

On Moist Potential Temperatures and Their Ability to Characterize Differences in the Properties of Air Parcels

PASCAL MARQUET^a AND BJORN STEVENS^b

^a CNRM, Université de Toulouse, Météo-France, CNRS, Toulouse, France

^b Max Planck Institute for Meteorology, Hamburg, Germany

(Manuscript received 2 April 2021, in final form 23 November 2021)

ABSTRACT: A framework is introduced to compare moist “potential” temperatures. The equivalent potential temperature θ_e , the liquid water potential temperature θ_ℓ , and the entropy potential temperature θ_s are all shown to be potential temperatures, in the sense that they measure the temperatures of certain reference-state systems whose entropy is the same as that of the air parcel. They only differ in the choice of reference-state composition— θ_ℓ describes the temperature a condensate-free state, θ_e a vapor-free state, and θ_s a water-free state—required to have the same entropy as the given state. Although in this sense θ_e , θ_ℓ , and θ_s are all different flavors of the same thing, only θ_ℓ satisfies the stricter definition of a “potential temperature,” as corresponding to a reference temperature accessible by an isentropic and closed transformation of a system in equilibrium; both θ_e and θ_ℓ measure the “relative” enthalpy of an air parcel at their respective reference states, but only θ_s measures air-parcel entropy. None mix linearly, but all do so approximately, and all reduce to the dry potential temperature θ in the limit as the water mass fraction goes to zero. As is well known, θ does mix linearly and inherits all the favorable (entropic, enthalpic, and potential temperature) properties of its various—but descriptively less rich—moist counterparts. All involve quite complex expressions, but admit relatively simple and useful approximations. Of the three moist “potential” temperatures, θ_s is the least familiar, but the most well mixed in the broader tropics, a property that merits further study as a possible basis for constraining mixing processes.

KEYWORDS: Conservation equations; Entropy; Thermodynamics

1. Introduction

The strong pressure dependence of many state variables can complicate attempts to compare the properties of atmospheric air parcels. For dry air, approximated as an ideal gas, the potential temperature θ elegantly describes an air parcel’s state. It does so by accounting for the effect of pressure on the state of the air parcel, which then facilitates comparisons of the properties of air parcels independent of their ambient pressure.

Physically, θ describes the temperature dry air would attain, were it brought adiabatically to a reference pressure, usually (but not necessarily) taken to be the standard pressure, $P_0 = 1000$ hPa. Mathematically,

$$\theta = T \left(\frac{P_0}{P} \right)^{\kappa_d}, \quad (1)$$

where T is temperature (in K), P pressure, and $\kappa_d = R_d/c_{p_d}$. Values of the dry-air gas constant, R_d , and the isobaric specific heat c_{p_d} depend on how dry air is defined—usually as N_2 , O_2 , Ar, and sometimes CO_2 , approximated as an ideal mixture of ideal gases specified in some fixed proportion.¹ As has been appreciated for some time (von Bezold 1888; Bauer 1910), θ is much more than a way to compensate for the effects of pressure

on temperature, it measures the buoyancy of air parcels (on isobars), the enthalpy of the air at a reference pressure, and it mixes linearly. It is also linearly proportional to the exponential of the dry air-parcel entropy s divided by c_{p_d} .

For a variable composition fluid, even for the limiting case of an ideal mixture of ideal gases, the situation is more complicated. Admitting condensable phases for the minor constituent, what we call moist air, complicates matters further. Earth’s atmosphere is, however, fundamentally composed of moist air—it cannot be understood without considering the water it contains. This makes it necessary to address these complications, and explains the rich literature that has developed, proposing one or the other generalization of the idea of the potential temperature to moist air. As it turns out, these *moist potential temperatures* all measure slightly different quantities, and while this point is generally well understood (see Pauluis 2018), physical understanding of exactly what they measure remains rudimentary.

Given the prominence of a literature that has made statements to the contrary (cf. Emanuel 1994; Pauluis et al. 2008; Raymond 2013; Romps 2015), it may come as a surprise that the equivalent potential temperature θ_e does not measure the entropy of an air parcel—not even approximately. Figure 1, which presents vertical profiles of the liquid-water potential temperature θ_ℓ the entropy potential temperature θ_s , and θ_e as calculated from thermodynamic measurements made during the recent Elucidating the Role of Clouds-Circulation Coupling in Climate (EUREC⁴A) field study, substantiates this point. All quantities are invariant for isentropic transformations of closed air parcels (viz., with a constant total water content), but this adiabatic invariance, as the figure demonstrates, does not mean that their differences (e.g., with altitude) are indicative of

¹ For the treatment of the thermodynamics it is common to neglect changing CO_2 and O_2 from burning fossil fuels.

Corresponding author: Bjorn Stevens, bjorn.stevens@mpimet.mpg.de

DOI: 10.1175/JAS-D-21-0095.1

© 2022 American Meteorological Society. For information regarding reuse of this content and general copyright information, consult the AMS Copyright Policy (www.ametsoc.org/PUBSReuseLicenses).

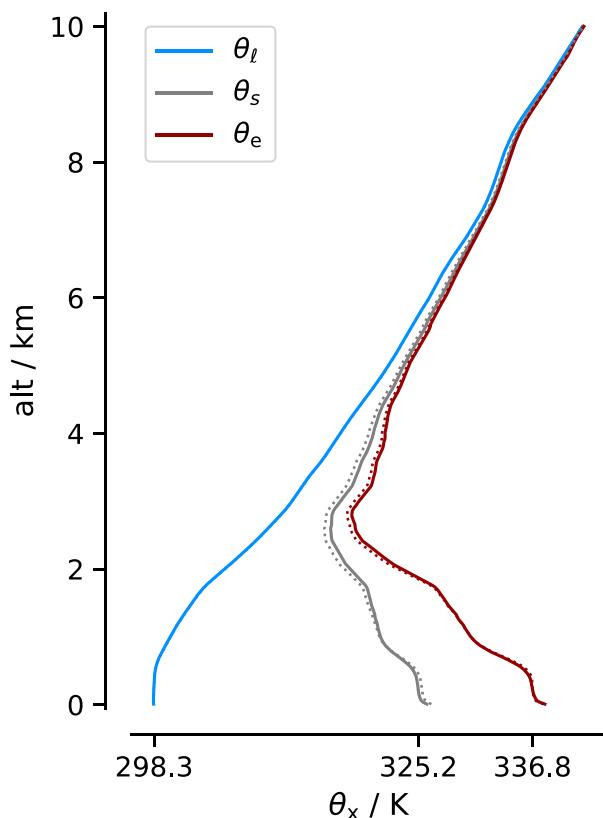


FIG. 1. Mean profiles of the liquid water (θ_l), entropy (θ_s), equivalent (θ_e) potential temperatures from 757 dropsondes launched along the EUREC⁴A circle (Stevens et al. 2021; George et al. 2021). Dashed lines are from slight approximations to the same quantities, as discussed later in the manuscript.

differences in entropy, nor does it guarantee that their isopleths are isentropes. Were this the case, then θ_e or θ_l could not take on different values for the same value of θ_s .

As it turns out, only $\theta_s \propto \exp(s/c_{p,d})$, and hence only its differences measure differences in s . Why this is so, how θ_s and the other moist potential temperatures relate to one another, and hence what precisely one compares when one compares their different values, are the subject of this paper. We begin by constructing a framework (section 2) that allows us to define precisely what we mean by the term potential temperature. This framework is used in section 3 to derive exact (within the framework of the given assumptions) expressions for θ_l , θ_s , and θ_e . These are physically interpreted, and compared to common simplified expressions of the same variables. The ability of the different moist potential temperatures to measure different air-parcel properties is evaluated in section 4. In section 5 examples are chosen to substantiate some of our main points, before concluding in section 6.

2. Terminology and definitions

a. Moist air

We idealize the atmosphere as *moist air*, i.e., as a mixture of dry air and water, allowing a portion of the latter to condense

TABLE 1. Subscript notation for the specification of particular states.

| Subscript | Description |
|-----------|---|
| 0 | Standard values, or quantities evaluated at standard values |
| r | A nonstandard reference value |
| 1, 2 | To distinguish different values or states, indexed by j |
| v, l, t | Vapor, liquid, and total water |
| * | Value at vapor–liquid (water) saturation |
| d | Dry component ($q_d = 1 - q_t$) for the two components system) |
| e | Equivalent (liquid) reference state ($q_l = q_t$) |
| l | Liquid-free reference state ($q_v = q_t$) |
| s | Absolute entropy value |
| x | Unspecified reference state defining the moist potential temperature θ_x |

as conditions dictate. In equilibrium, the thermodynamic state of the moist air is completely specified by three thermodynamic coordinates. For these we adopt the temperature T , the pressure P , and the water mass fraction (total-water specific humidity) q_t . A guide to the subscript notation adopted is given in Table 1.

To arrive at an analytically tractable description, and to facilitate precise statements, we make four further assumptions: (i) the specific heats are approximated as constant, i.e., not varying with temperature; (ii) the noncondensate phase (gas/vapor) is approximated to behave as an ideal mixture of ideal gases; (iii) the contribution of the condensate to the total volume is negligible; and (iv) only a single condensate phase is admitted, and this is treated as an ideal liquid, whose mass fraction is denoted q_l .

Assumptions (i) to (iii) are a common starting point for atmospheric thermodynamics (Emanuel 1994; Stevens and Siebesma 2020; Romps 2021), which facilitates analytic work (Ooyama 1990; Raymond 2013; Romps 2017). Approximation (iv) is adopted because including the ice phase introduces formal complexity that is not relevant to our arguments. Approximations (i) and (ii) can be relaxed by using the variable values of specific heat and nonideal effects based on International Association for the Properties of Water and Steam (IAPWS) and International Thermodynamic Equation Of Seawater—2010 (TEOS-10) tools (IAPWS 2010; Feistel 2018), but sacrifices analytic clarity for accuracy.

b. Reference states and notation

Many thermodynamic state functions, such as the entropy or the enthalpy are defined with respect to some reference-state value. For ice-free moist air in thermal equilibrium, a reference state can be fully characterized by specifying a reference temperature T_r , and the reference-state composition $\{P_{d,r}, q_{v,r}, q_{l,r}\}$. Here P_d denotes the partial pressure of the dry air, and the roman subscript “r” denotes a reference value. A description in terms of three (rather than two) additional state variables anticipates the possibility of

mechanical disequilibrium.² This possibility is required to accommodate the derivation of some of the moist potential temperatures in the proposed framework.

The specification of the reference state already illustrates how notation can be a challenge. In the present manuscript, subscripts are used to give specificity to a class of variables. For instance, roman subscripts *d*, *v*, and *l* are used to distinguish properties of dry air versus water vapor or liquid water. Roman subscript *t* is used to denote total water, whereby in an ice-free system $q_t = q_v + q_l$. In addition, we introduce the roman subscript *r* to identify a reference-state value, and *x* to denote quantities associated with a particular choice of reference-state composition. As a rule, and as summarized in Table 1, numeric subscripts are used to distinguish different air-parcel states (with 0 denoting standard values), and letters are used to denote a particular disposition of matter.

