

Eulerian Available Energetics in Moist Atmospheres

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ABSTRACT

A new derivation of local available energy for a compressible, multicomponent fluid that allows for frictional, diabatic, and chemical (e.g., phase changes) processes is presented. The available energy is defined relative to an arbitrary isothermal atmosphere in hydrostatic balance with uniform total chemical potentials. It is shown that the available energy can be divided into available potential, available elastic, and available chemical energies. Each is shown to be positive definite.

The general formulation is applied to the specific case of an idealized, moist, atmospheric sounding with liquid water and ice. The available energy is dominated by available potential energy in the troposphere but available elastic energy dominates in the upper stratosphere. The available chemical energy is significant in the lower troposphere where it dominates the available elastic energy. The total available energy increases with increasing water content.

1. Introduction

Gibbs (1873, 1875) introduced the concept of available energy as the maximum amount of work that can be extracted from a system relative to a reservoir at constant temperature, pressure, and chemical composition. This available energy is the maximum amount of work that can be done on the system undergoing reversible processes and is given by the difference in the Gibbs function G of the system and that of the reservoir evaluated at the temperature, pressure, and chemical potential of the reservoir. For a particularly lucid explanation of the concept of available energy, the reader is referred to Reif (1965, section 8.3), though Reif uses the term maximum work rather than available energy). Since its introduction, available energy has appeared in many different guises with many different appellations in the physics and engineering literature. Marquet (1991, 1993) presents good historical reviews of the literature and overviews of the nomenclature. Dutton (1973) and Livezey and Dutton (1976) applied the concept to geophysical fluid systems. Their term entropic energy for the available energy was defined in a global context as the maximum amount of work that can be

extracted from a fluid system relative to an isothermal, hydrostatic system having the same mass and energy of the original fluid system with uniform total chemical potentials. The total chemical potential is the sum of the intrinsic chemical potential and a geopotential contribution. Pichler (1977) developed a local budget equation for available energy for a dry atmosphere. More recently, Karlsson (1990) developed a local version for a moist atmosphere using an isothermal reference atmosphere in hydrostatic balance with nonuniform intrinsic chemical potentials. In contrast, Marquet (1991, 1993, 2003) developed local dry and moist versions of a function he termed the available enthalpy. Marquet followed many earlier investigators (e.g., Gibbs 1873; Keenan 1951; Haywood 1974) and assumed constant values for the reference pressure field and intrinsic chemical potentials.

It is important to note that the present use of the concept of available energy is distinct from the available potential energy of Margules (1905) and Lorenz (1955, 1978, 1979) (see Dutton and Johnson 1967 for a thorough discussion) in which the reference state is obtained by a mass-conserving, isentropic adjustment to a barotropic, hydrostatic state that need not be isothermal.

The purpose of the present paper is to present a derivation of available energy in a local context for a compressible, multicomponent, geophysical fluid defined relative to an isothermal hydrostatic reference state

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with uniform total chemical potentials. The derivation emphasizes the use of available energy in Eulerian applications and it thus complements a recent work (Bannon 2004) that presents a Lagrangian perspective of available energy. Section 2 presents the derivation and the energy partitioning. The derivation is a direct extension of that of Fortak (1998) but for multicomponent flows. In addition, the present derivation differs from that of Karlsson (1990) in the choice of reference state and in its compactness and its generality. Similarly, the partitioning of the available energy into potential, elastic, and chemical energies is an extension of that of Andrews (1981). Section 2 also differentiates the present formulation from the exergy approach of Karlsson (1990) and from the available enthalpy approach of Marquet (1991, 1993). Section 3 presents numerical calculations of the available energy and its components for idealized atmospheric soundings containing water vapor as well as liquid water and ice. Unlike Livezey and Dutton (1976), Karlsson (1990), and Marquet (1993), the reference atmosphere is assumed to be a dry one. This choice assures that the isothermal reference atmosphere is convectively dead with no possibility of moist nonlinear conditional instability. However this choice necessitates that the absolute value of the thermodynamic state variables be calculated. Section 4 presents some conclusions. Appendix A summarizes the thermodynamics of a moist atmosphere with liquid water and ice and provides the necessary thermodynamic constants. Appendix B provides an algorithm to calculate the enthalpy given the entropy, pressure, and total water mixing ratio of the cloudy air.

2. Eulerian available energetics with chemical reactions and phase changes

a. General derivation

This section presents a simple derivation of the general result for the available energy for a multicomponent, compressible fluid from an Eulerian perspective. The specific available energy (ae) is

$$ae \equiv \Delta h - T_r \Delta s - \alpha \Delta p - \mu_{rj} \Delta \chi_j, \quad (2.1)$$

where h is the specific enthalpy, s is the specific entropy, α is the specific volume, p is the pressure, T is the temperature, and μ_j is the total chemical potential of the j th constituent with concentration χ_j (i.e., the mass of the j th constituent per total mass). The summation convention holds for repeated subscripts j . Here a subscript r refers to a reference atmosphere in hydrostatic balance that is assumed to be isothermal ($T_r = \text{const}$) with constant concentrations ($\chi_{rj} = \text{const}$) and constant

chemical potentials ($\mu_{rj} = \text{const}$). Unsubscripted variables are function of position $\mathbf{x} = (x, y, z)$ and time t but the reference entropy and pressure are functions of only height z . Reif (1965) notes that multiple separate reservoirs are permissible. The symbol Δ defines a finite departure from that reference state. For example, $\Delta h = h - h_r$.

The available energy (2.1) is mathematically equivalent to the static entropic energy of Livezey and Dutton (1976) who wrote (2.1) in terms of the internal energy. It is shown below that the enthalpy (as opposed to internal energy) formulation of (2.1) leads to an interesting partitioning of the available energy. Karlsson (1990, p. 22) defines the static exergy in a form equivalent to (2.1). In contrast to the available energy (2.1), Marquet (1993) defines the moist available enthalpy as the sum of the first, second, and fourth terms on the right-hand side of (2.1) using intrinsic chemical potentials and takes the reference temperature, pressure, and entropy as constants. Here T_r is a constant but p_r and s_r are functions of height z . In addition Marquet's (1993) Eq. (17) includes an extra chemical potential term associated with the difference in the reference chemical potentials between the ice and liquid water.

The rate of change of the energy following the three-dimensional, mass-weighted, mean velocity \mathbf{v} is

$$\begin{aligned} \frac{Dae}{Dt} \equiv & \frac{Dh}{Dt} - T_r \frac{Ds}{Dt} + T_r \frac{Ds_r}{Dt} - \Delta p \frac{D\alpha}{Dt} - \alpha \frac{Dp}{Dt} \\ & + \alpha \frac{Dp_r}{Dt} - \mu_{rj} \frac{D\chi_j}{Dt}, \end{aligned} \quad (2.2)$$

where the material derivative is

$$\frac{D}{Dt} \equiv \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla,$$

and $\mathbf{v} = \sum_j m_j \mathbf{v}_j / \sum_j m_j$, and m_j and \mathbf{v}_j are the mass and velocity of the j th constituent. In writing (2.2), the fact that the reference temperature, concentrations, and total chemical potentials are constants has been used. The continuity equation is

$$\frac{D\rho}{Dt} = -\rho \nabla \cdot \mathbf{v} \quad \text{or} \quad \frac{D\alpha}{Dt} = \alpha \nabla \cdot \mathbf{v}, \quad (2.3)$$

where ρ is the total density. For a hydrostatic reference state at rest, the force balance is

$$0 = -\nabla p_r - \rho_r \nabla \Phi, \quad \text{or} \quad \alpha_r \nabla p_r = -\nabla \Phi, \quad (2.4)$$

where Φ is the geopotential. The Gibbs relation in the form $dh = T ds + \alpha dp + \mu_j d\chi_j$ for the reference state implies

$$\nabla h_r - \mu_{rj} \nabla \chi_{rj} = T_r \nabla s_r + \alpha_r \nabla p_r = 0, \quad (2.5)$$

where the second equality holds because the reference temperature and chemical concentrations are constants. Together (2.4) and (2.5) imply

$$T_r \nabla s_r = \nabla \Phi, \quad \text{or} \quad T_r \frac{Ds_r}{Dt} = \frac{D\Phi}{Dt}, \quad (2.6)$$

because the reference atmosphere is static. Substituting (2.3) and (2.6) into (2.2) yields

$$\begin{aligned} \frac{Dae}{Dt} &= \frac{Dh}{Dt} - T_r \frac{Ds}{Dt} + \frac{D\Phi}{Dt} - \alpha \Delta p \nabla \cdot \mathbf{v} - \alpha \frac{Dp}{Dt} \\ &+ \alpha \frac{Dp_r}{Dt} - \mu_{rj} \frac{D\chi_j}{Dt}. \end{aligned} \quad (2.7)$$

