Eq. (29). The computations of \( δ Q^+ \) for \( Q_1, Q_2, Q_{1(d)}, \) or \( Q_{2(d)} \) are especially uneasy because they rely on accurate definitions of all the enthalpies (\( h/\rho_q \)), the entropies (\( s/\rho q \)), and the Gibbs functions (\( \mu_u, \mu_d, \) or \( g_u \)). Moreover, whereas \( \frac{δ}{d} h = 0 \) for a closed cycle, the integral of \( dh \) is different from zero if it is computed only for those points where \( δ h > 0 \).

The enthalpy (\( h/\rho_q \)), entropy (\( s/\rho q \)), and Gibbs functions (\( g_u \)) appearing in Eqs. (27) and (28) are those defined in P11. The specific entropy involved in Eqs. (26) is the third-law value defined in M11 and recalled in Eq. (10). The specific enthalpy in Eq. (25) is the one defined in Marquet (2015 a,c):

\[
\begin{align*}
  h &= h_{ref} + c_{pd} T + \left( L_h q_d - L_v q_d - L_s q_d \right) + L_h (T_i) - L_v (T_i) - L_s (T_i) \\
  L_h &= h_{v} - h_d = L_h (T_i) + (c_{pu} - c_{pd}) (T - T_i).
\end{align*}
\]

where \( L_h(T_i) \approx 2603 \) kJ kg\(^{-1}\) and \( h_{ref} \approx 256 \) kJ kg\(^{-1}\). The Gibbs functions \( \mu_u \) and \( \mu_d \) are computed by \( h_u = T S_u \) and \( h_d - T S_d \), where \( h_d(T_i) \approx 530 \) kJ kg\(^{-1}\) and \( h_u(T_i) \approx 3133 \) kJ kg\(^{-1}\).

The latent heat \( L_h(T) \) defined in Eq. (31) depends on the values of \( L_u(T_i) \), in the same way as \( L_v \) depends on \( L_v(T_i) \approx 2501 \) kJ kg\(^{-1}\), and in the same way as the entropy potential temperature \( \theta_{SM11} \) defined in Eq. (6) depends on the third-law values \( \Lambda_r, (s_u)_r, \) and \( (s_d)_r \).

However, \( L_h(T) \) is independent of the reference temperature \( T_r \) because \( L_h(T_r) + (c_{pu} - c_{pd}) T_r \) is a constant, in the same way as \( L_v \) and \( L_s \) are independent of the value \( T \) used to compute them, and in the same way as \( \theta_{SM11} \) does not depend on \( T_r, p_r \), and \( r_e = r_{sm}(T_r, p_r) = ee \Delta p_r - e_r \) provided that \( e_r = e_{sm}(T_r) \).

The efficiency factors shown in the last column of Table 6 are almost the same for \( Q_1 \) and \( Q_2 \) on the one hand and for \( Q_{1(d)} \) and \( Q_{2(d)} \) on the other hand. However, the values, respectively close to 2.2% and 3.4%, are not compatible. Although these two efficiency values are close to those derived in Palmén and Riehl (1957), only the former value is close to the approximate value \( X_S \approx 0.020 \) derived in P11. The explanation for this important difference seems to come from the energy input terms \( Q_{in1} \) and \( Q_{in2} \), which are only 1% smaller than \( Q_{in1(d)} \) and \( Q_{in2(d)} \), whereas the full work functions \( Q_{1(d)} \) and \( Q_{2(d)} \) are 50% larger than \( Q_1 \) and \( Q_2 \).

The definitions of Palmén and Riehl (1957) or P11 for the efficiency factor may not be the most relevant ones. It is thus probably necessary either to change these definitions in order to be independent in the choice of the reference values of entropies and enthalpies or to use the third-law potential temperature, with all specific quantities expressed per unit of moist air, in order to comply with the recommendations of open-system thermodynamics.

### 4. Discussion and conclusions

Isentropic analysis is probably a powerful tool for investigating moist-air energetics by plotting moist-air isentropes or by computing isentropic mass fluxes. However, the quality and the realism of such an analysis rely on a clear definition of the moist-air entropy. It has been shown, here, that the way the potential temperatures \( \theta_s, \theta_e, \) or \( \theta_{es} \) are defined as “equivalents” of the moist-air entropy significantly impacts the computations and plots of isentropic surfaces, making “isentropic” analyses similar to those published in MPZ or P11 uncertain.