Three special compositions of the reference state are defined as special cases of *x*. These correspond to end-member (or limiting) situations whereby:

- e state:** denotes the “equivalent” composition of the reference state, whereby $x \rightarrow \{P_{d,0}, 0, q_t\}$, and hence is vapor free;
- ℓ state:** denotes the “liquidless” composition of the reference state, whereby $x \rightarrow \{P_{d,0}, q_t, 0\}$, and hence is condensate free;
- s state:** denotes the “entropic” composition of the reference state, whereby $x \rightarrow \{P_{d,0}, 0, 0\}$, and hence is water-free (dry).

Dalton’s law and state equations specify the partial pressures of the ideal gases in terms of the total pressure and the specific humidities, such that

$$P_{d,0} \equiv P_0 \left(\frac{1 - q_{tr}}{1 + \varepsilon q_{v,r} - q_{l,r}} \right), \quad \text{with} \quad \varepsilon = \frac{R_v}{R_d} - 1, \quad (2)$$

and correspondingly for $P_{v,0} = P_r - P_{d,0}$. The names (equivalent, liquidless, entropic) are not especially informative nor intuitive in this context, but chosen to keep consistency with historical usage.

c. The entropy temperature ϑ

For an ideal gas the specific entropy is given as

$$s(T, P) = s(T_r, P_r) + c_p \ln \left(\frac{T}{T_r} \right) - R \ln \left(\frac{P}{P_r} \right), \quad (3)$$

where $s(T_r, P_r)$, alternatively written as s_r , is the entropy at the reference temperature, T_r , pressure, P_r , and gas constant R (Fermi 1937). The entropy for the condensed phase can be expressed similarly, except that the dependence on pressure vanishes by virtue of the assumed incompressibility. The sum of the constituent entropies defines the system entropy,

$$s = q_d s_d + q_v s_v + q_l s_l. \quad (4)$$

Combining Eq. (3) with Eq. (4) results in a long expression for the entropy [see, for instance, Pauluis et al. (2010), Marquet (2011), Raymond (2013), and Stevens and Siebesma (2020), where however the dry-air and liquid-water or water-vapor reference entropies are sometimes set to zero]. By referring the component systems to a common reference temperature, the remaining terms can be combined into a single function ϑ such that without any further loss in generality:

$$s(T, P, q_t) - s_r = c_{p,r} \ln \left(\frac{\vartheta}{T_r} \right), \quad (5)$$

where $s_r \equiv s(T_r, P_r, q_{v,r}, q_{l,r})$, with $P_r = P_{d,r} + P_{v,r}$, and $c_{p,r}$ is the isobaric specific heat of the system in the reference state. Expanding Eq. (4) shows ϑ to be a function of both the state (T, P, q_t) and those aspects of the reference state that determine its composition, i.e., $\{P_r, q_{v,r}, q_{l,r}\}$.

Using the subscript *x* to remind us of how quantities depend on the composition of the reference state, allows us to write Eq. (5) as

$$s(T, P, q_t) - s_x(T_r) = c_x \ln \left[\frac{\vartheta_x(T, P, q_t)}{T_r} \right]. \quad (6)$$

Readers familiar with the Hauf and Höller (1987) entropy temperature will recognize it as the special case of ϑ_x with $x = e$, i.e., the vapor-free reference state $\{P_r = P_0, q_{v,r} = 0, q_{l,r} = q_t\}$. Leaving the composition of the reference state open (as indicated by *x*), enables a more general treatment of the moist potential temperatures ϑ_x . Notwithstanding this generalization, and the fact that ϑ_x measures entropy differences $[s - s_x(T_r)]$ rather than the entropy *s* itself, we also refer to ϑ_x as an “entropy temperature.” Calling it a “generalized entropy-difference temperature” would be more precise, but unwieldy and ahistorical.

d. Potential temperatures

Based on Eq. (6) we formalize the Stevens and Siebesma (2020) definition of potential temperature as follows:

Given a reference state whose *composition* is denoted by *x*, the potential temperature θ_x is the temperature (T_r) this reference state must adopt to have the same entropy as the given state.

Mathematically this defines θ_x , implicitly to satisfy $s - s_x(\theta_x) = 0$, for some given specification of *x*. It follows that $\theta_x = \vartheta_x$. The adjective “potential” describes how θ_x is the temperature the system *would* adopt were it brought to the reference state without changing its entropy. The potential temperature as defined above is thus a generalization of the Hauf and Höller (1987) entropy temperature.

By definition, θ_x is invariant for any isentropic transformation that does not imply a change in the reference-state composition. For dry air, the reference state is completely specified by P_r the reference-state pressure, usually taken to be standard pressure P_0 . A stricter form of the above definition, and one satisfied by the dry-air potential temperature θ would additionally require the transformations to be closed and reversible, but by this definition there can be at most one moist potential temperature.

² What we call mechanical equilibrium, which is a force (pressure) balance between phases, is sometimes referred to as phase equilibrium.

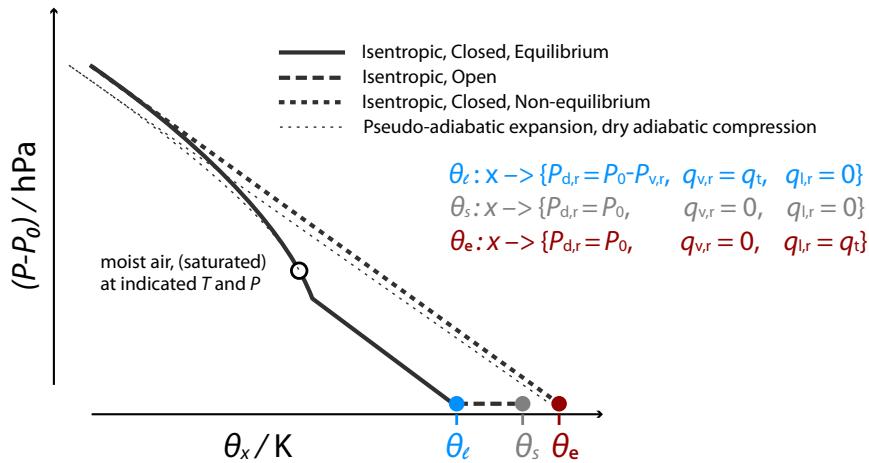


FIG. 2. Schematic of the moist potential temperatures as projected in (θ_x, P) coordinates. All connected points share the same entropy, with their different reference temperatures reflecting differences in the reference-state composition. The types of isentropic transformations that connect the different moist potential temperatures are indicated in the legend. That θ_s is in position 2/3 between θ_l and θ_e is explained further in the text.

The three moist potential temperatures θ_l , θ_s , and θ_e are shown below to correspond to the three limiting reference states (e, l, s) described above. Each is illustrated schematically in Fig. 2, whereby all of the points connected by lines in the figure share the same entropy, but the transformations that bring them to their respective reference states differ. Reversible transformations of the closed system are shown along the solid line, and the dashed–dotted lines show either nonequilibrium transformations (for instance associated with the condensate for $x = e$), or open transformations as associated with removing the water substance at constant entropy, for $x = s$.

3. Moist potential temperatures

a. The equivalent potential temperature θ_e

The oldest, and most familiar, moist potential temperature θ_e was introduced by Rossby (1932) as the value of θ for a parcel undergoing an infinite pseudoadiabatic ascent toward $P = 0$, with all the water removed by precipitation (Fig. 2). Hence it measures the potential temperature required of dry air, such that following an adiabatic expansion its temperature asymptotically approaches that of moist air expanded pseudoadiabatically—herein lies the modern idea of equivalence.³

In the present paper, and following contemporary usage, θ_e is defined as the temperature of a vapor-free (equivalent) reference state, with the same entropy, but for which all the

water is in the condensate phase at the standard pressure P_0 . This differs from Rossby’s definition by virtue of being isentropic (condensate is not precipitated from the parcel), hence “equivalence” is being drawn to a system in which the specific heat of the water mass is retained. Retaining the condensate maintains a closed system, but comes at the cost of the reference state being in a state of mechanical disequilibrium [$P_{v,r} \neq P_*(T_r)$].

In the equivalent (vaporless) reference state the specific heat and gas constants become

$$c_e = c_{p_d}(1 - q_t) + c_l q_t \quad \text{and} \quad R_e = R_d(1 - q_t). \quad (7)$$

With $q_l = q_t - q_v$, Eq. (4) becomes

$$s - s_e(T_r) = c_e \ln \left(\frac{T}{T_r} \right) - R_e \ln \left(\frac{P_d}{P_0} \right) + q_v(s_v - s_l) \quad (8)$$

where

$$s_e(T_r) = (1 - q_t) s_d(T_r, P_0) + q_t s_l(T_r) \quad (9)$$

is the reference entropy of the “equivalent” state at temperature T_r . The “equivalent” reference state, defined earlier as a dry-air and vapor-free fluid parcel with all water content in the liquid state, results from this Eq. (9) for $s_e(T_r)$ which depends only on s_d and s_l , as in Hauf and Höller (1987). A possible physical process for realizing such a state would be to separate the condensate as it forms, maintaining it in condensate form in thermal equilibrium with the gas—for instance by separating it from the gas with the help of a perfectly conducting membrane whose own heat capacity is vanishingly small.

At the temperature T , the entropy difference between two phases can be written relative to the saturation entropy s_* :

$$s_v - s_l = (s_v - s_*) + (s_* - s_l) = -R_v \ln \left(\frac{P_v}{P_*} \right) + \frac{\ell_v}{T}, \quad (10)$$

³ Marquet and Dauhut (2018) traces the idea of an “equivalent” potential temperature, to Normand (1921), who introduced it as a generalization of Schubert (1904, p. 18) and Knoche (1906, p. 3), and ultimately von Bezold’s concept of (“higher” or “supplemented” or “complete”) “equivalent” temperature (T_e). Normand’s equivalent potential temperature (θ_e) was defined using $c_{p_d} T_e = c_{p_d} T + \ell_v q_v$ and $\theta_e \approx \theta(T_e/T)$, where the T_e was the “moist equivalent” of T with the impact of q_v taken into account via the moist “total energy.”

where P_* is the saturation vapor pressure and $\ell_v = h_v - h_l$ is the vaporization enthalpy (or latent heat of vaporization). Recasting the above in the form of Eq. (6), and defining θ_e as the value of the reference temperature that satisfies $s_e(\theta_e) = s$, yields

$$\theta_e = \vartheta_{x=e} = T \left(\frac{P_0}{P} \right)^{\kappa_e} \exp \left(\frac{q_v \ell_v}{c_e T} \right) \Omega_e, \quad (11)$$

where

$$\Omega_e = \left(\frac{R}{R_e} \right)^{\kappa_e} \left(\frac{P_v}{P_*} \right)^{-q_v R_v / c_e} \quad (12)$$

and $R = R_d(1 - q_t) + R_v q_v$ is the moist-air gas constant. Equation (11) is identical to that found in modern textbooks (e.g., Emanuel 1994; Stevens and Siebesma 2020). The factor Ω_e , which is close to 1, is often neglected in practical applications. Its first term, proportional to the ratio of gas constants, absorbs the effect of defining θ_e in terms of P rather than P_d , and its exponent, $\kappa_e = R_e/c_e$, which also appears in Eq. (11), generalizes the analogous quantity for dry air to the equivalent reference system.