The specific kinetic energy (ke) and enthalpy equations are

$$\frac{Dke}{Dt} = -\alpha \mathbf{v} \cdot \nabla p - \mathbf{v} \cdot \nabla \Phi + \alpha \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\sigma}), \quad (2.8)$$

$$\frac{Dh}{Dt} = \alpha \frac{Dp}{Dt} + T \frac{Ds}{Dt} + \mu_j \frac{D\chi_j}{Dt}, \quad (2.9)$$

where $\boldsymbol{\sigma}$ is the viscous stress tensor. Then (2.7), (2.8), and (2.9) sum to give

$$\begin{aligned} \frac{\partial \rho(ke + ae)}{\partial t} &= -\nabla \cdot [\rho(ke + ae)\mathbf{v}] - \nabla \cdot (p'\mathbf{v}) \\ &+ \rho(T - T_r) \frac{Ds}{Dt} + \rho(\mu_j - \mu_{rj}) \frac{D\chi_j}{Dt} \\ &+ \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\sigma}), \end{aligned} \quad (2.10)$$

where $p' = \Delta p$ is the perturbation pressure relative to the reference pressure. The equation for the concentration rate of change is

$$\rho \frac{D\chi_j}{Dt} = \rho \dot{\chi}_j \equiv -\nabla \cdot (\rho_j \mathbf{v}'_j) + \dot{r}_j, \quad (2.11)$$

where ρ_j is the density of the j th constituent whose velocity relative to the mass-weighted average velocity \mathbf{v} is \mathbf{v}'_j , and whose rate of production by chemical reactions and/or phase changes is \dot{r}_j . The entropy equation is (e.g., Landau and Lifshitz 1959)

$$\rho T \frac{Ds}{Dt} = \rho T \dot{s} \equiv \rho \dot{q} - \rho \mu_j \dot{\chi}_j, \quad (2.12)$$

where \dot{q} is the heating rate due to radiation, conduction, viscous dissipation, and diffusion (i.e., the convergence of the enthalpy flux of the constituents with enthalpy h_j

relative to the mean velocity). Then, the final form of the Eulerian energetics equation is

$$\begin{aligned} \frac{\partial \rho(ke + ae)}{\partial t} &= -\nabla \cdot [\rho(ke + ae)\mathbf{v}] - \nabla \cdot (p'\mathbf{v}) \\ &+ \rho(T - T_r) \dot{s} + \rho(\mu_j - \mu_{rj}) \dot{\chi}_j \\ &+ \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\sigma}), \end{aligned} \quad (2.13a)$$

or, using (2.12),

$$\begin{aligned} \frac{\partial \rho(ke + ae)}{\partial t} &= -\nabla \cdot [\rho(ke + ae)\mathbf{v}] - \nabla \cdot (p'\mathbf{v}) \\ &+ \rho \frac{(T - T_r)}{T} \dot{q} + \rho T_r \left(\frac{\mu_j}{T} - \frac{\mu_{rj}}{T_r} \right) \dot{\chi}_j \\ &+ \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\sigma}). \end{aligned} \quad (2.13b)$$

This completes the derivation. Equation (2.13) reduces to Fortak's (1998) result [see his Eq. (14'')] for the specific exergy of internal energy for a single-component fluid. It is evident that the global conservation of $\rho(ke + ae)$ holds for adiabatic, inviscid flow in a closed volume that undergoes no local chemical or phase changes. The coefficients multiplying the rates of change of the heat and concentration in (2.13b) may be interpreted as the thermal and chemical efficiencies. It is emphasized that the available energetics is here defined in an Eulerian sense such that the energy is defined at a point in space relative to a reference atmosphere at the same height. It is therefore distinct from the formulation of the available energetics of Bannon (2004) that defines it in a Lagrangian sense such that the energy is defined for a parcel relative to its initial conditions.

The exergy formulation of Karlsson (1990) is similar to, but different than, the present formulation developed independently. Karlsson's specific static exergy b_s is, in the present notation,

$$b_s \equiv u + \alpha p_r - T_r s - \mu'_{rj} \chi_j = h - T_r s - \alpha \Delta p - \mu'_{rj} \chi_j, \quad (2.14)$$

where u is the specific internal energy and the reference intrinsic chemical potentials μ'_{rj} are functions of height. The governing equation for the exergy is given by (2.13b) if b_s replaces the available energy ae and μ'_{rj} replace μ_{rj} . Thus though the two formulations yield similar equations, the physics is distinct. In particular, the relation (2.6) is not invoked in Karlsson's formulation where instead it is assumed that the reference intrinsic chemical potentials are such that $\chi_{rj} \nabla \mu'_{rj} = -\nabla \Phi$. In addition the sources and sinks of entropy are different from the current derivation that utilizes the mass-

weighted mean velocity from the outset. A second expression (Karlsson 1990, p. 71) for the flow exergy is consistent with (2.13b) provided one recognizes that the reference variables are not functions of time and the reference chemical potentials are height dependent as discussed above.

b. Linearized form

It is of some interest to examine the linearized form of the available energy. For simplicity, this section specializes to the case of a binary fluid. Noting that the enthalpy is a function of the entropy, pressure, and concentration $h = h(s, p, \chi)$, the enthalpy is expanded in a Taylor series expansion about the reference state denoted here with a subscript zero

$$\begin{aligned} ae \equiv & h_0 - h_0 + h_{s0}\Delta s + h_{p0}\Delta p + h_{\chi0}\Delta\chi + \frac{1}{2}h_{ss0}(\Delta s)^2 \\ & + \frac{1}{2}h_{pp0}(\Delta p)^2 + \frac{1}{2}h_{\chi\chi0}(\Delta\chi)^2 + h_{sp0}\Delta s\Delta p \\ & + h_{s\chi0}\Delta s\Delta\chi + h_{p\chi0}\Delta p\Delta\chi - T_0\Delta s - \alpha\Delta p - \mu_0\Delta\chi, \end{aligned} \tag{2.15}$$

where a subscript with respect to a state variable denotes differentiation and a subscript zero denotes evaluation in the reference state. But $h_s = T$, $h_p = \alpha$, and $h_\chi = \mu$, then (2.15) reduces to

$$\begin{aligned} ae \equiv & \frac{1}{2}h_{ss0}(\Delta s)^2 + \frac{1}{2}h_{pp0}(\Delta p)^2 + \frac{1}{2}h_{\chi\chi0}(\Delta\chi)^2 + \alpha_{s0}\Delta s\Delta p \\ & + T_{\chi0}\Delta s\Delta\chi + \alpha_{\chi0}\Delta p\Delta\chi - \Delta\alpha\Delta p. \end{aligned} \tag{2.16}$$

Noting that the specific volume is a function of entropy, pressure, and concentration, one has

$$\Delta\alpha = \alpha_{s0}\Delta s + \alpha_{p0}\Delta p + \alpha_{\chi0}\Delta\chi, \tag{2.17}$$

and substituting yields

$$\begin{aligned} ae \equiv & \frac{1}{2}h_{ss0}(\Delta s)^2 - \frac{1}{2}h_{pp0}(\Delta p)^2 + \frac{1}{2}h_{\chi\chi0}(\Delta\chi)^2 \\ & + h_{s\chi0}\Delta s\Delta\chi. \end{aligned} \tag{2.18}$$

The last term in (2.18) vanishes because the chemical potential is uniform in the base state and does not vary with height z or, by (2.6), entropy s . Mathematically, $h_{s\chi0} = \mu_{s0} = 0$. Then the available energy (2.18) is positive definite. To demonstrate this, note that the coefficients of the three remaining terms are positive:

$$\begin{aligned} -h_{pp0} &= -\left(\frac{\partial\alpha}{\partial p}\right)_0 = \frac{1}{\rho_0^2}\left(\frac{\partial\rho}{\partial p}\right)_0 = \frac{1}{\rho_0^2c_0^2} > 0, \\ h_{ss0} &= T_{s0} = \frac{T_0}{c_p} > 0, \\ h_{\chi\chi0} &= \mu_{\chi0} > 0, \end{aligned} \tag{2.19}$$

where c_0 is the speed of sound and c_p is the specific heat at constant pressure. Thus, each term is positive definite. The last inequality follows from the assumption that the reference state is in chemical equilibrium (Landau and Lifshitz 1980, section 96). In particular, for dry air, one can show with some effort that

$$ae \equiv \frac{1}{2N_0^2}\left(\frac{g\theta'}{\theta_0}\right)^2 + \frac{p'^2}{2\rho_0^2c_0^2}, \tag{2.20}$$

where θ denotes potential temperature, g is the acceleration due to gravity, and N is the buoyancy frequency. This result implies that the available energy (2.1) is the nonlinear extension of the traditional linear energetics (e.g., Eckart 1960, sections 20 and 21).