It has been pointed out that the streamfunction, the heat input, and the efficiency factor may be largely modified by the way in which the entropy and the enthalpy are defined: \( s \) or \( s/\rho q \); \( h \) or \( h/\rho q \); modified reference values for entropies and enthalpies; the choice of \( \theta_s, \theta_e, \) or \( \theta_{es} \); the choice of \( c_{pd} \) or \( c_{pd}' \) as a factor of the logarithm; etc.

The issue associated with the “per unit mass of dry air” view can be understood as follows. If isentropic
processes are defined as in E94, MPZ, and P11, with constant values of $s/q_d$, the definitions of the geopotential, the wind components, or the kinetic energy one should modify accordingly by plotting, for instance, $gz/q_d, u/q_d, v/q_d$, or $(u^2 + v^2)/(2q_d)$. These definitions are unusual in the thermodynamics of open systems. Moreover, if $s/q_d$ could be defined within a global constant $C$, the specific value $s$ would depend on $q_dC$, which varies with $q_d$ and renders the integral $S = \int \int \int q_dC \, d\tau$ indeterminate, because it would depend on $\int \int \int q_dC \, d\tau$, where $C$ is an unknown term. This is not realistic.

The third law of thermodynamics, which can be based on calorimetric, quantum, or statistical physics, can now be considered as well established. It provides a fortunate opportunity to compute, describe, analyze, and possibly understand several features of atmospheric energetics in a new way.

It is important to clearly differentiate the wish to define conserved variables like $\theta_t, \theta'_t, \theta_e$, or $\theta_{eo}$, on the one hand, from the need to define the specific moist-air entropy by computing the third-law value $\theta_s$, on the other hand.

These two aspects are complementary because a given process which might correspond to the law of conservation of $\theta_e$, for instance, may correspond to a change of entropy that can be precisely computed by using the third-law value $s(\theta_t)$. Conversely, a nontrivial isentropic process where $\theta_t$ is conserved, but where both $\theta_t$ and $q_t$ vary with time and space, might not correspond to a conservation of any of $\theta'_t, \theta_e$, or $\theta_{eo}$.

Moist-air isentropic surfaces are not subject to uncertainty in the natural world and it is likely that the third-law definitions $\theta_t$ and $s(\theta_t)$ given by Eqs. (6) and (10) are the most relevant, since they are based on general thermodynamic principles and use specific values expressed per unit mass of moist air, as with all other variables in fluid dynamics.

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APPENDIX A

The History of the Third Law of Thermodynamics

It is surprising that so many potential temperatures may serve to compute the moist-air entropy at the same time. Since the moist-air entropy is a state function, the status of the isentropic or diabatic evolution of a given parcel of moist air is an observable feature and, in the words of Richardson (1922, p. 157), “approximations are not here permissible.” The only way to solve this problem is to rely on general thermodynamics where the aim of the third law is precisely to provide an absolute and nonambiguous definition of the entropy state function. According to reviews of the old treatises and papers of thermodynamics (Lewis and Randall 1923; Wilks 1961; Barkan 1999; Coffey 2006; Klimenko 2012), there are three ways to express the third law.

In the mid- and late nineteenth century, an important problem in chemistry was how to improve the understanding of chemical reactions and to predict their spontaneity. The answer given by Gibbs (1878a,b) was to compute the sign of the Gibbs function (or free enthalpy) of reaction

$$\Delta G = \Delta H - T\Delta S = -T(\Delta S)_{tot},$$

where $\Delta H$ and $\Delta S$ are the enthalpy and entropy of reaction and $T$ is the temperature. Negative values of $\Delta G$ would make the reaction proceed spontaneously because, according to the second law of thermodynamics, the total entropy of the system and its surroundings, $(\Delta S)_{tot}$, would increase.