Physically, θ_e measures the temperature air would have if all of its vaporization enthalpy were used to warm the parcel (accounting for the specific heat of the condensate) at standard pressure. It does not satisfy our stricter definition of a potential temperature as the reference state is not in mechanical equilibrium, and complete condensation through expansional cooling can only be realized asymptotically.

b. The liquid-water potential temperature θ_ℓ

The liquid-water potential temperature θ_ℓ was introduced by Betts (1973) to study reversible changes of phase in nonprecipitating shallow convection. Following Stevens and Siebesma (2020) it can be derived from Eq. (6) by adopting a liquid-free reference state, denoted ℓ , in which all the condensate is assumed to be in the vapor phase at standard pressure and at temperature $T_{r,\ell}$. The corresponding specific heat and gas constants are

$$c_\ell = c_{p_d}(1 - q_t) + c_{p_v} q_t, \text{ and } R_\ell = R_d(1 - q_t) + R_v q_t, \quad (13)$$

and the reference entropy becomes

$$s_\ell = (1 - q_t) s_d(T_r, P_{d,0}) + q_t s_v(T_r, P_{v,0}), \quad (14)$$

where $P_{v,0} = P_0 - P_{d,0}$ with $P_{d,0}$ defined by Eq. (2). As the ℓ state is composed of a dry air and water vapor alone, a state of mechanical (phase) equilibrium is ensured as long as

$$q_t < \frac{R_d P_*(T_r)}{R_v P_0 - \varepsilon R_d P_*(T_r)}.$$

By substituting $q_t = q_v + q_l$, Eq. (4) can be written as

$$s - s_\ell(T_r) = c_\ell \ln \left(\frac{T}{T_r} \right) - R_d(1 - q_l) \ln \left(\frac{P_d}{P_{d,0}} \right) - R_v q_l \ln \left(\frac{P_v}{P_{v,0}} \right) - q_l(s_v - s_l). \quad (15)$$

In equilibrium $q_l(s_v - s_l) = q_l \ell_v / T$, namely, with either $q_l = 0$ or $P_v = P_*$. Recasting the above in the form of Eq. (6), and defining θ_ℓ as the value of the reference temperature that satisfies $s_\ell(\theta_\ell) = s$, yields

$$\theta_\ell = \vartheta_{x=\ell} = T \left(\frac{P_0}{P} \right)^{\kappa_\ell} \exp \left(- \frac{q_l \ell_v}{c_\ell T} \right) \Omega_\ell, \quad (16)$$

where

$$\Omega_\ell = \left(\frac{R}{R_\ell} \right)^{\kappa_\ell} \left(\frac{q_t}{q_v} \right)^{q_t R_v / c_\ell} \quad (17)$$

and $\kappa_\ell = R_\ell/c_\ell$. This equation differs slightly from the one derived by Betts (1973) as his Eq. (8) makes the tacit approximation that $d \ln P_v = d \ln P$, which neglects contributions from changes in q_v for saturated perturbations. Accounting for these effects gives rise to the small correction represented by Ω_ℓ , which departs from unity only when condensate is present in equilibrium. Equation (16) differs fundamentally from Hauf and Höller (1987), who by limiting themselves the e-state composition for the reference state, proposed a θ_ℓ -like quantity as an approximation to θ_e .

Physically, θ_ℓ measures the temperature the air would have were any (here liquid) condensate evaporated through a process of isentropic warming by compression. To the extent its reference state is in equilibrium, it is thus a potential temperature in the same (strict) sense as θ , provided that all condensed water can be evaporated in this reference state.

c. The entropy potential temperature θ_s

Despite frequent statements to the contrary, neither θ_ℓ nor θ_e are indicative of the specific entropy s of moist air. To address this shortcoming, Marquet (2011) introduced the entropy potential temperature θ_s . The insight required to ensure that θ_s measures entropy, is the necessity to completely standardize the reference-state composition, denoted by x . For a multicomponent system, doing so introduces a dependency on the absolute entropies, and a role for the third law in atmospheric physics (appendix B).

To adapt the various derivations of θ_s to our purposes we begin with the same form of the entropy equation as was used to derive θ_ℓ , namely, Eq. (15), which corresponds also to Eq. (B.10) (with $q_i = 0$) of Marquet (2011). Adopting a reference state for a dry atmosphere, at standard pressure, and defining θ_s as the value of the reference temperature that satisfies $s_d(\theta_s, P_0) = s$ implies that

$$\theta_s = \vartheta_{x=s} = \theta \exp \left(- \frac{q_l \ell_v}{c_{p_d} T} + \Lambda q_t \right) \Omega_s, \quad (18)$$

where

$$\Omega_s = \left(\frac{R}{R_e} \right)^{\kappa_d} \left(\frac{P_d}{P_{d,0}} \right)^{q_t \kappa_d} \left(\frac{P_{v,0}}{P_v} \right)^{q_t \gamma} \left(\frac{T}{T_0} \right)^{q_t \lambda}, \quad (19)$$

$$\gamma = R_v/c_{p_d}, \lambda = c_{p_v}/c_{p_d} - 1, \text{ and}$$

TABLE 2. Thermodynamic constants calculated with dry air composed with a CO₂ concentration of 420 ppmv.

| Constant | Value |
|----------------------------|---|
| T_0 | 273.15 K |
| P_0 | 100 000 Pa |
| $P_{s,0} = P_s(T_0)$ | 611.21 Pa |
| c_{p_d} | 1004.66 J kg ⁻¹ K ⁻¹ |
| c_{p_v} | 1865.01 J kg ⁻¹ K ⁻¹ |
| c_l | 4179.57 J kg ⁻¹ K ⁻¹ |
| R_d | 287.04 J kg ⁻¹ K ⁻¹ |
| R_v | 461.52 J kg ⁻¹ K ⁻¹ |
| $s_{d,0} = s_d(T_0, P_0)$ | 6776.2 J kg ⁻¹ K ⁻¹ |
| $s_{v,0} = s_v(T_0, P_0)$ | 10 319.7 J kg ⁻¹ K ⁻¹ |
| $s_{l,0} = s_l(T_0)$ | 3516.7 J kg ⁻¹ K ⁻¹ |
| $\ell_{v,0} = \ell_v(T_0)$ | 2500.93×10^3 J kg ⁻¹ |

$$\Lambda = \frac{s_v(T_0, P_{s,0}) - s_d(T_0, P_{d,0})}{c_{p_d}} \approx 5.867. \quad (20)$$

Reference entropies for water vapor, $s_v(T_0, P_{s,0}) \approx 12\,672$ J kg⁻¹ K⁻¹, and dry air, $s_d(T_0, P_{d,0}) \approx 6778$ J kg⁻¹ K⁻¹, are known up to ± 1.5 J kg⁻¹ K⁻¹. These uncertainties arise from uncertainties in the standard values (Table 2) from which they are computed. The accuracy of Λ is thus of about ± 0.003 unit.

Physically, θ_s is the temperature that dry air must have to have the same entropy as the moist system at standard pressure. Like θ_e and θ_ℓ , θ_s shares the property of reducing to θ for $q_{t,1} = 0$; however, in the form of Eq. (18) it does so more transparently. This can also be understood due to the relationship

$$s = s_{d,0} + c_{p_d} \ln \left(\frac{\theta_s}{T_0} \right), \quad (21)$$

which generalizes the dry-air formula derived by Bauer (1908) to moist air.

d. Reference states and pseudoentropies

A substantial and enduring body of literature (Pauluis et al. 2008, 2010; Raymond 2013; Romps 2015), which dates back to Emanuel (1994), introduces the moist potential temperatures, θ_e and θ_ℓ , as a measure of the entropy that would arise if the reference entropies in Eqs. (8) and (15)—respectively depending on $s_e(T_r)$ and $s_\ell(T_r)$ —were assumed to be zero. By adopting this approach one can arrive at expressions for θ_e and θ_ℓ that are equivalent to Eqs. (11) and (16), with the seemingly attractive property that $\theta_e \propto T_r \exp(s/c_e)$, and equivalently $\theta_\ell \propto T_r \exp(s/c_\ell)$. This has led many authors to conclude that θ_e and θ_ℓ measures the entropy, or at least a closely related quantity which Pauluis (2018) calls the “relative” entropy.⁴

A difficulty with defining the moist air entropy as a “relative” entropy, in the sense of Pauluis (2018), is that it is then measured relative to a reference state that varies with

⁴ As pointed out by Marquet and Dauhut (2018), this terminology risks confusion with the paper where the Shannon (1948) entropy is defined, but with another different quantity with the same name of “relative” entropy.

the composition of the system, so that comparing “relative” entropies of fluid parcels invariably conflates differences in their reference-state entropies. In a single component fluid, where the composition is fixed, this problem vanishes. To finesse this difficulty, some of the above cited studies have asserted that $s_{v,0} - s_{d,0}$, which defines Λc_{p_d} in Eq. (20), or analogously $s_{l,0} - s_{d,0}$ as determines $s_e(T_r)$, can be set arbitrarily without breaking the more general links between θ_ℓ , θ_e , and the moist-air entropy. For moist air, the matter-change entropies differentiate how different forms of matter contribute to the entropy, analogously to the phase-change entropies for different phases of matter. While this is important for specifying the entropy, the absence of conversions (chemical reactions) between the different forms of matter (water and dry air) makes the dynamic role of these matter change entropies less obvious than for the phase change entropies. This does not, however, ameliorate the difficulty, which is that if θ_e and θ_ℓ purport to measure the entropy relative to something, that *something* needs to be meaningfully specified.