The proof given here (that the linear moist available energy is positive definite and that it can be expressed as the sum of three positive definite components) is readily extended using the approach of Dutton (1973) to invoke a Taylor series expansion with remainder. One finds that the nonlinear moist available potential energy and its components are positive definite. This proof is distinct from that of Fortak (1998, appendix 2) that follows Andrews (1981) whose approach is Lagrangian (Bannon 2004). The current proof is distinctly Eulerian.

c. Energy partitioning

This linear result suggests that the available energy can be divided into three parts: available potential, available elastic, and available chemical energy. Specifically

$$ae = ape + aee + ace, \tag{2.21}$$

where the available potential energy is

$$ape \equiv h(s, p_r, \chi) - h(s_r, p_r, \chi) - T_r\Delta s, \tag{2.22}$$

the available elastic energy is

$$aee \equiv h(s, p, \chi) - h(s, p_r, \chi) - \alpha\Delta p, \tag{2.23}$$

and the available chemical energy is

$$ace \equiv h(s_r, p_r, \chi) - h(s_r, p_r, \chi_r) - \mu_{rj}\Delta\chi_j, \tag{2.24}$$

and $\chi = (\chi_1, \chi_2, \dots, \chi_N)$ is the concentration vector for the N constituents where χ_j is the concentration of the

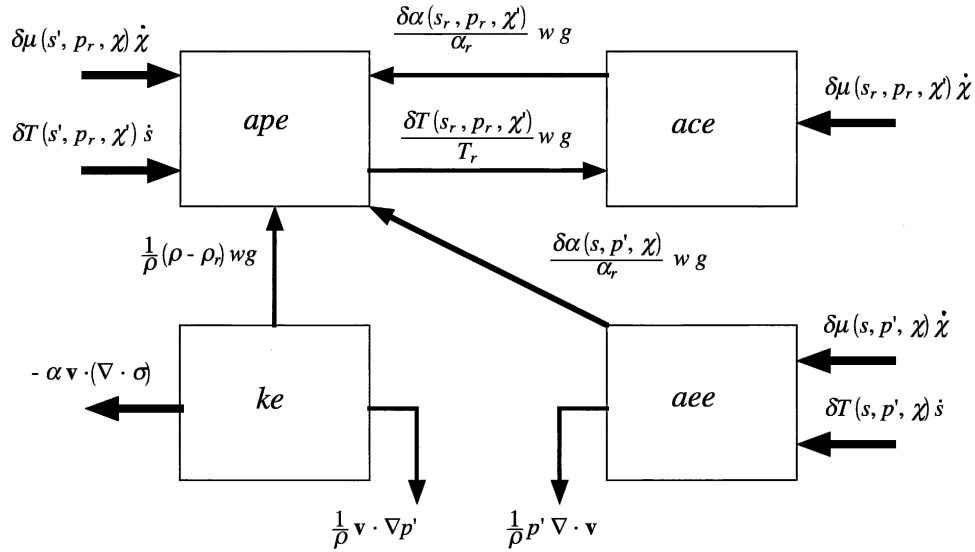


FIG. 1. Schematic box diagram of the available energetics. The heavy arrows depict generation mechanism; the thin arrows depict conversion mechanisms. The direction of the arrow indicates the direction of positive conversion/generation.

j th constituent. Using the Gibbs relation, the hydrostatic relation (2.4), and the relation (2.6), and defining the gradient of the geopotential as the acceleration due to gravity g in the vertical, the rate of change of the individual components of the available energy may be determined. For example, the rate of change of the available potential energy is

$$\begin{aligned} \frac{Dape}{Dt} = & [T(s, p_r, \chi) - T_r] \dot{s} + \frac{1}{\rho} (\rho - \rho_r) gw \\ & - [T(s_r, p_r, \chi) - T_r] gw \\ & + [\mu_j(s, p_r, \chi) - \mu_j(s_r, p_r, \chi)] \dot{\chi}_j \\ & - \frac{[\alpha(s, p_r, \chi) - \alpha(s, p, \chi)]}{\alpha_r} gw \\ & - \frac{[\alpha(s_r, p_r, \chi_r) - \alpha(s_r, p_r, \chi)]}{\alpha_r} gw. \end{aligned} \quad (2.25)$$

That for the available elastic energy is

$$\begin{aligned} \frac{Daee}{Dt} = & [T(s, p, \chi) - T(s, p_r, \chi)] \dot{s} \\ & - \frac{[\alpha(s, p, \chi) - \alpha(s, p_r, \chi)]}{\alpha_r} gw \\ & + [\mu_j(s, p, \chi) - \mu_j(s, p_r, \chi)] \dot{\chi}_j - \alpha p' \nabla \cdot \mathbf{v}, \end{aligned} \quad (2.26)$$

and that for the available chemical energy is

$$\begin{aligned} \frac{Dace}{Dt} = & \frac{[T(s_r, p_r, \chi) - T_r]}{T_r} gw - \frac{[\alpha(s_r, p_r, \chi) - \alpha_r]}{\alpha_r} gw \\ & + [\mu_j(s_r, p_r, \chi) - \mu_{rj}] \dot{\chi}_j. \end{aligned} \quad (2.27)$$

The individual components of the available energetics are summarized in Fig. 1 based on the above equations and the kinetic energy equation in the form

$$\frac{Dke}{Dt} = -\frac{1}{\rho} \mathbf{v} \cdot \nabla p_r - \frac{1}{\rho} \mathbf{v} \cdot \nabla p' - \mathbf{v} \cdot \nabla \Phi + \frac{1}{\rho} \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\sigma}), \quad (2.28a)$$

or

$$\frac{Dke}{Dt} = -\frac{1}{\rho} (\rho - \rho_r) wg - \frac{1}{\rho} \mathbf{v} \cdot \nabla p' + \frac{1}{\rho} \mathbf{v} \cdot (\nabla \cdot \boldsymbol{\sigma}), \quad (2.28b)$$

which sum to give (2.13). Here δ denotes a partial finite difference. For example,

$$\begin{aligned} \delta T(s, p', \chi) & \equiv T(s, p, \chi) - T(s, p_r, \chi), \\ \delta T(s', p_r, \chi') & \equiv T(s, p_r, \chi) - T(s_r, p_r, \chi_r). \end{aligned} \quad (2.29)$$

Inspection of the equations and of Fig. 1 indicates that it is convenient to combine the available potential and chemical energies into a single available potential energy, $ape' = ape + ace$. Then $ae = ape' + aee$ and

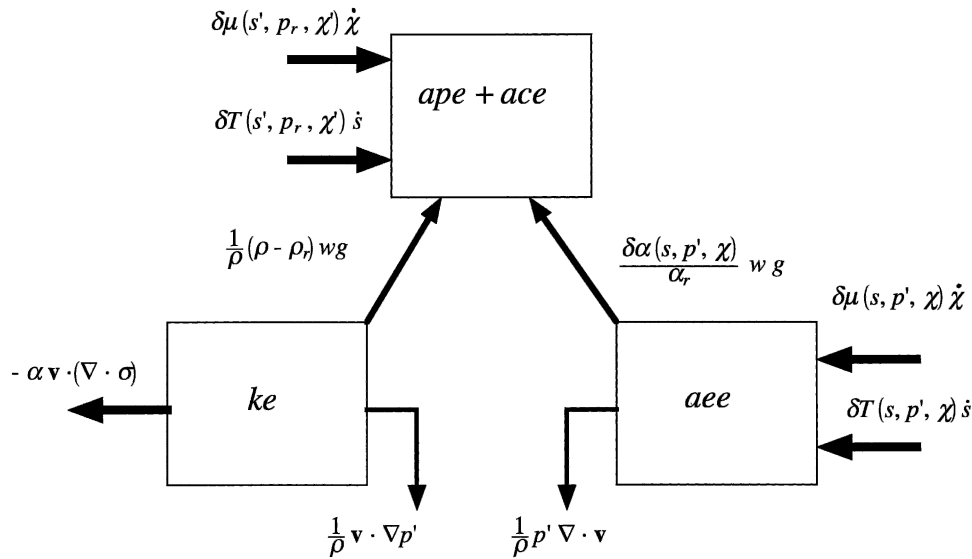


FIG. 2. As in Fig. 1 but for the case of the combined available potential and chemical energies.

$$\begin{aligned} \frac{Dape'}{Dt} = & [T(s, p_r, \chi) - T_r] \dot{s} - \left[\frac{1}{\rho} - \frac{1}{\rho_r} \right] \rho_r g w \\ & - \frac{[\alpha(s, p_r, \chi) - \alpha(s, p, \chi)]}{\alpha_r} g w \\ & + [\mu_j(s, p_r, \chi) - \mu_{rj}] \dot{\chi}_j, \end{aligned} \quad (2.30)$$

and the schematic simplifies to Fig. 2.

3. Application to moist atmospheres

This section applies the general formulation of the preceding section to specific examples of moist atmospheres that can contain liquid water and ice as well as water vapor and dry air. The explicit thermodynamic relations for this situation are summarized in appendix A.