Gibbs (1878a, 150–152) explicitly introduced two constants of integration appearing in the computation of the specific energy, entropy, free energy, and free enthalpy for an ideal gas. He then arrived at the definitions of the entropy, free energy, and free enthalpy of a mixture of ideal gases [Eqs. (278), (279) and (293); p. 156 and 163]. These definitions depend on the constants of integration, which, a priori, are different for each individual gas and are multiplied by the individual variable concentrations. Moreover, since $\Delta S$ is multiplied by the variable temperature in the computation of $\Delta G$ given by Eq. (A1), the free enthalpy computed in Eq. (293) of Gibbs (1878a) must depend on the constants of integration for the specific entropies.

The problem of finding the numerical values of $\Delta H$, $\Delta S$, and $\Delta G$ was next considered by Le Chatelier (1888), Lewis (1899), Richards (1902), van’t Hoff (1904), and Haber (1905) with an alternative version of Eq. (A1). They all focused on the free energy $A = \Delta G$ on both sides of Eq. (A1) by using the Helmholtz equations

$$A = \Delta H + T \frac{dA}{dT} \text{ or } \frac{d}{dT} \left( \frac{A}{T} \right) = \frac{\Delta H}{T^2},$$

where $A$ represents the maximum available work (“maximaler Arbeit”). Comparison of Eqs. (A1) and (A2) shows that the derivative at constant pressure $dA/dT$ is equal to $-\Delta S$ (the opposite of the entropy of reaction).
The advantage of Eq. (A2) is that it provides the actual possibility of measuring the heat of reaction \( \Delta H(T) \) for different absolute temperatures from laboratory experiments, and then of finding the value of \( A(T)/T \) by an integration of Eq. (A2) between \( T_0 \) and \( T \), leading to

\[
A(T) = -T \int_{T_0}^{T} \frac{\Delta H(T')}{(T')} dT' + T \left[ \frac{A(T_0)}{T_0} \right].
\] (A3)

The knowledge of \( A(T) \) from Eq. (A3) should allow the spontaneity of any chemical reaction to be predicted, for a given temperature \( T \); it depends on the sign of \( A(T) = \Delta G \). However, the constant of integration \( A(T_0)/T_0 \) is multiplied by \( T \) and influences the value of \( A(T) \) and, thus, possibly the sign of \( \Delta G(T) \). This cannot be true because it would bring some arbitrariness into the spontaneity of the chemical reaction, making it possible to modify at will the behavior of chemical reactions like \( \text{H}_2 + \text{O}_2 = \text{H}_2\text{O} \) in the atmosphere by choosing any arbitrary value for the constant of integration \( A(T_0)/T_0 \) for the temperature \( T_0 \).

This problem was solved by Nernst (1907) in 1906 by assuming (page 49) a “new hypothesis,” which is nowadays called the “heat theorem”:

\[
\lim \frac{dA}{dT} = \lim \frac{d(\Delta H)}{dT} = 0 \quad \text{when} \quad T = 0 \text{ K}. \] (A4)

The heat theorem was not expressed in terms of the entropy but, instead, was based on the Helmholtz function \( A \), leading to \( A(T_0)/T_0 \to 0 \) as \( T_0 \to 0 \) K in Eq. (A3). This is the third law of thermodynamics in its original formulation suggested by Nernst.

Nernst tested the consequences of his theorem by computing the theoretical values of the affinities or the reaction rates of several chemical reactions. The good agreement he showed with experimental results supported his theorem. The hope of Nernst was then to demonstrate his theorem starting from the observed anomalous behavior of specific heats, which tend to zero at low temperature and with \( C(T)/T \) remaining finite at absolute zero, which implied that the entropy itself defined by \( ds = [C(T)/T]dT \) remained finite at 0 K.

In response to Einstein’s objections to the heat theorem, expressed during the First Solvay Congress in Brussels in the fall of 1911, Nernst (1912) suggested the alternative principle of unattainability of \( T = 0 \) (“Ünerreichbarkeit des absoluten Nullpunktes”), namely that absolute zero temperature cannot be reached in a finite time interval and in a finite number of steps. A proof for this second way to express the third law of thermodynamics is given in the recent paper Masanes and Oppenheim (2017).