To circumvent these difficulties Marquet (2011) derived θ_s . In terms of the present interpretative framework, θ_s can be understood as the result of an open-process that transforms the moist-air to a dry-air reference state by removing the water while heating to maintain constant entropy—isentropic desiccation. This then defines θ_s in terms of a reference state whose composition can be fixed absolutely ($q_{r,t} = 0$), thereby fixing $s_{r,x}$ and c_x independently of the state of the parcel, and recovering the desired property whereby $\theta_s \propto T_{r,s} \exp(s/c_s)$, as described by Eq. (21).

e. Simplified expressions

The moist potential temperatures are often approximated by neglecting the minor effects of water, i.e., on the thermodynamic constants, or the contribution of the partial vapor pressure to the total pressure. With this approximation $\Omega_x \rightarrow 1$ and

$$\tilde{\theta}_e = \theta \exp \left(\frac{+q_v \ell_v}{c_{p_d} T} \right), \quad (22)$$

$$\tilde{\theta}_\ell = \theta \exp \left(\frac{-q_l \ell_v}{c_{p_d} T} \right), \quad (23)$$

$$\tilde{\theta}_s = \tilde{\theta}_\ell \exp(\Lambda q_t), \quad (24)$$

with tilde denoting the approximation. Errors introduced by the use of Eqs. (22)–(24) in lieu of Eqs. (11), (16), and (18) are on the order of 1%, and tend to increase with differences in the pressure from the reference state (see Fig. A1 in appendix A). A sense of the errors associated with these approximations is given by Fig. 1, which also plots the approximations (dashed) alongside the actual values for the EUREC⁴A soundings.

Equations (22)–(24) are informative as to the differences in the magnitude of the different forms of θ_x . Taking $\ell_v/(c_{p_d} T) \approx 9$ and $\Lambda \approx 6$ yields

$$\ln\left(\frac{\theta_\ell}{\theta}\right) \approx \ln\left(\frac{\theta_s}{\theta}\right) - 6q_t \approx \ln\left(\frac{\theta_e}{\theta}\right) - 9q_t. \tag{25}$$

Because q_t is positive definitive, this positions θ_s at roughly the two-thirds position between θ_ℓ and θ_e , as observed in Fig. 1.

The different magnitudes of the moist potential temperatures reflect the different degree to which temperature has to compensate differences in the composition of the chosen reference state to maintain the same entropy. Comparing θ_e to θ_ℓ , for instance, shows that a system with all its water in the liquid phase must be much warmer, than the same system with all its water in the vapor phase, if it is to have the same entropy.

Keeping in mind that each of the moist potential temperatures describe the same system, with the same entropy, Eq. (25) shows how, due to q_t , none of the moist potential temperatures are proportional to one another. And although each describes (approximately) a system with the same entropy, at most one can actually be proportional to entropy, which is a state function whose difference between two points (i.e., states) takes a unique value.

4. Properties of the moist potential temperatures

By virtue of their derivation, the moist potential temperatures, θ_ℓ , θ_s , and θ_e are all potential temperatures in the weak sense of the term, i.e., being the temperature of a reference system with the same entropy as the actual system. Only θ_ℓ qualifies as a potential temperature in the strict sense of the term, i.e., corresponding to a reference temperature accessible by an isentropic and closed transformation of a system in equilibrium.

For θ_s the reference state has a different composition and thus cannot be attained by a closed system. For θ_e the reference state is in mechanical (phase) disequilibrium. Even for θ_ℓ , mechanical equilibrium of the reference state is only guaranteed for under or just-saturated water vapor pressure at $T_r = \theta_\ell$, which corresponds to $q_t < q_s(P_0, \theta_\ell)$, a restriction that is satisfied for most atmospheric conditions. Whereas the composition of the reference state with respect to which θ_s is defined is independent of the composition of the system it measures, the reference state for both θ_ℓ and θ_e is set equal to the composition of the system whose state they measure.

When comparing how differences in properties are measured by differences in the potential temperatures, it simplifies notation to introduce the difference operator Δ defined such that

$$\Delta[f(\chi)] \equiv f(\chi_2) - f(\chi_1) \tag{26}$$

for two states (enumerated by 1 and 2) of any variable χ and for any function f . Hence $\Delta[f(\chi)] = 0$ if $\chi_2 = \chi_1$. What distinguishes θ_s from θ_ℓ and θ_e is that $q_{r,s}$ is absolute, i.e., it is the same (zero in our case) for all states. Hence $\Delta(q_{r,s}) = 0$ by definition.

a. Entropy

For moist air and from Eq. (6), denoting by θ_x the temperature for the reference state whose composition is chosen by x such that $s = s_x(\theta_x)$, it follows that

$$\Delta s = \Delta[s_x(\theta_x)]. \tag{27}$$

For the case of dry air, the reference entropy (as measured relative to standardized values) with the temperature chosen in this way, satisfies

$$s_{d,r} = s_d(\theta, P_r) = s_{d,0} + c_{p_d} \ln\left(\frac{\theta}{T_0}\right) - R_d \ln\left(\frac{P_r}{P_0}\right). \tag{28}$$

Hence the difference between two reference states is given by

$$\Delta s_{d,r} = c_{p_d} \Delta[\ln(\theta)] - R_d \Delta[\ln(P_r)]. \tag{29}$$

These equations show that by standardizing the reference pressures (so that $P_{r,1} = P_{r,2}$), $\Delta s \propto \Delta(\ln\theta)$, hence differences in the dry-air potential temperature measure dry-air entropy differences.

Let us show that the same is not true for θ_ℓ and θ_e . Consider first the entropy differences between two liquidless ($q_t = q_v$) reference states (per the definition of the ℓ state, both are defined relative to standardized pressures, but can differ in composition, i.e., $q_{t,1} \neq q_{t,2}$). In this case, after a little bit of algebra, one can show that

$$\Delta[s_\ell(\theta_\ell)] = c_{\ell,2} \Delta[\ln(\theta_\ell)] + \Phi_\ell(q_{t,2}, q_{t,1}), \tag{30}$$

where

$$\begin{aligned} \Phi_\ell(q_{t,2}, q_{t,1}) = & \left[c_{p_d} \Lambda + (c_{p_v} - c_{p_d}) \ln\left(\frac{\theta_{\ell,1}}{T_0}\right) \right] \Delta q_t \\ & + R_d \Delta[(1 + \varepsilon q_t) \ln(1 + \varepsilon q_t) \\ & - (1 - q_t) \ln(1 - q_t)] \\ & + R_v \Delta[q_t \ln q_t - q_t \ln(\varepsilon + 1)]. \end{aligned}$$

Equation (30) shows that, even after standardizing the reference-state pressures the relationship between Δs and $\Delta(\ln\theta_\ell)$ is modified by Φ_ℓ , whose value depends on differences in the composition of the two states. Because $\Phi_\ell(q_{t,2}, q_{t,1}) = 0$ only if $q_{t,2} = q_{t,1}$, differences in θ_ℓ can only measures the entropy differences of systems with the same composition ($q_{t,2} = q_{t,1}$). The same is true for θ_e although the form of Φ_e differs from that of Φ_ℓ .

In contrast, for θ_s , by virtue of adopting a dry reference state (and standardizing the pressures),

$$\Delta[s_s(\theta_s)] = c_{p_d} \Delta[\ln(\theta_s)]. \tag{31}$$

To attain this property it is necessary to standardize the reference-state composition, i.e., to pick a reference-state composition x that is fixed independently of the composition of the given state. This of course means that isentropic transformations to this state cannot be closed. So while it is possible to define a moist potential temperature (in the weak sense) that measures entropy (θ_s), no moist potential temperature defined in the strict sense of the term can do so.

b. Enthalpy

Here we investigate to what extent the choice of a moist potential temperature influences its ability to measure enthalpy differences. For the dry potential temperature, $T = \theta$ at the

reference-state pressure, and so differences in θ measure differences in the reference-state enthalpies, i.e.,

$$\Delta h = c_{p_a} \Delta \theta. \quad (32)$$

It was in this sense that Helmholtz identified θ with what he called the Wärmegehalt (heat content).

Similar to the case for entropy, for moist air, compositional differences influence enthalpy differences in ways that the moist potential temperatures do not fully account for. For moist air,

$$h = c_\ell(T - T_0) - \ell_v q_t + h_{d,0} + (h_{v,0} - h_{d,0}) q_t \quad (33)$$

$$= c_e(T - T_0) + \ell_v q_v + h_{d,0} + (h_{1,0} - h_{d,0}) q_t, \quad (34)$$

where a discussion of the reference enthalpies are given in Marquet (2017). In atmospheric studies the “relative” enthalpies

$$h_\ell = c_\ell T - \ell_v q_t \quad \text{and} \quad h_e = c_e T + \ell_v q_v, \quad (35)$$

which form parts of Eqs. (33) and (34), are often introduced, and serve as the enthalpic contributions to the liquid water and moist static energies, respectively.

Given that θ_ℓ and θ_e respectively measure the temperature T at condensate-free and vapor-free reference states, it follows that changes in the reference-state enthalpy (not to be confused with the reference quantities, which are denoted by subscript 0) can be written as

$$\Delta(h) = \Delta(c_\ell \theta_\ell) + L_{\ell,0} \Delta(q_t) \quad (36)$$

$$= \Delta(c_e \theta_e) + L_{e,0} \Delta(q_t), \quad (37)$$

with $L_{\ell,0}$ and $L_{e,0}$ constant reference quantities readily deduced from Eqs. (33) and (34).

Equations (36) and (37) demonstrate how the dependence of the reference-state enthalpy on q_t conflates the relationship between $\Delta(h)$ in the reference state and $\Delta(c_e \theta_e)$. The situation for θ_ℓ is no different. However, for many purposes (e.g., measuring temperature changes from mixing) differences in reference temperatures and enthalpies play no role—knowledge of differences in “relative” enthalpies and q_t is sufficient. From Eq. (35) we note that in the reference state $\Delta(h_e) \rightarrow \Delta(c_e \theta_e)$ and $\Delta(h_\ell) \rightarrow \Delta(c_\ell \theta_\ell)$. This gives a weak form of correspondence between θ_e or θ_ℓ and their dry air counterpart θ .

Because θ_s defines the temperature dry air must have to have the same entropy as the moist system, differences in $\Delta\theta_s$ measure differences in the enthalpy of dry air with the same entropy as the moist systems being compared, but the meaning of this enthalpy is not especially informative. This is not unexpected given that $\Delta(\theta_s)$ was designed to measure changes in entropy, not enthalpy.

c. Linear mixing

Entropy S and enthalpy H for a given mass (m) are both extensive variables, whereas specific values for both entropy

($s = S/m$) and enthalpy ($h = H/m$) are intensive variables. The total entropy and enthalpy embodied in two parcels of air of mass m_1 and m_2 is the sum of the entropy and enthalpy of each parcel, respectively. When the parcels mix, the total entropy increases because the process is irreversible, but the total enthalpy does not change. Therefore, the specific enthalpy is linearly mixing, but the specific entropy is not.