The reference atmosphere is taken to be a dry, isothermal atmosphere of temperature $T_r = 250$ K and a surface pressure of 1000 hPa. This choice of reference temperature is compatible with Livezey and Dutton (1976) and Marquet (2003). The reference chemical potentials are constants and are given by (A.12) evaluated for moist air saturated with respect to ice at the reference temperature and pressure and corresponds to the chemical potential of saturated air at the surface temperature T_r and surface pressure p_{00} ($=1000$ hPa). The choice of a dry reference atmosphere assures that it is in a convectively dead state. Figure 3 summarizes the situation. The present choice differs from that of Livezey and Dutton (1976) who used an isothermal, hydrostatic system having the same mass and energy of the original

fluid system. However, Kucharski (1997) emphasizes that the choice of reference state is arbitrary. Clearly, the analysis of section 2 does not hinge on the particular attributes of the reference state other than that it be isothermal, hydrostatic, and with uniform chemical concentrations. In contrast to Livezey and Dutton (1976), Lorenz (1978, 1979), and Marquet (1993) who all want to conserve the total mass of water, the current work treats the atmosphere as an open system and water can enter it through evaporation and leave it through pre-

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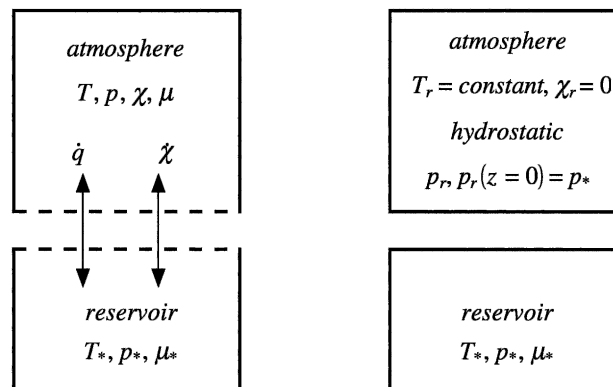


FIG. 3. Schematic diagram depicting (left) an atmosphere (rectangle) that is in thermal and chemical contact (dashed horizontal lines) with an infinite reservoir (open rectangle) of fixed temperature, pressure, and chemical potential. (right) The reference "convectively dead" state of the atmosphere that is dry, isothermal, and hydrostatic and is not in thermal and chemical contact (solid horizontal lines) with the infinite reservoir.

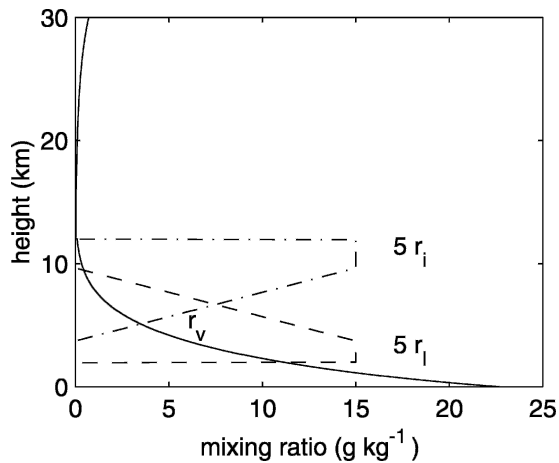


FIG. 4. Mixing ratio as a function of height for the moist cases. The solid and dotted curves are the water vapor mixing ratio for the saturated and moist atmospheres. The dashed and dash-dotted curves are the liquid water and ice mixing ratios multiplied by 5 for the case of a cloud with ice. In the case of a cloud with no ice (not shown), the liquid water mixing ratio is 3 g kg^{-1} from 2 to 12 km.

TABLE 1. Vertically integrated densities for the five atmospheres. Units are kg m^{-2} .

	Dry	Moist	Saturated	Cloud	Cloud with ice
Dry air	10 073.7	10 021.2	10 015.8	9999.3	9999.3
Vapor	0	50.8	56.0	55.9	55.9
Liquid	0	0	0	18.0	10.6
Ice	0	0	0	0	7.5
Total	10 073.7	10 072.1	10 071.9	10 073.3	10 073.3

precipitation. Such a choice is more relevant to applications to moist convection.

The available potential, elastic, and chemical energies are evaluated using the expressions

$$ape = h(s, p_r, r) - h(s_r, p_r, r) - T_r \Delta s, \quad (3.1)$$

$$aee = h(s, p, r) - h(s, p_r, r) - \alpha \Delta p, \quad (3.2)$$

$$ace = h(s_r, p_r, r) - h(s_r, p_r, 0) - \mu_{rj} \chi_j. \quad (3.3)$$

Dry Atmosphere

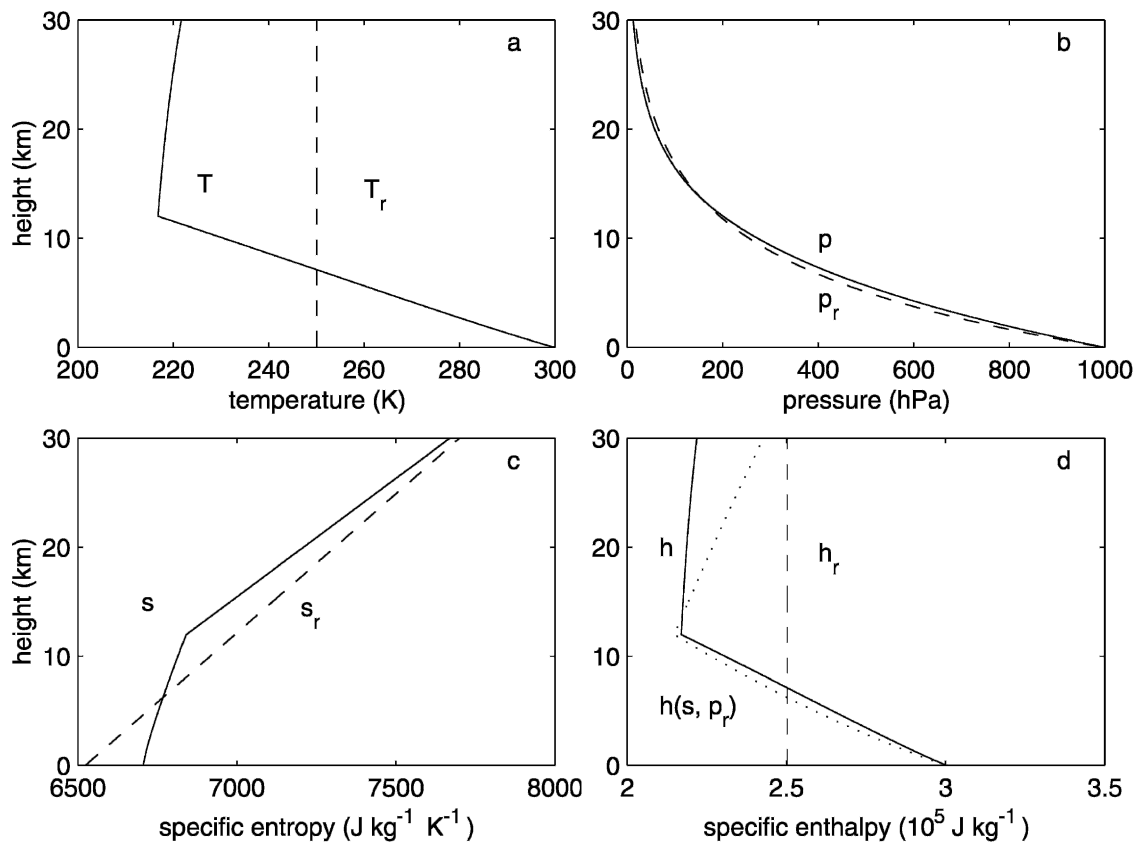


FIG. 5. (a) Temperature, (b) pressure, (c) entropy, and (d) enthalpy as a function of height z for the dry atmosphere. The solid curves refer to the sounding and the dashed curves to the reference atmosphere. Subscript r refers to the reference atmosphere. In (d) the hybrid enthalpy $h(s, p_r)$ is the dotted curve.