Planck made the heat theorem more general in his third (1911) and fifth (1917) German editions of his Treatise on Thermodynamics (Planck 1917). The third formulation of the third law expressed by Planck was clearly based on the entropy and was written in two parts:

1) “The gist of the (heat) theorem is contained in the statement that, as the temperature diminishes indefinitely the entropy of a chemical homogeneous body of finite density approaches indefinitely near to a definite value, which is independent of the pressure, the state of aggregation and of the special chemical modification” (p. 273).

2) “…without loss of generality, we may write [this definite value] \( \lim(T \to 0) \) entropy \( = 0 \). We can now in this sense speak of an absolute value of the entropy” (p. 274).

The “finite density” hypothesis clearly excludes applications to perfect gases at 0 K and the third law must only be applied to the solid state. Planck wrote in the preface of the fifth edition in 1917, “The theorem in its extended form has in the interval (since 1911) received abundant confirmation and may now be regarded as well established.” However, it was discovered after 1917 that a residual entropy may exist for anomalous species like Ice-Ih at 0 K owing to quantum effects explained by Pauling (1935) and Nagle (1966) (proton disorder and remaining randomness of hydrogen bonds at 0 K). For these reasons, Planck’s formulation must now be amended and applied to the “most stable form of pure crystalline solid substances.”

Accordingly, the standard third-law values of entropies at temperature \( T \) and pressure \( p_0 \) can be written as

\[
s(T, p_0) = \int_{0}^{T} c_p(T, p_0)\frac{dT}{T} + \sum_{k} L(T_k, p_0) \] (A5)

The integral of the piecewise function \( c_p(T, p_0) \) is computed from 0 K to \( T \) for all solid(s), liquid, and gaseous states. The sum over \( k \) is extended to all transitions of phases occurring at \( T_k \) with the latent heats \( L(T_k) \).

The validity of the third law is now considered as established by the relevance of the computations of \( \Delta G \), which provide accurate predictions of the constants of chemical reactions and of the spontaneity of these reactions with respect to temperature. This is why thermochemical tables include absolute values for entropy \( S_0 \), whereas only relative standard enthalpies of reactions \( \Delta H^\circ \) are provided.

According to the results already available in Kelley (1932) and in more recent tables, the absolute values of entropies determined from the calorimetric method
(A5) and with the third law are in good agreement with the other available methods: 1) by using the statistical-physics method—that is, by computing the translational partition function and the corresponding Sackur–Tetrode equation valid for monoatomic gases only, and thus for Argon in the atmosphere (Grimus 2013); 2) by computing the partition functions valid for more complex molecules (like O2, N2, H2O, and CO2), including the impact of possible rotational, vibrational, or anharmonic vibration corrections or electronic states of molecules (Gordon and Barnes 1932; Gordon 1934, 1935, and subsequent works); 3) by analyzing residual-ray frequencies and infrared absorption spectra of crystals or by using calculations from spectroscopic data for gases; and 4) by measuring both $\Delta S$ and $\Delta H$, leading from Eq. (A1) to $\Delta S = (\Delta H - \Delta G)/T$.

It is important to note that the third law corresponds to a similar hypothesis, which is implicitly assumed in Boltzmann’s entropy written as $S = S_0 + k \ln(W)$, namely that $S_0$ is a constant, which is usually set to zero. It is clearly explained in Schrödinger (1989, lectures delivered in 1944 at Dublin) that the second part of the third-law assumption suggested by Planck (1917), to write $S_0 = 0$ without loss of generality, must not be regarded as the essential thing. This would create confusion and would draw attention away from the point really at issue, namely that $S_0$ is a universal constant that has no physical meaning only if it is independent of any internal physical parameters of any species, no matter what the value of $S_0$ might be.

The entropies of the five most frequent atmospheric species are listed in Table A1 for the values computed with either the third-law quantum statistical-physics (theoretical) method or with the third-law calorimetric (experimental) method. Good agreement can be observed between theoretical and experimental values. The larger discrepancy observed for H2O and GR96 (45.132 vs 44.31) is not observed for MG15 (45.2). The explanation for the larger value observed for O2 and N2 is similar (45.132 vs 44.31) is not observed for MG15 (45.2).