Therefore, in addition to labeling entropy, being conserved along isentropes and measuring enthalpy differences at constant pressure, $\theta = (p_0/p)^{\kappa} T$ also mixes linearly for dry air at constant pressure. By this it is meant that if one lets m_1 and m_2 denote the specific masses of two air parcels, whose states are indicated by the enumeration (1 or 2), then upon mixing masses of dry air the value of θ is just the mass-fraction weighted sum of the constituents, i.e.,

$$\theta = \theta_1 + \eta \Delta(\theta) \quad \text{where} \quad \eta = \frac{m_2}{m_1 + m_2}. \quad (38)$$

This property of linear mixing is desirable of quantities used in numerical models. It is verified for the mixing of both enthalpy, and “relative” enthalpy, for dry and moist air, and extends to θ for the case of dry air. For this property to also be transferable to the θ_x thus requires $\Delta h_x = c_x \theta_x$.

From the discussion of the previous section, this would seem to be the case for $x \in \{e, \ell\}$. However, as pointed out there, $\Delta(h_x) \rightarrow c_x \theta_x$ only for the reference state. For mixing of air in a different state it is additionally required that the work done to move the mixed system from its reference state to the given state is the same as the work done on the component systems to move them to their reference state, that this is not generally satisfied is also why the moist static energies do not mix linearly (Bretherton 1987).

5. Examples

In this section we present several examples chosen to further illustrate the properties of various choices of θ_x . The first compares the structure of the tropical atmosphere as seen through profiles of θ_e , θ_ℓ , and θ_s . The second explores the ability of θ_x to measure changes in the state of the atmosphere resulting from the isobaric mixing of air parcels, using a challenging but relevant example of cloud-top mixing. The third compares the ASTEX observed vertical profiles of θ_e , θ_ℓ , and θ_s to study the transition from stratocumulus to cumulus.

a. Contrasting the wet and dry tropics

For the first example we compare the representation of the thermodynamic state in the troposphere in terms of θ_e , θ_ℓ and θ_s . Composite temperature and humidity profiles are derived from global storm-resolving (2.5 km) simulations from the Dynamics of the Atmospheric general circulation Modeled On Nonhydrostatic Domains (DYAMOND) project (Stevens et al. 2019) using the Icosahedral Nonhydrostatic (ICON) model (Hohenegger et al. 2020). The composite soundings are taken points over the ocean within the deep (10°S–10°N) tropics. Two soundings are constructed, the first by compositing over regions drier than the 10th percentile of precipitable water, the second by compositing over columns moister than

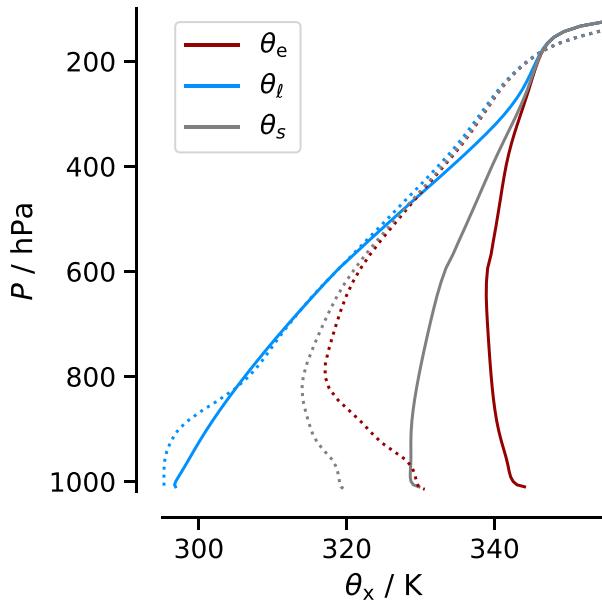


FIG. 3. Profiles of θ_e , θ_l , and θ_s for a composite sounding over the dry (dotted) and moist (solid) tropics.

the 99th percentile of precipitable water (to capture the very moistest convective regions). They thereby contrast the thermodynamic structure of the dry and wet tropics, the latter being indicative of regions of active convection.

Figure 3 complements Fig. 1 to more generally show how different expressions for θ_x have neither the same values, nor even the same structure. If each expression for θ_x were proportional to the entropy (or the entropy as measured relative to some reference), as is sometimes maintained, then how in the case of the moist atmosphere (solid lines) could θ_s increase in the lower atmosphere (between 800 and 600 hPa) while θ_e decreases. Likewise, how can θ_s decrease below 800 hPa in the dry sounding (left panel) where θ_l increases. This provides a vivid example of how differences in θ_e and θ_l measure differences in the entropy of the reference states of each profile, rather than differences in the entropy of the actual state. Put another way, if two gas quanta have the same entropy, but differ in composition, their values of θ_e and θ_l will vary to reflect these differences in composition.

In contrast, by virtue of being defined relative to an absolute reference state, θ_s is proportional to $\exp(s/c_{p,d})$. For both the dry and the moist soundings, profiles of θ_s vary less with height than profiles of θ_l or θ_e . The inference being that the entropy s is better mixed in the lower troposphere than one would surmise by associating it with θ_e or θ_l . And whereas in the dry atmosphere a surface thermal source and an above-PBL radiative sink of entropy are associated with an entropy minimum near (800 hPa), the entropy is everywhere increasing in the convective sounding. The profile of θ_s in particular emphasizes that the entropy of the lower troposphere is relatively constant, but that the dry regions have an entropy deficit as compared to the moist regions, presumably due to the radiant energy sink as air slowly subsides away from regions

of active convection. These properties are only possible to ascertain from the profile of θ_s .

As evident from Eq. (25) θ_e is consistent with constant θ_x , only for the case of constant q_t . Homogenizing θ_e while reducing q_t , as the moist profiles in Fig. 3 show to be the case in the convective state, increases θ_s .

b. Cloud-edge isobaric mixing

For the second example we compare isobaric mixing between two air masses at a cloud-top interface. The mixing of saturated and unsaturated air is nonlinear, so this provides a challenging but relevant test of the properties of the various forms of θ_x . The case we explore is based on measurements of marine stratocumulus made as part of the DYCOMS II field study, wherein a stratocumulus layer was topped by warmer and much drier air (Stevens et al. 2003). The conditions sampled during the first research flight satisfied the buoyancy reversal criteria, whereby the air aloft, which we designated by subscript 1, had a higher density temperature, $T_{\rho,1}$ than the air in the cloud, designated by subscript 2. This situation, whereby $T_{\rho,1} > T_{\rho,2}$, corresponds to a stable stratification in the absence of mixing. For the observed conditions, mixtures of the warmer drier air aloft with the cooler saturated air in the cloud layer, would (for a range of mixing fractions) result in air parcels denser than the air in the cloud layer. This is a mixing instability whose importance for the dynamics of marine stratocumulus continues to be debated (Deardorff 1980; Randall 1980; Mellado 2017).

We calculate $\Delta T_{\rho} = T_{\rho}(\eta) - T_{\rho,2}$ as a function of the mixing fraction η . As defined as in Eq. (38), η denotes the specific mass of one component (which we denote by subscript 2) of a binary mixture. For the reference (black line) we calculate the properties of the mixed air by virtue of both q_t and h_e [as given by Eq. (34)] mixing linearly at constant pressure P , leading to

$$q_t = q_{t,1} + \eta\Delta(q_t), \quad (39)$$

$$h_e = h_{e,1} + \eta\Delta(h_e). \quad (40)$$

Together with the fixed pressure P , this defines the state of the system, from which T and T_{ρ} can be calculated.

Figure 4 confirms our earlier arguments that none of the formulations for θ_x linearly mix. Although our particular example involves phase changes, the structure of the error in Fig. 4 (right panel), which is on the order of 5%–10% and maximizes (near $\eta = 0.6$) for unsaturated mixtures, is primarily due to the effect of Δq_t rather than from phase changes.

This analysis serves as a reminder that isentropic invariance (conservation) of a thermodynamic quantity does not guarantee that it mixes linearly. For the case of θ_s this should be clear, as the mixing itself is a source of entropy and $s \propto \ln(\theta_s)$. Adopting a log mixing rule, i.e.,

$$\theta_s(\eta) = \exp\left\{\ln(\theta_{s,1}) + \eta\Delta\left[\ln(\theta_s)\right]\right\}, \quad (41)$$

is thus equivalent to (incorrectly) assuming linear mixing of s . This, at least, gives the resultant temperature errors a physical

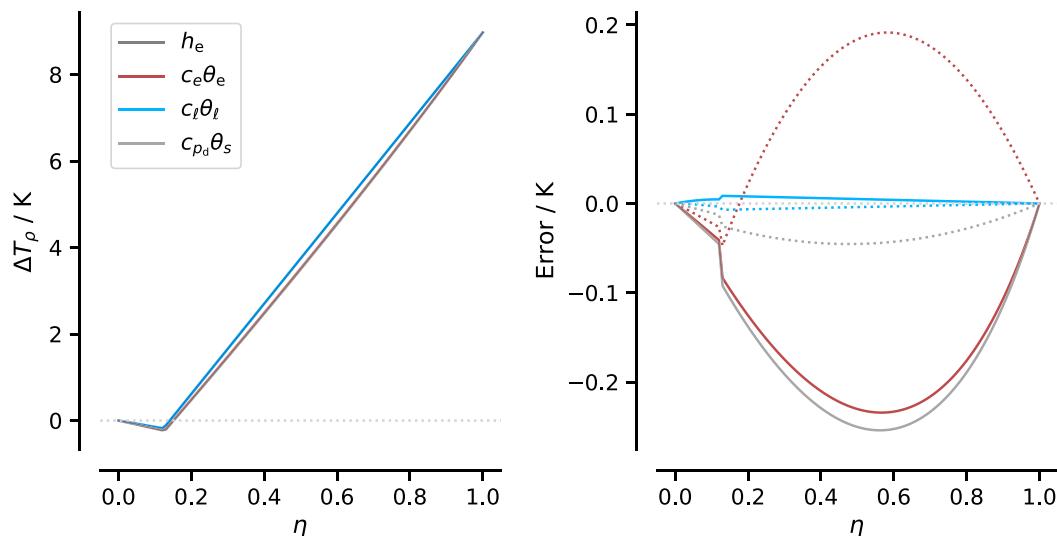


FIG. 4. Buoyancy perturbation between isobaric mixing of saturated ($T = 283.02$ K and $q_t = 9.0$ g kg $^{-1}$) and unsaturated air ($T = 292.94$ K and $q_t = 1.5$ g kg $^{-1}$) at 920 hPa with a cloud-top water content of 0.7 g kg $^{-1}$. (left) The buoyancy temperature derived by mixing parcels based on their moist “relative enthalpy” h_e is plotted vs mixing fraction, along with the error. (right) Errors are compared for the mixing of the exact $c_x\theta_x$ (solid) vs the simplified $c_{p_d}\theta_x$ (dotted) versions. Color coding is indicated in the key in the left panel.

interpretation, i.e., that which arises from neglecting the entropy production through mixing (Richardson 1919). Errors incurred by linearly mixing θ_e or θ_l are more challenging to interpret.

c. Stratocumulus–cumulus transition

For the third example we study profiles of θ_x for the 43 observed sounding profiles of the first ASTEX Lagrangian experiment described in Bretherton and Pincus (1995) and de Roode and Duynkerke (1997). The profiles are shown for the respective values of θ_x in Fig. 5. The sets of profiles are subjectively associated with different cloud regimes. Stratocumulus profiles (colored blue) are associated with mixing from cloud top to the surface and have extensive cloud cover. Profiles associated with cumuliform cloud regimes, are colored black. The transition between the two, often associated with stratocumulus whose thermodynamic properties are differentiated (decoupled) from the thermodynamic state of the subcloud layer, are colored red.