Dry Atmosphere

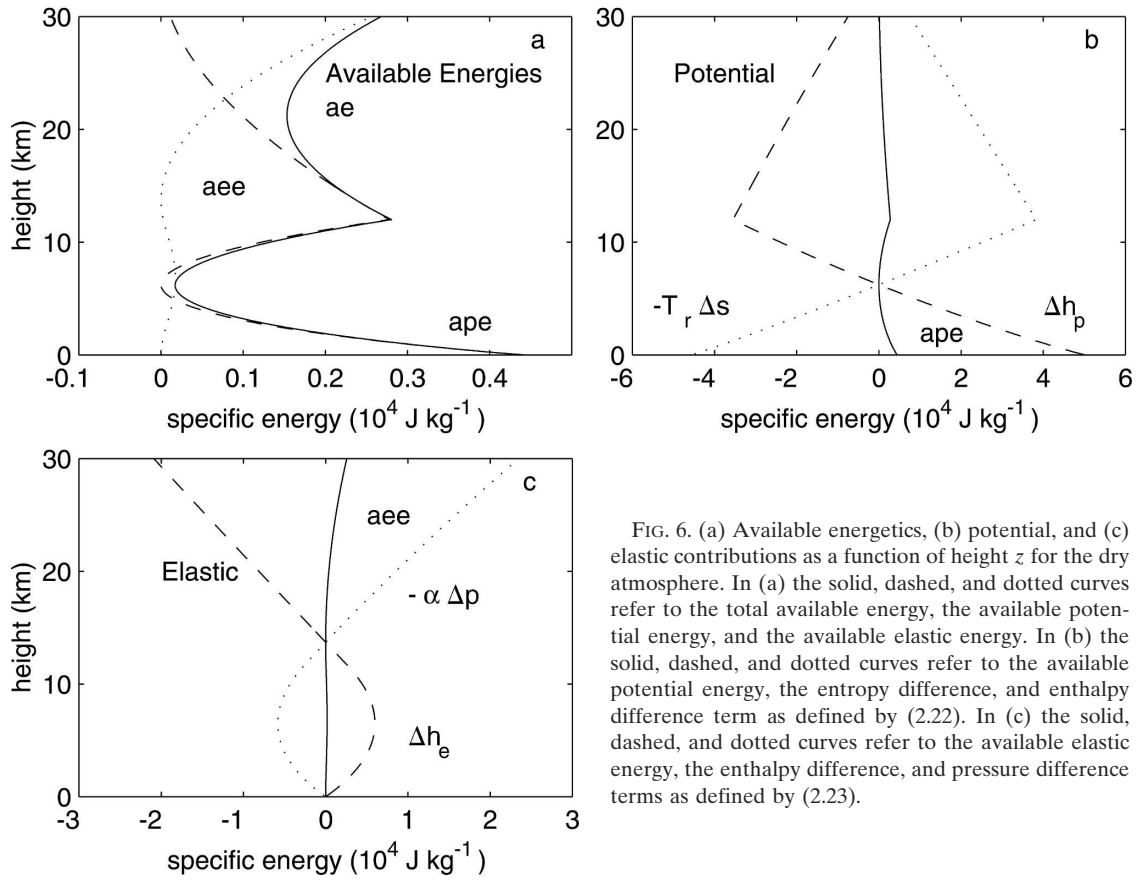


FIG. 6. (a) Available energetics, (b) potential, and (c) elastic contributions as a function of height z for the dry atmosphere. In (a) the solid, dashed, and dotted curves refer to the total available energy, the available potential energy, and the available elastic energy. In (b) the solid, dashed, and dotted curves refer to the available potential energy, the entropy difference, and enthalpy difference term as defined by (2.22). In (c) the solid, dashed, and dotted curves refer to the available elastic energy, the enthalpy difference, and pressure difference terms as defined by (2.23).

These expressions differ from the definitions in section 2 by the replacement of the vector of concentrations χ with the total water mixing ratio r . Thus in, say, the calculation of the available potential energy we require that the total water is the same for the two enthalpies $h(s, p_r, r)$ and $h(s_r, p_r, r)$ but the definition (2.22) would require that the individual concentrations in the two cases would be the same. The latter approach could possibly lead to huge supersaturations or supercooled water contents. The approach with the restriction on the total water content prevents these situations. It is noted that the total available energy is the same using either the set (2.22)–(2.24) or (3.1)–(3.3). Appendix B describes the algorithm used to calculate the enthalpy from the entropy, pressure, and total mixing ratio.

The analytic sounding of Weisman and Klemp (1982) that has been employed in several idealized studies of deep convection is used here. Specifically, the environmental potential temperature θ and relative humidity H_l are given by

$$\theta(z) = \begin{cases} \theta_0 + (\theta_{tr} - \theta_0) \left(\frac{z}{z_{tr}}\right)^{5/4}, & z \leq z_{tr} \\ \theta_{tr} \exp\left[\frac{g}{c_{pa} T_{tr}} (z - z_{tr})\right], & z \geq z_{tr} \end{cases} \quad (3.4)$$

and

$$H_l(z) = \begin{cases} 1 - \frac{3}{4} \left(\frac{z}{z_{tr}}\right)^{5/4}, & z \leq z_{tr} \\ 0.25, & z \geq z_{tr} \end{cases}, \quad (3.5)$$

where $\theta_0 = 300$ K is the surface potential temperature, and the tropopause height is $z_{tr} = 12$ km with potential temperature $\theta_{tr} = 343$ K and a reference temperature $T_{tr} = 213$ K. In addition to water vapor given by (3.5), the sounding may also be modified by the prescription of profiles of liquid water and ice mixing ratios (defined below). The atmosphere is assumed to be hydrostatic with a surface pressure of 1000 hPa. The atmospheric temperature and water vapor mixing ratio are derived

Moist Atmosphere

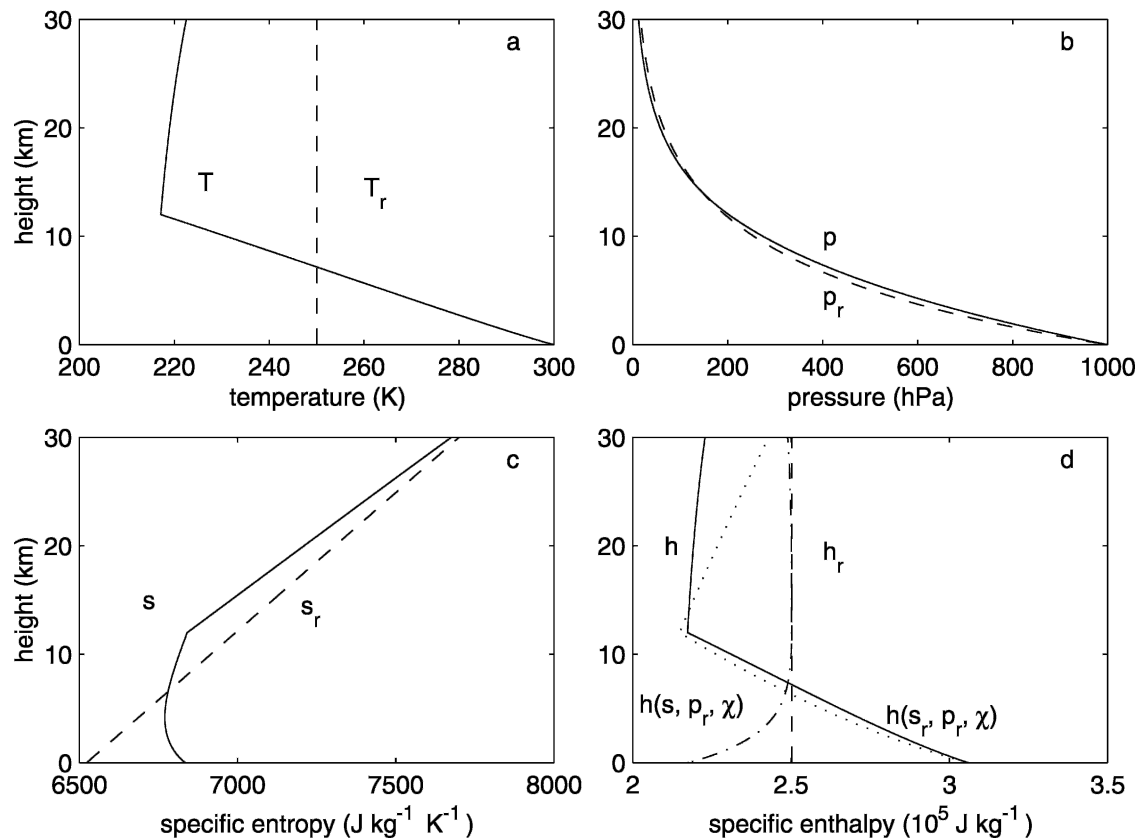


FIG. 7. As in Fig. 5 but for the moist atmosphere. (d) The hybrid enthalpy $h(s_r, p_r, \chi)$ is the dash-dotted curve.

iteratively from (3.4) and (3.5) by integrating the hydrostatic relation upward from the surface ($z = 0$) to the top of the atmosphere ($z = 30$ km) and using the ideal gas law. The numerical integration has a resolution of 50 m.

Five different atmospheres are examined: a dry atmosphere with no water; a moist atmosphere with water vapor given by (3.5); a saturated atmosphere with a relative humidity of 100% in the troposphere and 25% in the stratosphere; and two cloudy atmospheres. The two cloudy atmospheres have a relative humidity distribution identical to the saturated atmosphere with a hydrometeor mixing ratio specified to be 3 g kg^{-1} from $z = 2$ to 12 km. In the first cloudy atmosphere, the hydrometeors are all liquid water. In the second, the hydrometeors are partitioned according to temperature as described in appendix B. Specifically, the fraction of ice increases from zero at a temperature 0°C to one at -40°C . Figure 4 summarizes the water profiles for the various cases. Table 1 demonstrates that each atmosphere has approximately the same total mass but differing relative amounts of dry air and water. In addition,

the method described in the preceding paragraph implies that each temperature profile is slightly different for the five atmospheres considered.