### APPENDIX B

#### Applications of the Third Law to Atmospheric Studies

The apparent paradox is that, while there is no chemical reaction, the third law discovered in thermochemistry must be applied if the moist-air entropy is to be computed in the atmosphere.

The close link between the two subjects can be understood by analyzing the simple case of mixing dry air and water vapor, both of them considered as perfect gases. If the gas constants $R_0$ and $R$, and specific heats $c_p$ and $c_v$, are assumed to be constant in the range of atmospheric temperatures (from 170 to 340 K), the entropies for dry air, water vapor, and moist-air mixing can be written as

$$
s_d(T, p_d) = c_p \ln(T/T_0) - R_d \ln(p_d/p_0) + s_{d0},
$$

$$
s_v(T, e) = c_v \ln(T/T_0) - R_v \ln(e/e_0) + s_{v0},
$$

$$
s(T, p, e, q_v) = q_d s_d(T, p - e) + q_v s_v(T, e),
$$

and

$$
s(T, p, e, q_v) = c_p \ln(T/T_0) - q_d R_d \ln[p - e/p_d] + q_v R_v \ln[e/e_0] + [q_d s_{d0} + q_v s_{v0}],
$$

where $p = p_d + e, q_d = 1 - q_v, and c_p = q_d c_{pd} + q_v c_{pv}$ and with the use of the partial pressures $p, e, p_d, and e_0$, which automatically takes the entropy of mixing of the two gases into account.

The impact of the last bracketed terms in Eq. (B4) is similar to the impact of the last bracketed terms in Eq. (A3). These terms are the product of the constants of integration $A(T_0)/T_0, s_{d0}$, and $s_{v0}$ by the variable terms $T(x, y, z), q_d(x, y, z)$, and $q_v(x, y, z)$, respectively.

Therefore, the same consequences as described for thermochemistry hold true for the atmosphere: in order to determine if a process is diabatic or isentropic, or for making isentropic analyses, it is necessary to compute local values of moist-air entropy with Eq. (B4) and, in particular, $q_d(x, y, z)s_{d0}$ and $q_v(x, y, z)s_{v0}$. Consequently,
the two reference values \( s_{d0} \) and \( s_{e0} \) must be known and the use of the third-law values would be in full agreement with general thermodynamics recommendations.

Bjerknes (2009) may well have been the first to imagine in 1904 to using entropy in weather prediction, as a prognostic variable in one of his seven basic equations. It is recalled in Marquet (2016a) that the consequences of the third law on atmospheric thermodynamics was described soon after in Richardson (1922, 158–160), who was already aware of the problem of the constant of integration in the entropy. Richardson suggested 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.” This corresponds to the use of the third-law values for \( s_{d0} \) and \( s_{e0} \).

However, Richardson was not able to continue accurate computations of the moist-air entropy in 1922 because values of \( c_p(T) \) were not available at that time for an absolute temperature varying from near zero to 350 K. These measurements were made later on for all atmospheric species by using the magnetic refrigeration method to attain extremely low temperatures far below 1 K (Giauque 1964 in 1949; Tiselius 1949). It is now possible to find the absolute values of entropies for all atmospheric species: \( \text{N}_2, \text{O}_2, \text{Ar}, \text{H}_2\text{O}, \text{CO}_2, \text{etc.} \) in thermodynamic tables. All these third-law values were already available in Kelley (1932).

The use made of entropy by Rossby et al. (1937) for a moist-air isentropic analysis was based on the use of the dry-air value \( \theta \). This seems unrealistic.

The first application of the third law for computing the moist-air entropies in atmospheric science was probably that of Hauf and Höller (1987), who wrote that “the entropy reference value \( q_v s_{d0} + q_s s_{e0} \) is not a constant,” and that “the values of the zero entropies have to be determined experimentally or by quantum statistical considerations,” namely from the third law or spectroscopic methods. They used the numerical values \( s_{e0} \approx 10320 \text{ J K}^{-1} \text{ kg}^{-1} \) and \( s_{d0} \approx 6675 \text{ J K}^{-1} \text{ kg}^{-1} \) for \( T_0 = 273.15 \text{ K} \) and \( p_{d0} = e_0 = 1000 \text{ hPa} \).