As a consequence of the changing profile of q_t , the cloud transition admits very different interpretations depending on which form of θ_x it is viewed from. Transition profiles are associated with a weakening of the negative θ_l gradients in the hydrolapse⁵ regions that demarcates the top of the marine (moist) layer, and a reversal above a certain threshold value of the gradient as measured by θ_e . The latter is the basis for the cloud-top entrainment instability hypothesis (Randall 1980). The behavior of θ_s is somewhat different, as the transition is better demarcated by a homogenization of θ_s in the

lower troposphere and almost a null top-PBL jump. Whether this is the cause as once suggested by Richardson (1919), or an effect, of increased lower tropospheric mixing is difficult to say, particularly given the strong entropy sources and sinks in this region of the atmosphere. Nonetheless the observation, whereby θ_s gradients tend to vanish as stratocumulus gives way to shallow cumulus, has recently been used by Marquet and Bechtold (2020) to introduce an index for demarcating regions of stratocumulus from cumulus.

6. Conclusions

Our main conclusion is that it is hard to avoid accounting for composition when comparing air parcels whose composition varies. While this might seem trivial, a poor recognition of this fact can, and has, led to considerable confusion—for instance, the idea that somehow θ_e measures entropy.

In retrospect it seems obvious that composition matters for varied air-parcel properties in ways that the introduction of a single moist potential temperature cannot account for—a point also emphasized by Pauluis et al. (2008). Recognizing this fact raises the question as to whether the different moist potential temperatures measure the same thing, and if not, then what precisely do they measure?

We answer these questions first by showing that the equivalent potential temperature (θ_e) of Rossby (1932), the liquid-water potential temperature (θ_l) of Betts (1973), and the entropy potential temperature (θ_s) of Marquet (2011) all share the property of describing the temperature air in some specified reference state would need to have, to have the same entropy as the air parcel they characterize. Each of these adopt standard pressure for the reference state, but differ in the disposition of the variable component. The reference state

⁵ The term hydro-lapse is used to demarcate the trade wind inversion region as the falloff of moisture with height is often more pronounced than the increase of temperature at the top of the trade wind cloud layer.

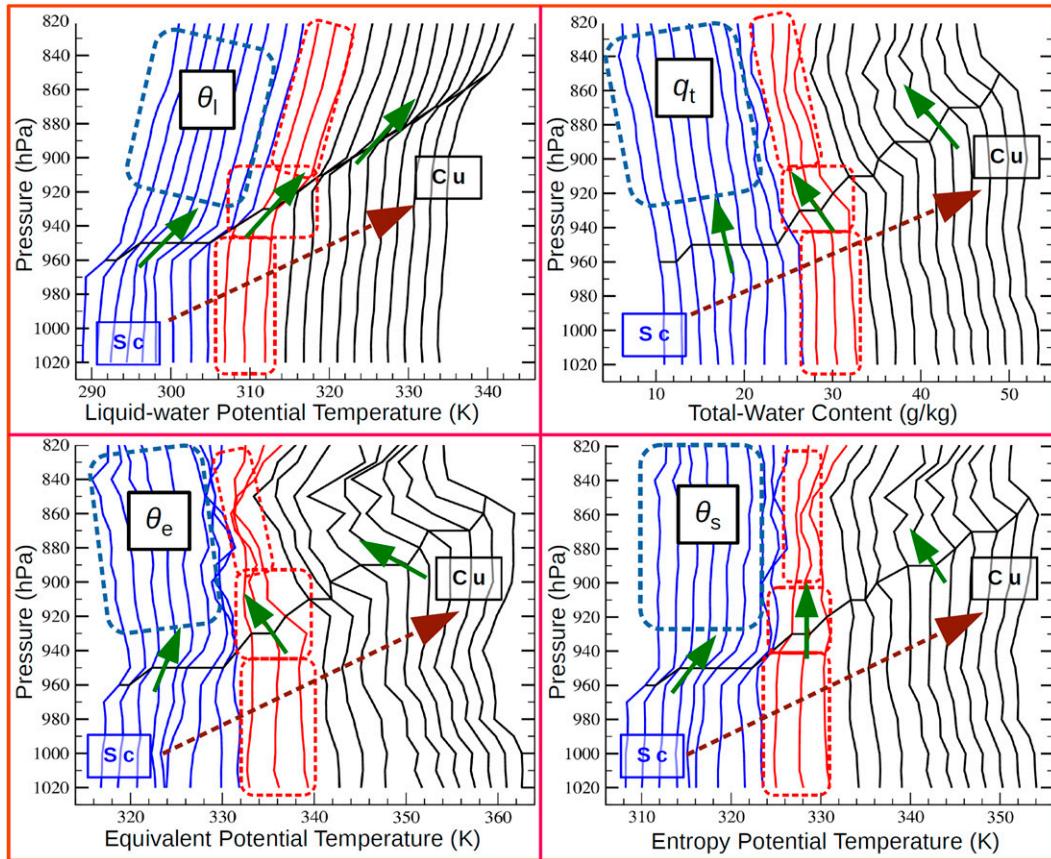


FIG. 5. Vertical profiles of θ_e , θ_ℓ , and θ_s plotted for half of the observed sounding of the first ASTEX Lagrangian experiment (with a shift of 2 K or 2 g kg⁻¹ between each profiles). Stratocumulus (Sc) profiles are colored blue, whereas cumulus (Cu) profiles are colored black. Transition profiles 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 compensates with the special value of Λ given by the third law.

for θ_s is water-free, the reference state for θ_ℓ is condensate free, and the reference state for θ_e is vapor-free.

Even if it is not crucial to the validity of its definition, only the θ_ℓ reference state is attainable through an isentropic, reversible, and closed transformation, as is the case for the dry potential temperature, θ , and then only in the case when the mass fraction of the water mass in the air parcel is less than the saturated mass fraction at the reference-state temperature and pressure. The reference state for θ_e is one of mechanical (phase) disequilibrium of the water phase, and the reference state for θ_s can only be accessed by an open process (to remove the water mass entirely).

The reference states that define θ_ℓ and θ_e are variable, which means they depend on the composition of the parcel which they characterize. In contrast, the reference state of θ_s is absolute; it is independent of the composition of the air parcel it characterizes. The latter is a necessary condition for a moist potential temperature to measure entropy. Put differently, θ_e (and θ_ℓ) only measures entropy differences of air parcels with the same composition, hence in a variable

composition atmosphere, only isopleths of θ_s coincide with isentropes. Compositional contributions to the entropy are substantial and can only be accounted for by accounting explicitly for the entropy difference between dry air and water vapor (via Λ), similar to the well-appreciated fact that condensational effects can only be accounted for by explicitly accounting for entropy differences between water vapor and condensate, which in equilibrium is proportional to ℓ_v , the vaporization enthalpy. This is why $\ln(\theta_e/\theta_\ell) \propto q_t \ell_v$, and why $\ln(\theta_s/\theta_\ell) \propto \Lambda q_t$, with Λ measuring the difference between the entropy of water vapor and dry air.

It should come as no surprise that each of the moist potential temperatures are useful for precisely measuring something, and each usefully approximates several air-parcel properties, but none usefully approximate all important properties. θ_ℓ and θ_e are poor measures of entropy, but accurately measure the reference-state “relative” enthalpy. In the case of θ_e whose reference state has already valorized the vaporization enthalpy of its water, the addition or removal of condensate, has a relatively minor effect. Likewise θ_ℓ is relatively insensitive to changes in

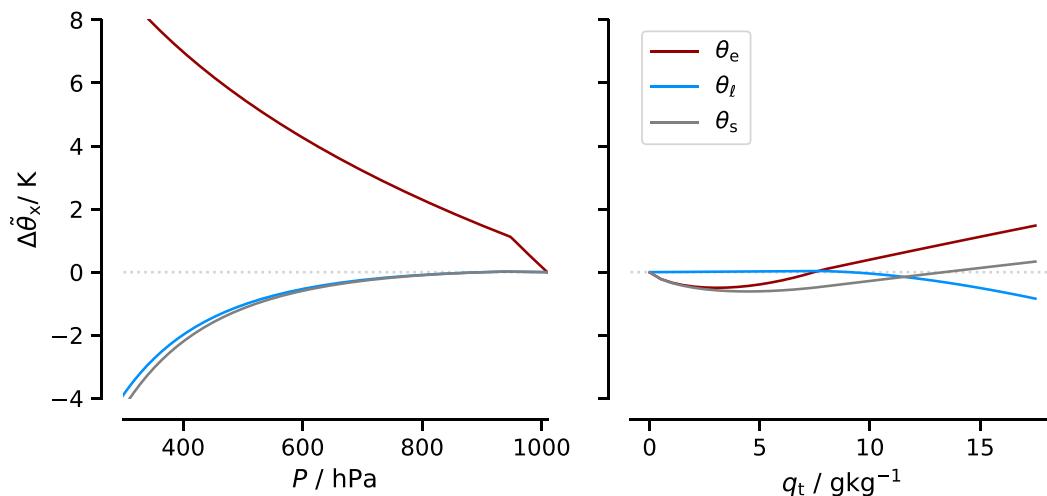


FIG. A1. Approximation errors associated with expressions of $\tilde{\theta}_x$. (left) Variations of $\tilde{\theta}_x - \theta_x (P=1010 \text{ hPa})$ along a saturated isentrope; (right) $\tilde{\theta}_x - \theta_x$ as a function of q_t for $(T, P) = (280 \text{ K}, 800 \text{ hPa})$. Lines in the left panel share the color key in the right panel.

vapor. This explains the popularity of θ_e as a basis for tracking air parcels in the presence of precipitation, or the use of θ_l in studies more interested in isolating an air mass's thermal properties—for instance, as a component of a mixing diagram. In contrast, θ_s measures the entropy of moist air. None of the moist potential temperatures mix linearly, and the errors encountered by assuming they do so can be substantial (ranging from a few to 10%).

Several examples are explored as a basis for exploring trade-offs in the use of different forms of θ_x to interpret the structure of the tropical atmosphere. These examples show how θ_s is generally better mixed through the tropical troposphere than is either θ_e or θ_l , and that the transition from stratocumulus to cumulus is associated with a transition of the troposphere to a state where θ_s becomes mixed through the lower troposphere, despite considerable gradients in moisture—whether or not this structure, which is also corroborated by many other observations (see Marquet 2011), is indicative of a process that acts to homogenize entropy, or occurs by chance, is an open question.