Figure 5 plots several thermodynamic state variables for the sounding (3.4) for a dry atmosphere $H = 0$ and the reference atmosphere. The sounding values for temperature, pressure, entropy, and enthalpy are greater than that of the reference atmosphere below 7.15, 13.60, 6.25, and 7.15 km, respectively. These transition points are reflected in the various difference terms that make up the components of the available energy (Fig. 6). For example, the pressure difference term $-\alpha\Delta p$ exhibits a transition from negative to positive values at 13.60 km in Fig. 6c. Inspection of Figs. 6b and 6c indicates that the two terms that make up the available potential and elastic energies have similar magnitudes and opposite sign. The available potential energy is positive definite with its largest values near the surface and a secondary maximum at the tropopause $z = 12$ km. In contrast, the available elastic energy is largest in the stratosphere and has a secondary maximum near 7 km in the troposphere. Their sum

Moist Atmosphere

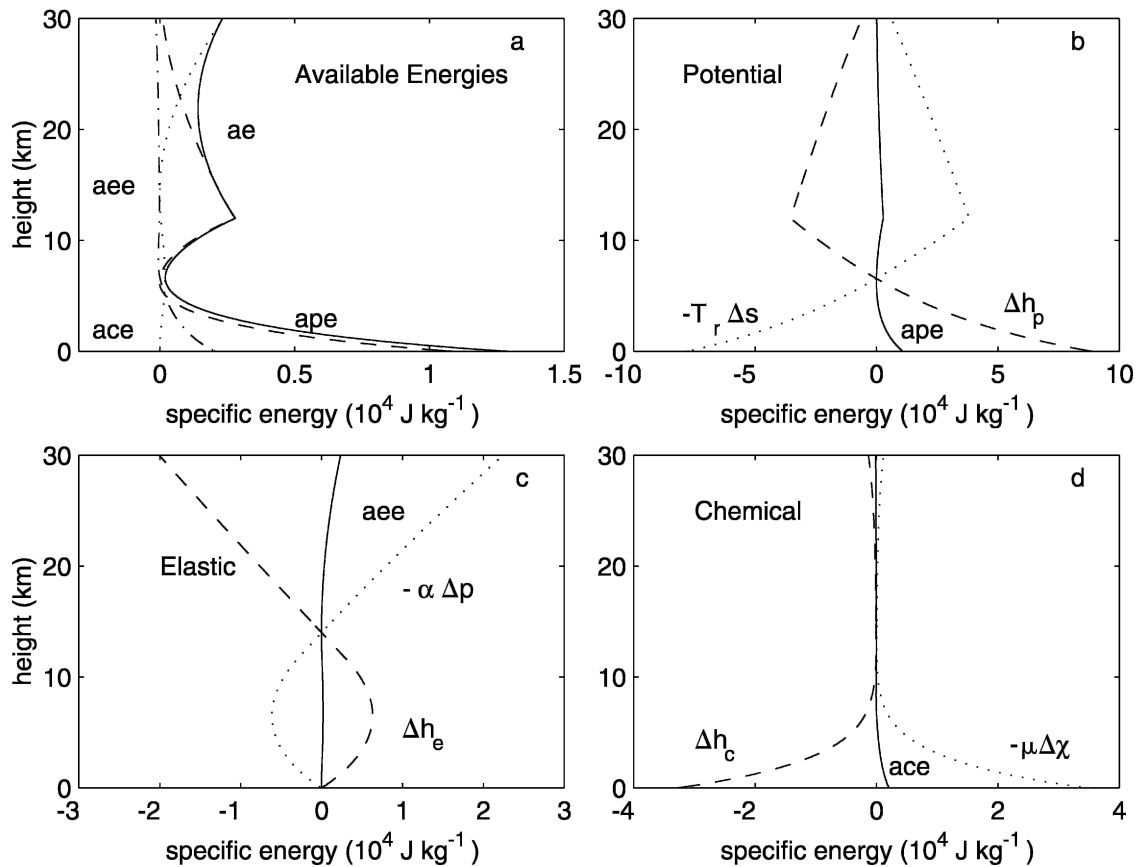


FIG. 8. As in Fig. 6 but for the moist atmosphere. (a) The dash-dotted curve is the available chemical energy. (d) The solid, dashed, and dotted curves refer to the available chemical energy, the enthalpy difference, and the concentration difference terms as defined in (2.24).

yields the available energy (Fig. 6a) that is dominated by the available potential energy below 20 km.

The corresponding situation for the moist case with (3.5) is given in Figs. 7 and 8. The temperature field is quite similar and the pressure field has a slightly higher transition, $z = 14.05$ km, in the moist case. The presence of moisture has significantly increased the entropy of the sounding in the lower atmosphere below 5 km (Fig. 7c). The structure of the available potential and elastic energies and their components are similar in the moist case (Figs. 8b and 8c) to the dry case (Figs. 6b and 6c) but the moist case has a greater available potential energy due to the increased entropy at low levels. The available chemical potential exhibits a significant contribution (Figs. 8d and 8a) to the available energy only in the lower troposphere.

The three remaining cases add refinements to the moist case. Plots for the saturated case (not shown) are similar to the moist case. The plots for the cloudy atmospheres with and without ice are similar to each

other. Figures 9 and 10 show the fields for the cloudy atmosphere with ice. The major differences from the moist case of Figs. 7 and 8 are the shifts in the entropy and enthalpy at cloud base and cloud top. The terms that comprise the available chemical energy are enlarged (Fig. 10d).

Table 2 compares the vertically integrated available energies for the five cases. For example,

$$APE \equiv \int_0^D \rho a p e \, dz, \quad (3.6)$$

where $D = 30$ km is the depth of the atmosphere. There is a clear monotonic increase in the available potential and chemical energies as the amount of water is increased in the profile. The reduction in available elastic energy in going from clear to a cloudy atmosphere reflects the fact that the pressure for the cloudy atmospheres is closer to the reference pressure.

In contrast to the available energetics of Table 2, the

Cloudy Atmosphere with Ice

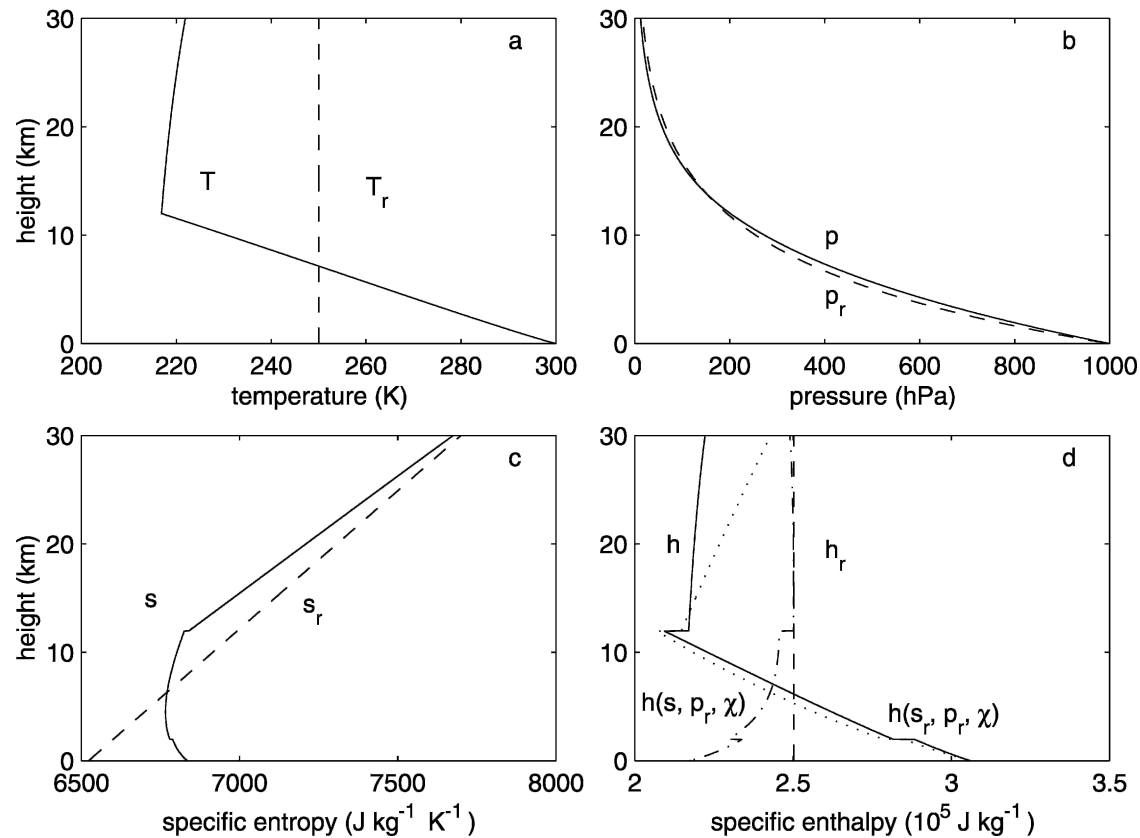


FIG. 9. As in Fig. 7 but for the cloudy atmosphere with ice.

traditional energetics (Table 3) provides no clear signal on the impact of increasing water to the profile.