Another application of the third law to the atmosphere was that of Bannon (2005), who used the reference entropies given by Chase (1998) with the same value of \( s_{e0} \) but with a smaller value \( s_{d0} \approx 6612 \text{ J K}^{-1} \text{ kg}^{-1} \) for dry air.

The term \( \Lambda_r \) appearing in Eq. (6) depends on the standard values at 273.15 K and 1000 hPa considered in Hauf and Höller (1987) including a correction made in M11 to account for the impact of changes in partial pressures: \( e_r \approx 6.11 \text{ hPa for water vapor and } p_{d0} \approx 1000 - 6.11 \approx 994 \text{ hPa for dry air.} \) The reference entropies are \( s_{e0} \approx 12673 \text{ J K}^{-1} \text{ kg}^{-1} \) and \( s_{d0} \approx 6777 \text{ J K}^{-1} \text{ kg}^{-1} \), leading to \( \Lambda_r = [(s_{e0} - s_{d0})/c_{pd} = 5.87 \).

The third-law reference entropies given by A5 are explicitly computed in Marquet (2015c) and Marquet and Geleyn (2015) for \( \text{N}_2, \text{O}_2, \text{and H}_2\text{O} \). A larger value \( s_{d0} \approx 6848 \text{ J K}^{-1} \text{ kg}^{-1} \) for dry air is derived by considering the change in \( c_p(T, p_0) \) for \( O_2 \) at the second-order solid \( \alpha-\beta \) transition occurring at 23.85 K, forming a kind of Dirac pulse with no latent heat (Fagerstroem and Hollis Hallett 1969). The corresponding term \( \Lambda_r \approx 5.80 \) is 1.1% smaller than the one considered in M11. The reference entropies considered in Chase (1998) lead to a 2.7% larger value, \( \Lambda_r \approx 6.03 \), where the second-order transition for \( O_2 \) at 23.85 K is not taken into account in Joint Army–Navy–Air Force (JANAF) tables.

It is shown in Marquet (2015c, section 2.4) and Marquet and Geleyn (2015, section 5.3) that the linear combination \( (1 - a)s(\theta_e) + as(\theta) \) described in appendix C of Pauluis et al. (2010) can lead to the third-law value of entropy \( s(\theta_{eM11}) \) if the weighting factor is set to the value \( a = [(s_{e0} - s_{d0})/T/L_s(T_0) = 0.356. \) Another value for \( a \) would lead to a definition of the specific moist-air entropy which would disagree with the third law. The case \( a = 1 \) corresponds to \( S(\theta) \) if it is assumed that both \( (s_{e0}) \) and \( (s_{d0}) \) vanish at 0°C (\( T = 272.15 \text{ K} \)). The case \( a = 0 \) corresponds to \( S(\theta) \) if it is assumed that both \( (s_{e0}) \) and \( (s_{d0}) \) vanish at 0°C.

The definitions of entropy of moist air selected in the IAPWS guidelines (http://www.iapws.org/) are mostly based on reference-state conditions of vanishing entropies of both dry air and liquid water at the standard ocean state 273.15 K and 1013.25 hPa (IAPWS 2010; Feistel et al. 2010). However, an absolute (third-law) definition for entropy of ice-lh is envisaged in Feistel and Wagner (2006). It is based on Gordon (1934) and a value of \( 10320.7 \text{ J K}^{-1} \text{ kg}^{-1} \), which is close to that taken in Hauf and Höller (1987) and M11 for water vapor at 273.15 K and 1000 hPa.

The advantage of Eq. (10) is that both \( s_{e0} \) and \( c_{pd} \) are constant, making \( \theta_e \) a true equivalent of \( s \). Other definitions of \( \theta_l \) and \( \theta_s \), and even \( \theta_g \) defined in Hauf and Höller (1987), have the disadvantage of using values of \( s_{e0} \) and \( c_{pd} \) as factors of the logarithm, which both depend on \( q_r \) or \( r_s \), thus preventing these potential temperatures from being an equivalent of the moist-air entropy if \( q_r \) is not a constant.

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