Acknowledgments. The ideas were developed jointly by the authors and hence ordered alphabetically by last name. The research was made possible by generous public support for the scientific activities of the Max Planck Society, Météo-France, and the CNRS—sometimes research is still possible without third party funding. The authors thank Dave Raymond, Martin Singh, and an anonymous reviewer, as well as the editor William Boos, for their constructive and critical comments, which led to substantial improvements in the presentation of our ideas.

Data availability statement. Profiles used for the cumulus to stratocumulus transition are available at <http://www.atmos.washington.edu/~breth/astex/lagr/README.hourly.html> and <ftp://eos.atmos.washington.edu/pub/breth/astex/lagr/>

<http://www.atmos.washington.edu/~breth/astex/lagr1/hourly/>. EUREC⁴A data for Fig 1 are available from the JOANNE dataset as cited. The temperature soundings used Fig. 2 are provided courtesy of the DYAMOND project; it and a notebook containing the calculations presented in the manuscript are made available by the host authors corresponding institutions by contacting publications@mpimet.mpg.de.

APPENDIX A

Numerical Evaluation

We tested the numerical implementation of expressions for the different forms of θ_x . To do so we numerically integrated the adiabatic form of the first law for our composite system, along the (300 K, 1010 hPa, 17 g kg⁻¹) isentrope, which also served as the initial condition. The integration was terminated when P reached 150 Pa, at which point $T = 207.42 \text{ K}$. We then calculated θ_e , θ_l , and θ_s for different tuples of (T, P) , along this isentrope. If properly constructed, the different versions of θ_x should adopt different values, but each should be invariant on this isentrope. Variations were verified to be smaller than the tolerance of the ODE solver (lsoda) used for the numerical integration of the adiabatic form of the first law. To achieve this level of accuracy it was necessary to use a relationship for $P_*(T)$ consistent with the approximations outlined in section 2, and to ensure the adequacy between the definition of $P_*(T)$ and the variations, or not, of $\ell_v(T) = (c_{p_v} - c_1)(T - T_0) + \ell_v(T_0)$ with temperature, due to

$$\frac{1}{P_*(T)} \frac{dP_*(T)}{dT} = \frac{\ell_v(T)}{R_v T^2}.$$

Using more exact approximations to P_* , which account for variations in the specific heats c_{p_v} and c_1 with temperature, introduces inconsistencies in the form of centikelvin

discrepancies between the temperatures derived by direct integration, and those implied by constant θ_x .

The approximations given by Eqs. (22)–(24) introduce errors on the order of 1%, or about 4 K. The left panel of Fig. A1 shows how $\tilde{\theta}_x$ changes from its value at 1010 hPa as pressure is reduced and θ_x is held constant. Through most of the lower troposphere ($P > 600$ hPa) both $\tilde{\theta}_\ell$ and $\tilde{\theta}_s$ are approximately constant along the isentrope. Errors in $\tilde{\theta}_e$ are more severe and systematic with pressure. All forms of θ_x show errors in the upper troposphere, but in this region of the atmosphere strong departures from equilibrium associated with the ice phase likely introduce even larger errors, or at least substantial uncertainty.

The chosen forms for $\tilde{\theta}_x$ neglect humidity effects in all terms other than the ones carrying the dominant sensitivity to humidity. For this reason, in the right panel of Fig. A1 we present an evaluation of the errors in the expressions for $\tilde{\theta}_x$ as a function of q_t . The errors associated with each approximation are small (1%) and commensurate. Certainly we see no basis for choosing one or the other form of $\tilde{\theta}_x$ based on it being a better approximation to the true value.

The results shown in this appendix are in agreement with errors on the order of 0.6 K or 0.2% shown in Fig. 1. The larger errors in Fig. A1 are due to cumulative effects during the vertical ascents.

APPENDIX B

Historical Notes on the Application of the Third Law

The dependence of θ_s on the absolute entropy, through the factor Λ in Eq. (18), arises because from the need to characterize a multicomponent system whose relative composition (in our case between dry air and water vapor) is allowed to vary.

The recognition that the absolute value of the entropy are important for reacting, or multicomponent systems, dates to [Le Chatelier \(1888\)](#), who first described the need to know the absolute values of entropy of reactants and products in order to be able to predict the stability of all chemical processes. Then [Nernst \(1906\)](#) derived his “theorem of heat,” but it is [Planck \(1914, 1917\)](#) who really derived what is nowadays known as the Boltzmann equation $S = k \ln(W)$ with k the Boltzmann constant. The absence of an additive constant corresponds to cancelling the entropy of all perfect crystalline state at zero Kelvin temperature (third law of thermodynamics), due to the unique remaining number of configuration $W = 1$ at 0 K. [Pauling \(1935\)](#) and [Nagle \(1966\)](#) computed the residual entropy for ice at 0 K ($\Delta S \approx 189 \text{ J K}^{-1} \text{ kg}^{-1}$), which must be taken into account for computing the entropy of water at any finite positive absolute temperature. The link between the third law of Planck and the principle of unattainability of absolute zero temperature derived by [Nernst \(1912\)](#) and studied by [Simon \(1927\)](#) has been recently clarified by [Masanes and Oppenheim \(2017\)](#).

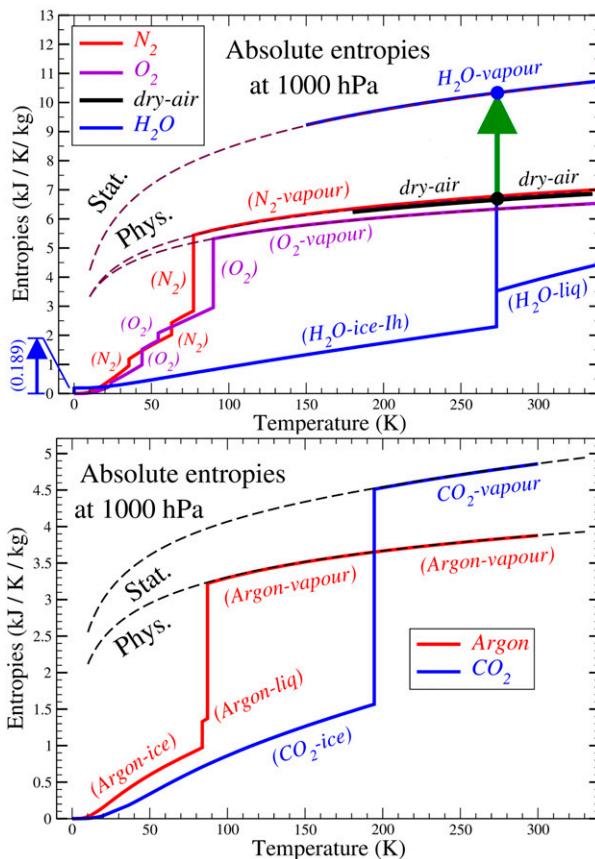


FIG. B1. Entropies for dry-air (N_2 , O_2 , Ar, CO_2 , and water H_2O) species plotted against the absolute temperature and computed at 1000 hPa. The calorimetric method $\left[\int_0^T c_p(T') d\ln(T') + \sum_j \ell(T_j)/T_j \right]$ corresponds to the colored solid lines. The third-law hypothesis is 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 $\ell(T_j)$ between solids phases (for N_2 and O_2), then from solid to liquid phases, then from liquid to vapor phases. The statistical-physics values (black dashed lines) are computed from $S = k \ln(W)$ and $F = -kT \ln(Z)$ for the vapor phases according to the method described in [Chase \(1998\)](#) for translational, rotational, vibrational, and electronic partition functions (Z).

Values of absolute reference entropy of atmospheric gases (N_2 , O_2 , Ar, H_2O , CO_2) used in [Hauf and Höller \(1987\)](#), [Marquet \(2011\)](#), and [Stevens and Siebesma \(2020\)](#) were already available in [Kelley \(1932\)](#), [Lewis and Randall \(1961\)](#), and [Gokcen and Reddy \(1996\)](#). They are now accurately determined and available in the National Institute of Standards and Technology Joint Army–Navy–Air Force (NIST-JANAF) tables ([Chase 1998](#)). The agreement between the various way to compute the absolute entropies can be fairly appreciated in Fig. B1, where the

“calorimetric” and “statistical-physics” methods lead to the same results in the range of atmospheric temperatures up to better than $\pm 0.6\%$ for H_2O and N_2 and better than $\pm 0.1\%$ for O_2 , Ar, and CO_2 . The accuracy of the NIST-JANAF tables are indicated as being better than one tenth of the differences between calorimetric and the statistical methods.

It can be recalled that, if the third law is applied to 0 K, the consequences of this hypothesis impact the atmospheric temperatures domain via the calorimetric method and the integrations made between 0 K and any temperature T . The same is true for the statistical physics method, where the partition function Z is computed with the hypothesis $S = k \ln(W)$ with no additive constant and with $S = 0$ because $W = 1$ at 0 K.

The impacts of the hypotheses (i) and (ii) made at the end of section 2a concerning the constancy of the specific heats and the deviations from the ideal gas aspects remain small when compared to the data computed by the IAPWS and TEOS-10 software (not shown). Moreover, the absolute values of the entropies can easily be computed with TEOS-10 if one takes into account the data from the thermodynamic tables (Lewis and Randall 1961; Chase 1998), or at least the liquid-water and dry-air absolute entropies given by Millero (1983) and Lemmon et al. (2000), respectively.