Table 2 also assesses the impact of using reference chemical potentials evaluated for moist air saturated with respect to liquid water rather than ice at the reference temperature and pressure. In the latter, the vapor–ice reference chemical potential (A.12c) vanishes; in the former, the vapor–water reference chemical potential (A.12b) vanishes. Inspection of the table indicates that the available potential and elastic energies are unchanged. The available chemical energy is significantly reduced for all atmospheres with water. Again, there is a clear monotonic increase in available energy as the amount of water is increased.

The impact of the choice of the reference atmosphere merits some discussion. Table 4 summarizes the effect of varying the reference temperature on the available energetics. The available potential, available chemical, and total available energies decrease with increasing reference temperature for both the moist and dry cases. The available elastic energy exhibits a minimum near a reference temperature of 250 K. For a given reference

temperature, the moist sounding always has a greater available energy. If one follows the prescription of Livezey and Dutton (1976) and defines the reference atmosphere with the same mass of dry air and a temperature $T_r = 251$ corresponding to an isothermal atmosphere with the same sum of potential and internal energies, one finds very similar results (not shown). The sole qualitative difference is, because the surface pressure of the reference atmosphere differs from the sounding, there is a nonzero contribution to the elastic energy at the surface.

4. Conclusions

The major contributions of this investigation are the derivation of the equation for local Eulerian available energetics (2.13) and its partitioning (2.21)–(2.24) into available potential, available elastic, and available chemical energies. The derivation (section 2a) is simple but general and emphasizes its Eulerian nature. It complements the derivation of Karlsson (1990) and extends that of Fortak (1998) for multicomponent flows.

Cloudy Atmosphere with Ice

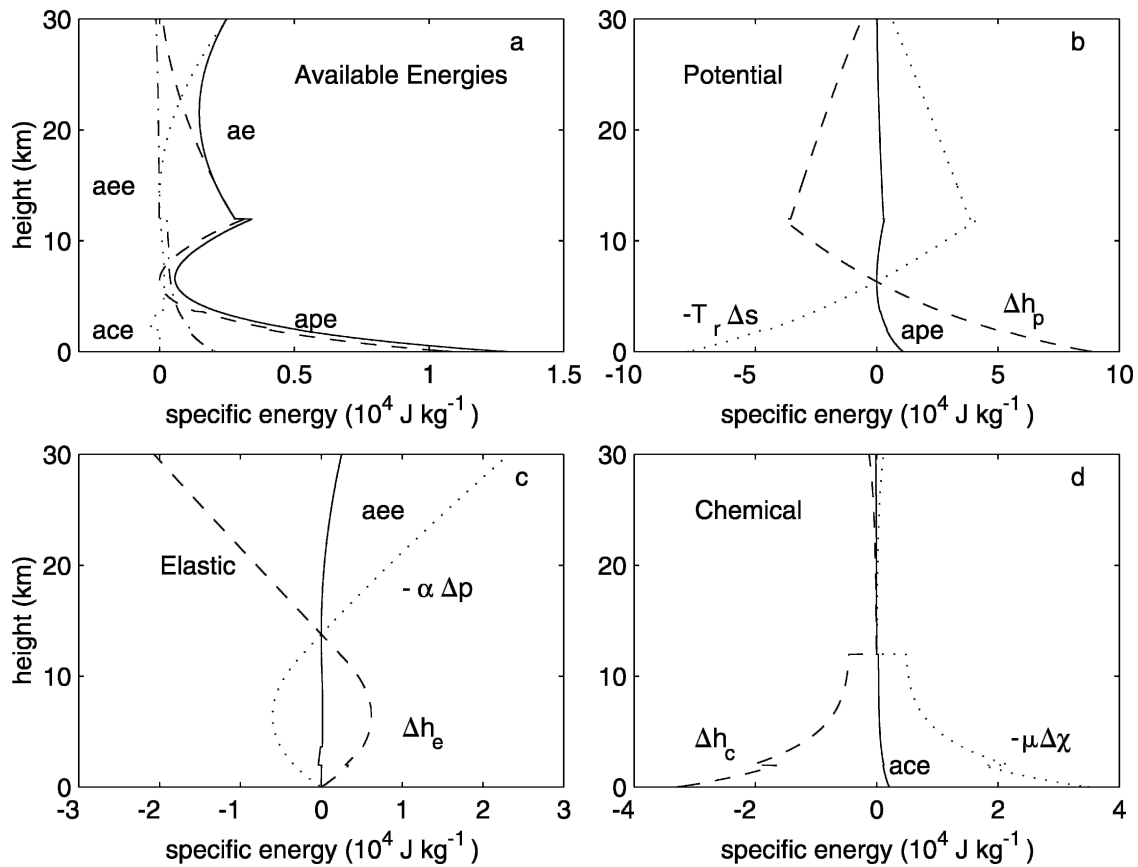


FIG. 10. As in Fig. 8 but for the cloudy atmosphere with ice.

The linear analysis of section 2b indicates that the available energy (2.1) is the nonlinear extension of the traditional linear energetics (e.g., Eckart 1960, sections 20 and 21).

The utility of the available energetics has been demonstrated in section 3 for the case of a moist atmosphere with liquid water and ice. Available energetics indicates that there is an increase in the available en-

ergy of an atmosphere as its water content increases. Karlsson (1990) and Marquet (1993) find a similar impact of an increase in water content on their static flow exergy and available enthalpy. In contrast, traditional energetics provides no insight into the impact of an increase in water content.

The results of section 3 may be applied to the temporal development of a moist convective system. As the water content of the system continues to grow with time, its available energy also grows, as does the possibility for the conversion of this available energy into

TABLE 2. Vertically integrated available energetics for the five atmospheres. The reference temperature is 250 K. Units are 10^6 J m^{-2} . The cases with water are for a reference vapor pressure for ice; numbers in parentheses are for a reference vapor pressure for liquid water.

	Dry	Moist	Saturated	Cloud	Cloud with ice
APE	14.2	24.1 (24.1)	24.9 (24.9)	25.5 (25.5)	25.7 (25.7)
ACE	0	4.3 (0.5)	4.9 (0.7)	5.8 (1.6)	6.3 (2.2)
AEE	1.4	1.4 (1.4)	1.4 (1.4)	1.0 (1.0)	0.9 (0.9)
AE	15.6	29.8 (26.0)	31.2 (27.0)	32.3 (28.2)	32.9 (28.8)

TABLE 3. Vertically integrated traditional energetics for the five atmospheres. Units are 10^9 J m^{-2} .

	Dry	Moist	Saturated	Cloud	Cloud with ice
Internal energy	1.848	1.859	1.860	1.814	1.816
Potential energy	0.707	0.709	0.709	0.708	0.708
Total energy	2.555	2.567	2.569	2.522	2.524

TABLE 4. Vertically integrated available energetics for the dry and moist atmospheres for various reference temperatures. Units are 10^6 J m^{-2} .

	Dry			Moist		
	240 K	250 K	260 K	240 K	250 K	260 K
T_r	240 K	250 K	260 K	240 K	250 K	260 K
APE	18.3	14.2	12.6	32.3	24.1	18.8
ACE	0	0	0	6.6	4.3	1.6
AEE	1.9	1.4	2.1	2.0	1.4	2.1
AE	20.2	15.6	14.7	40.9	29.8	22.5

kinetic energy. Research on this application is currently in progress.

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APPENDIX A

Moist Thermodynamics with Water and Ice

This appendix summarizes the thermodynamics of a multiphase, single-temperature parcel of cloudy air. Particular attention is paid to express the relations in absolute form. The entropy, s , per unit mass of cloudy air is

$$(1+r)s = s_a + rs_v + r_l(s_l - s_v) + r_i(s_i - s_v), \quad (\text{A.1})$$

where the total water mixing ratio $r = r_v + r_l + r_i$ is the sum of those for the water vapor, liquid water, and ice denoted with the subscripts v , l , and i . The specific entropies of each constituent are

$$s_a(T, p_a) = s_{a0} + c_{pa} \ln\left(\frac{T}{T_0}\right) - R_a \ln\left(\frac{p_a}{p_{00}}\right), \quad (\text{A.2})$$

$$s_v(T, e) = s_{v0} + c_{pv} \ln\left(\frac{T}{T_0}\right) - R_v \ln\left(\frac{e}{p_{00}}\right), \quad (\text{A.3})$$

$$s_l(T) = s_{l0} + c_l \ln\left(\frac{T}{T_0}\right), \quad s_i(T) = s_{i0} + c_i \ln\left(\frac{T}{T_0}\right), \quad (\text{A.4a,b})$$

where s_{a0} , s_{v0} , s_{l0} , and s_{i0} , are standard values of the entropy of dry air, water vapor, liquid water, and ice at the standard temperature T_0 and standard pressure p_{00} . The specific heats at constant pressure for the dry air,

water vapor, liquid water, and ice are c_{pa} , c_{pv} , c_l , and c_i . Here R_a and R_v are the ideal gas constants for dry air and water vapor, and p_a and e are the dry air and water vapor pressures.