REFERENCES

- Bauer, L. A., 1908: The relation between “potential temperature” and “entropy.” *Phys. Rev. Ser. I*, **26**, 177–183, <https://doi.org/10.1103/PhysRevSeriesI.26.177>.
- , 1910: The relation between “potential temperature” and “entropy.” *The Mechanics of the Earth's Atmosphere*, C. Abbe, Ed., Smithsonian, 495–500.
- Betts, A. K., 1973: Non-precipitating cumulus convection and its parameterization. *Quart. J. Roy. Meteor. Soc.*, **99**, 178–196, <https://doi.org/10.1002/qj.49709941915>.
- Bretherton, C. S., 1987: A theory for nonprecipitating moist convection between two parallel plates. Part I: Thermodynamics and “linear” solutions. *J. Atmos. Sci.*, **44**, 1809–1827, [https://doi.org/10.1175/1520-0469\(1987\)044<1809:ATFNMC>2.0.CO;2](https://doi.org/10.1175/1520-0469(1987)044<1809:ATFNMC>2.0.CO;2).
- , and R. Pincus, 1995: Cloudiness and marine boundary layer dynamics in the ASTEX Lagrangian experiments. Part I: Synoptic setting and vertical structure. *J. Atmos. Sci.*, **52**, 2707–2723, [https://doi.org/10.1175/1520-0469\(1995\)052<2707:CAMBLD>2.0.CO;2](https://doi.org/10.1175/1520-0469(1995)052<2707:CAMBLD>2.0.CO;2).
- Chase, M. W., 1998: *NIST-JANAF Thermochemical Tables*. 4th ed. Monogr., No. 40, American Chemical Society and American Institute of Physics, 1951 pp.
- Deardorff, J. W., 1980: Cloud top entrainment instability. *J. Atmos. Sci.*, **37**, 131–147, [https://doi.org/10.1175/1520-0469\(1980\)037<0131:CTEI>2.0.CO;2](https://doi.org/10.1175/1520-0469(1980)037<0131:CTEI>2.0.CO;2).
- de Roode, S. R., and P. G. Duynkerke, 1997: Observed Lagrangian transition of stratocumulus into cumulus during ASTEX: Mean state and turbulence structure. *J. Atmos. Sci.*, **54**, 2157–2173, [https://doi.org/10.1175/1520-0469\(1997\)054<2157:OLTOSI>2.0.CO;2](https://doi.org/10.1175/1520-0469(1997)054<2157:OLTOSI>2.0.CO;2).
- Emanuel, K. A., 1994: *Atmospheric Convection*. Oxford University Press, 580 pp.
- Feistel, R., 2018: Thermodynamic properties of seawater, ice and humid air: TEOS-10, before and beyond. *Ocean Sci.*, **14**, 471–502, <https://doi.org/10.5194/os-14-471-2018>.
- Fermi, E., 1937: *Thermodynamics*. Prentice Hall, 160 pp.
- George, G., and Coauthors, 2021: JOANNE: Joint dropsonde observations of the atmosphere in tropical North Atlantic meso-scale environments. *Earth Syst. Sci. Data*, **13**, 5253–5272, <https://doi.org/10.5194/essd-13-5253-2021>.
- Gokcen, N., and R. Reddy, 1996: The third law of thermodynamics. *Thermodynamics*, Springer Science and Business Media, 109–118.
- Hauf, T., and H. Höller, 1987: Entropy and potential temperature. *J. Atmos. Sci.*, **44**, 2887–2901, [https://doi.org/10.1175/1520-0469\(1987\)044<2887:EAPT>2.0.CO;2](https://doi.org/10.1175/1520-0469(1987)044<2887:EAPT>2.0.CO;2).
- Hohenegger, C., L. Kornbluh, D. Klocke, T. Becker, G. Cioni, J. F. Engels, U. Schulzweida, and B. Stevens, 2020: Climate statistics in global simulations of the atmosphere, from 80 to 2.5 km grid spacing. *J. Meteor. Soc. Japan*, **98**, 73–91, <https://doi.org/10.2151/jmsj.2020-005>.
- IAPWS, 2010: Guideline on an equation of state for humid air in contact with seawater and ice, consistent with the IAPWS formulation 2008 for the thermodynamic properties of seawater. International Association for the Properties of Water and Steam Doc. IAPWS G8-10, 21 pp., <http://www.iapws.org/relguide/SeaAir.pdf>.
- Kelley, K. K., 1932: Contributions to the data on theoretical metallurgy: I. The entropies of inorganic substances. Bureau of Mines Bulletin 350, 63 pp.
- Knoche, W., 1906: Ueber die räumliche und zeitliche Verteilung des Wärmegehalts der unteren Luftschicht (on the spatial and temporal distribution of the heat content of the lower air layer). Ph.D. thesis, Friedrich-Wilhelms-Universität, Berlin, 46 pp.
- Le Chatelier, M. H., 1888: *Recherches expérimentales et théoriques sur les équilibres chimiques*. Dunod Editeur, 229 pp.
- Lemmon, E. W., R. T. Jacobsen, S. G. Penoncello, and D. G. Friend, 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, <https://doi.org/10.1063/1.1285884>.
- Lewis, G. N., and M. Randall, 1961: *Thermodynamics*. McGraw-Hill, 723 pp.
- Marquet, P., 2011: Definition of a moist entropy potential temperature: Application to FIRE-I data flights. *Quart. J. Roy. Meteor. Soc.*, **137**, 768–791, <https://doi.org/10.1002/qj.787>.
- , 2017: A third-law isentropic analysis of a simulated hurricane. *J. Atmos. Sci.*, **74**, 3451–3471, <https://doi.org/10.1175/JAS-D-17-0126.1>.
- , and T. Dauhut, 2018: Reply to “Comments on ‘A third-law isentropic analysis of a simulated hurricane.’” *J. Atmos. Sci.*, **75**, 3735–3747, <https://doi.org/10.1175/JAS-D-18-0126.1>.
- , and P. Bechtold, 2020: A new estimated inversion strength (EIS) based on the moist-air entropy. WCRP Rep. 12/2020, 2 pp.
- Masanés, L., and J. Oppenheim, 2017: A general derivation and quantification of the third law of thermodynamics. *Nat. Commun.*, **8**, 14538, <https://doi.org/10.1038/ncomms14538>.
- Mellado, J. P., 2017: Cloud-top entrainment in stratocumulus clouds. *Annu. Rev. Fluid Mech.*, **49**, 145–169, <https://doi.org/10.1146/annurev-fluid-010816-060231>.
- Millero, F. J., 1983: The thermodynamics of seawater, part II. Thermochemical properties. *Ocean Sci. Eng.*, **8**, 1–40.

- Nagle, J. F., 1966: Lattice statistics of hydrogen bonded crystals. I. The residual entropy of ice. *J. Math. Phys.*, **7**, 1484–1491, <https://doi.org/10.1063/1.1705058>.
- Nernst, W., 1906: Ueber die berechnung chemischer gleichgewichte aus thermischen messungen. *Nachr. Ges. Wiss. Goettingen, Math.-Phys. Kl.*, **1**, 1–40.
- , 1912: Thermodynamik und spezifische Wärme. *Sitzungsberichte Sitzungsber. K. Preuss. Akad. Wiss. Berlin*, **6**, 134–140.
- Normand, C. W. B., 1921: Wet bulb temperatures and the thermodynamics of the air. India Meteorological Department Rep., 22 pp.
- Ooyama, K. V., 1990: A thermodynamic foundation for modeling the moist atmosphere. *J. Atmos. Sci.*, **47**, 2580–2593, [https://doi.org/10.1175/1520-0469\(1990\)047<2580:ATFFMT>2.0.CO;2](https://doi.org/10.1175/1520-0469(1990)047<2580:ATFFMT>2.0.CO;2).
- Pauling, L., 1935: The structure and entropy of ice and of other crystals with some randomness of atomic arrangement. *J. Amer. Chem. Soc.*, **57**, 2680–2684, <https://doi.org/10.1021/ja01315a102>.
- Pauluis, O. M., 2018: Comments on “A third-law isentropic analysis of a simulated hurricane.” *J. Atmos. Sci.*, **75**, 3725–3733, <https://doi.org/10.1175/JAS-D-18-0059.1>.
- , A. Czaja, and R. Korty, 2008: The global atmospheric circulation on moist isentropes. *Science*, **321**, 1075–1078, <https://doi.org/10.1126/science.1159649>.
- , —, and —, 2010: The global atmospheric circulation in moist isentropic coordinates. *J. Climate*, **23**, 3077–3093, <https://doi.org/10.1175/2009JCLI2789.1>.
- Planck, M., 1914: *The Theory of Heat Radiation*. Blakiston's Son and Co., 266 pp.
- , 1917: *Treatise on Thermodynamics*. Dover, 297 pp.
- Randall, D. A., 1980: Conditional instability of the first kind upside-down. *J. Atmos. Sci.*, **37**, 125–130, [https://doi.org/10.1175/1520-0469\(1980\)037<0125:CIOTFK>2.0.CO;2](https://doi.org/10.1175/1520-0469(1980)037<0125:CIOTFK>2.0.CO;2).
- Raymond, D. J., 2013: Sources and sinks of entropy in the atmosphere. *J. Adv. Model. Earth Syst.*, **5**, 755–763, <https://doi.org/10.1002/jame.20050>.
- Richardson, L. F., 1919: Atmospheric stirring measured by precipitation. *Proc. Roy. Soc. London*, **96A**, 9–18, <https://doi.org/10.1098/rspa.1919.0034>.
- Romps, D. M., 2015: MSE minus CAPE is the true conserved variable for an adiabatically lifted parcel. *J. Atmos. Sci.*, **72**, 3639–3646, <https://doi.org/10.1175/JAS-D-15-0054.1>.
- , 2017: Exact expression for the lifting condensation level. *J. Atmos. Sci.*, **74**, 3891–3900, <https://doi.org/10.1175/JAS-D-17-0102.1>.
- , 2021: Accurate expressions for the dewpoint and frost point derived from the Rankine–Kirchhoff approximations. *J. Atmos. Sci.*, **78**, 2113–2116, <https://doi.org/10.1175/JAS-D-20-0301.1>.
- Rossby, C.-G., 1932: Thermodynamics applied to air mass analysis. Massachusetts Institute of Technology Meteorology Papers 1, No. 3, 57 pp.
- Schubert, J., 1904: *Der Wärmeaustausch im festen Erdboden, in Gewässern und in der Atmosphäre (The Heat Exchange in the Solid Surface, in Water and in the Atmosphere)*. Springer Verlag, 30 pp.
- Shannon, C. E., 1948: A mathematical theory of communication. *Bell Syst. Tech. J.*, **27**, 379–423, <https://doi.org/10.1002/j.1538-7305.1948.tb01338.x>.
- Simon, F., 1927: Zum Prinzip von der Unerreichbarkeit des absoluten Nullpunktes. *Z. Phys.*, **41**, 806–809, <https://doi.org/10.1007/BF01395487>.
- Stevens, B., and P. Siebesma, 2020: Clouds as fluids. *Clouds and Climate: Climate Science's Greatest Challenge*, A. Siebesma et al., Eds. Cambridge University Press, 35–73.
- , and Coauthors, 2003: On entrainment rates in nocturnal marine stratocumulus. *Quart. J. Roy. Meteor. Soc.*, **129**, 3469–3493, <https://doi.org/10.1256/qj.02.202>.
- , and Coauthors, 2019: DYAMOND: The Dynamics of the Atmospheric general circulation Modeled On Non-hydrostatic Domains. *Prog. Earth Planet. Sci.*, **6**, 61, <https://doi.org/10.1186/s40645-019-0304-z>.
- , and Coauthors, 2021: EUREC⁴A. *Earth Syst. Sci. Data*, **13**, 4067–4119, <https://doi.org/10.5194/essd-13-4067-2021>.
- von Bezold, W., 1888: On the thermo-dynamics of the atmosphere (first communication). *The Mechanics of the Earth's Atmosphere*, C. Abbe, Ed., Smithsonian, 212–242.