The enthalpies of vaporization and sublimation are defined in terms of the difference in the entropies of the vapor at saturation (denoted with an asterisk) and those of the liquid water and ice

$$\frac{l_v(T)}{T} = s_{v^*}^*(T) - s_l(T), \quad \frac{l_s(T)}{T} = s_{i^*}^*(T) - s_i(T), \quad (\text{A.5a,b})$$

where l_v and l_s are the enthalpies of vaporization and sublimation. At saturation one has

$$s_{v^*}^* = s_{v0} + c_{pv} \ln\left(\frac{T}{T_0}\right) - R_v \ln\left(\frac{e_l^*}{p_{00}}\right), \quad (\text{A.6a})$$

$$s_{i^*}^* = s_{v0} + c_{pv} \ln\left(\frac{T}{T_0}\right) - R_v \ln\left(\frac{e_i^*}{p_{00}}\right). \quad (\text{A.6b})$$

Then the entropy may be written as

$$\begin{aligned} (1+r)s = & s_{a0} + rs_{v0} + (c_{pa} + rc_{pv}) \ln\left(\frac{T}{T_0}\right) \\ & - R_a \ln\left(\frac{p_a}{p_{00}}\right) - rR_v \ln\left(\frac{e}{p_{00}}\right) \\ & + r_l \left(R_v \ln H_l - \frac{l_v}{T} \right) + r_i \left(R_v \ln H_i - \frac{l_s}{T} \right), \end{aligned} \quad (\text{A.7})$$

because

$$s_{v^*}^* - s_v = R_v \ln\left(\frac{e}{p_{00}}\right) - R_v \ln\left(\frac{e_l^*}{p_{00}}\right) = R_v \ln H_l, \quad (\text{A.8a})$$

$$s_{i^*}^* - s_v = R_v \ln\left(\frac{e}{p_{00}}\right) - R_v \ln\left(\frac{e_i^*}{p_{00}}\right) = R_v \ln H_i, \quad (\text{A.8b})$$

where H_l and H_i are the relative humidities with respect to liquid water and ice.

Similarly, the specific enthalpy h is

$$\begin{aligned} (1+r)h = & h_{a0} + rh_{v0} + (c_{pa} + rc_{pv})(T - T_0) \\ & - r_l l_v - r_i l_s, \end{aligned} \quad (\text{A.9})$$

where h_{a0} and h_{v0} are the standard specific enthalpies of dry air and water vapor at the standard temperature T_0 .

It is straightforward to show that the thermodynamic identity

$$T ds - dh + \frac{1}{\rho} dp + \sum_{j=1}^4 \mu_j d\chi_j = 0, \quad (\text{A.10})$$

is satisfied. Here the subscripts 1–4 denote the dry air, water vapor, liquid water, and ice, respectively. The chemical potential contribution can be written in terms of the mixing ratios as

$$\begin{aligned} \sum_{j=1}^4 \mu_j d\chi_j &= \frac{(\mu_v - \mu_a)}{(1+r)^2} dr + \frac{(\mu_v - \mu_l)r_l}{(1+r)^2} dr \\ &+ \frac{(\mu_v - \mu_i)r_i}{(1+r)^2} dr - \frac{(\mu_v - \mu_l)}{(1+r)} dr_l \\ &- \frac{(\mu_v - \mu_i)}{(1+r)} dr_i, \end{aligned} \quad (\text{A.11})$$

where

$$\mu_v - \mu_a = (h_v - Ts_v) - (h_a - Ts_a), \quad (\text{A.12a})$$

$$\mu_v - \mu_l = R_v T \ln H_l, \quad \mu_v - \mu_i = R_v T \ln H_i. \quad (\text{A.12b,c})$$

The values of the constants are $T_0 = 273.15$, $p_{00} = 1000$ mb, $R_a = 287.04 \text{ J K}^{-1} \text{ kg}^{-1}$, $R_v = 461.50 \text{ J K}^{-1} \text{ kg}^{-1}$, $s_{a0} = 6.612 \times 10^3 \text{ J K}^{-1} \text{ kg}^{-1}$, $c_{pa} = 1004 \text{ J K}^{-1} \text{ kg}^{-1}$, $h_{a0} = 2.735 \times 10^5 \text{ J kg}^{-1}$, $s_{v0} = 1.032 \times 10^4 \text{ J K}^{-1} \text{ kg}^{-1}$, $c_{pv} = 1865 \text{ J K}^{-1} \text{ kg}^{-1}$, and $h_{v0} = 5.031 \times 10^5 \text{ J kg}^{-1}$ (Chase 1998). The number fractions of the components of the dry air are taken to be 78.1% nitrogen, 20.9% oxygen, and 1% argon. The latent heats of vaporization l_v and sublimation l_s are 2.501 and $2.835 \times 10^4 \text{ J kg}^{-1}$ at the standard temperature (Bohren and Albrecht 1998). In the calculations of section 3, the specific heats are constant but the latent heats vary linearly with temperature according to Kirchoff's relations.

APPENDIX B

Algorithm for $h(s, p, r)$

The definitions (2.22)–(2.24) for the components of the available energy require that the enthalpy be determined from the entropy, pressure, and total water mixing ratio. This appendix provides a recipe to do so. Given s , p , and r , all the other flow quantities must be diagnosed. As an initial guess, the temperature is taken to be the standard temperature $T = T_0$. Then the diagnosis proceeds in the following steps.

Step 1: The flow is assumed to be unsaturated. Then the mixing ratios are given by

$$r_v = r, \quad r_l = r_i = 0. \quad (\text{B.1})$$

Step 2: The partial pressures are found from the relations

$$p_a = p/(1 + r_v/\varepsilon), \quad e = \frac{r_v}{\varepsilon} p_a, \quad (\text{B.2})$$

where p_a is the dry air pressure, e is the water vapor pressure, and $\varepsilon = 0.622$.

Step 3: The temperature is found from the entropy relation (A.7) in the form

$$\begin{aligned} \ln\left(\frac{T}{T_0}\right) &= \left[(1+r)s - (s_{a0} + rs_{v0}) \right. \\ &+ R_a \ln\left(\frac{p_a}{p_{00}}\right) + rR_v \ln\left(\frac{e}{p_{00}}\right) \\ &- r_l \left(R_v \ln H_l - \frac{l_v}{T} \right) \\ &\left. - r_i \left(R_v \ln H_i - \frac{l_s}{T} \right) \right] / (c_{pa} + rc_{pv}). \end{aligned} \quad (\text{B.3})$$

Step 4: The density is determined from the ideal gas law

$$\rho = \frac{(1+r)p}{(1+r_v/\varepsilon)R_a T}. \quad (\text{B.4})$$

Step 5: The saturation vapor pressures are found from the temperature using the Clausius–Clapeyron equations

$$\frac{d \ln e_l^*}{dT} = \frac{l_v}{R_v T^2}, \quad \frac{d \ln e_i^*}{dT} = \frac{l_s}{R_v T^2}, \quad (\text{B.5})$$

where the latent heats are defined in appendix A and $e_{sat} = 6.11$ hPa at $T = 273.16$ K. Then the saturation mixing ratios with respect to liquid water and ice are determined from

$$r_{vl} = \frac{\varepsilon e_l^*(T)(1+r)}{\rho R_a T}, \quad r_{vi} = \frac{\varepsilon e_i^*(T)(1+r)}{\rho R_a T}, \quad (\text{B.6})$$

respectively.

Step 6: The total water is partitioned into vapor, liquid water, and ice.

If ice is permitted, then the partitioning proceeds as follows: If r is less than or equal to r_{vl} , the air is unsaturated with $r_v = r$ and $r_l = r_i = 0$ and the state variables have all been determined. If r is greater than r_{vl} and the temperature is above freezing, one has $r_v = r_{vl}$ and $r_l = r - r_{vl}$ and $r_i = 0$. If r is greater than r_{vl} and the temperature is below freezing, one partitions the liquid water and ice by setting $r_v = r_{vl}$, $r_l = (1 - f_{ice})(r - r_{vl})$ and

$r_i = f_{ice} (r - r_{ul})$. Here, f_{ice} is the fraction of the liquid water and ice that is ice. Its functional dependence in nature is not known. Let f_{ice} vary linearly with temperature such that $f_{ice} = 0$ at 0°C and $f_{ice} = 1$ for -40°C or colder. One must then repeat the loop and go back to step 2 and iterate until there is convergence. If no ice is permitted, then the partitioning proceeds as above but with $f_{ice} = 0$ for all temperatures.

The iteration is continued for a minimum of 10 iterations and is stopped when the absolute change in the temperature from one iteration to the next is 0.001 K or less. Typically convergence is reached in less than 100 iterations. Occasionally the iteration produces an oscillation between two temperatures. In such rare cases, step 3 is modified after 100 iterations so that the temperature is defined to be the old temperature plus 0.80 of the difference between the old and new temperatures. This approach breaks the oscillation and produces convergence.

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