Available Energy of Geophysical Systems

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ABSTRACT

An alternative derivation of the available energy for a geophysical fluid system is presented. It is shown that determination of the equilibrium temperature of the system by the minimization of an energy availability function is equivalent to that found by the vanishing of the entropy difference between the fluid and its equilibrium state. Applications to the atmosphere and the ocean are presented.

1. Introduction

The theories of the maximum energy available for conversion to kinetic energy developed by Karlsson (1990) and Bannon (2012) differ in the determination of the reference temperature of the isothermal reference atmosphere. [Tailleux (2013) provides a general review of available energy.] Karlsson (1990) uses a reference temperature that minimizes the entropy difference between the atmosphere and its reference atmosphere. Bannon (2012) argues that the reference temperature is that which minimizes an energy availability function (formerly a generalized Gibbs function). To be internally consistent with the argument in Bannon (2012, section 2), the entropy difference between the atmosphere and its equilibrium should vanish at the equilibrium temperature. Then the transition from the atmosphere to its equilibrium state is, in principle, achievable by an isentropic process.

The purpose of this paper is to demonstrate the equivalency of the two formulations. In particular, we prove that the energy availability δA of a system is related to the difference in total potential energy δTE between the system and its isothermal reference state by the difference in entropy δS between the two:

$$\delta A(T_r) = \delta \text{TE}(T_r) - T_r \delta S(T_r). \qquad (1.1)$$

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The specific availability is

$$\delta a = \delta u - T_r \delta s + p_r \delta \alpha - \mu_{rj} \delta \chi_j, \qquad (1.2)$$

where u, s, and α are the specific internal energy, entropy, and volume; T is the temperature; and p is the pressure. Here μ_j is the specific chemical potential of the jth component of mass m_j and χ_j is the concentration of the jth component (i.e., the mass of the jth component per total mass). The summation convention is assumed for repeated indices. The generalized Gibbs function of Bannon (2012) is here renamed availability for notational convenience and to emphasize its applicability to systems other than the atmosphere. A reference value is denoted by a subscript r. Unsubscripted variables are functions of position $\mathbf{x} = (x, y, z)$ and time t but the reference entropy, pressure, and chemical potentials are only functions of height z. The symbol δ defines a finite difference of the system from its isothermal reference state. For example, $\delta u = u(\mathbf{x}, t) - u_r(z)$. The total potential energy is the sum of the internal and potential energies $\text{TE} = U + \Phi$. The total mass of the system and that of its reference are the same:

$$\delta M = M - M_r = \int \rho \, dV - \int \rho_r \, dV_r \equiv \int (\rho - \rho_r) \, dV_t = 0, \qquad (1.3)$$

but the volumes of the two may differ. Here the last volume integral is over the volume V_t consisting of the union of the volumes of the system V and its isothermal reference state V_r. For example, the volume of an ocean with a tilted sea surface will differ from its reference

state that is dynamically dead with a sea surface corresponding to a geopotential. Similarly, the volume for an atmospheric system confined to lie below an isobaric surface will differ from its reference state also confined below the same isobaric surface. Then the difference in total entropy is $\delta S = S - S_r = \int (\rho s - \rho_r s_r) \, dV_t$, where the respective densities vanish in the appropriate regions of the total volume V_t.

The implications of the energy relation (1.1) are straightforward. If the entropy difference is negative $\delta S(T_r) < 0$, then it is impossible for the system to attain its reference state. If the difference is positive $\delta S(T_r) > 0$, then the availability is less than the difference in total potential energy $\delta A < \delta \text{TE}(T_r)$. Thus, the maximum available energy (AE) is that for the temperature T_0 where there is no entropy difference:

$$\text{AE} \equiv \delta A(T_0) = \delta \text{TE}(T_0), \quad \text{where} \quad \delta S(T_0) = 0. \quad (1.4)$$

It is noted that the equilibrium temperature and the available energy are thermodynamic state variables of the geophysical system.

Sections 2 and 3 present general proofs of the relation (1.1) for a moist atmosphere with hydrometeors and for an ocean of seawater. Specific examples are presented. The paper concludes in section 4 with some general comments.

2. Atmospheric available energy

The availability for the atmosphere can be expressed (Bannon 2012) as the sum of the contributions of its components as

$$\delta A = \int \rho_j \delta a_j \, dV_t, \quad \text{where} \quad \delta a_j = \delta u_j - T_0 \delta s_j + p_{rj} \delta \alpha_j. \quad (2.1)$$

The numeric subscripts $j = 1, 2, 3,$ and 4 (or alphabetical subscripts $j = d, v, l,$ and i) correspond to the dry air, water vapor, liquid water, and ice, respectively. The differences of the internal energy, entropy, and work term are (with no summation convention implied)

$$\delta U_j = \int \rho_j \delta u_j \, dV_t + u_{rj} \delta M_j, \quad (2.2)$$

$$T_r \delta S_j = \int \rho_j T_r \delta s_j \, dV_t + T_r s_{rj0} \delta M_j + \delta \Phi_j, \quad (2.3)$$

$$\int \rho_j p_{rj} \delta \alpha_j \, dV_t = -R_j T_r \delta M_j. \quad (2.4)$$

Unlike the total mass difference (1.3) that vanishes, the mass difference of an individual component δM_j may not vanish because of a difference in the distribution among the various phases. The entropy relation (2.3) is derived as follows. The entropy difference for the jth component is

$$\delta S_j = \int (\rho_j s_j - \rho_{rj} s_{rj}) \, dV_t = \int (\rho_j s_j - \rho_j s_{rj} + \rho_j s_{rj} - \rho_{rj} s_{rj}) \, dV_t$$

$$= \int (\rho_j \delta s_j + s_{rj} \delta \rho_j) \, dV_t. \quad (2.5)$$

The specific entropy in the equilibrium state is a constant s_{rj0} apart from a contribution owing to the exponential decay with height of the pressure field in the isothermal, hydrostatic, equilibrium atmosphere. Then, following Dutton (1973), we have $s_{rj} = s_{rj0} + \phi/T_r$, where ϕ is the geopotential. The result (2.3) follows where the difference in mass and potential energy are $\delta M_j = \int \delta \rho_j \, dV_t$ and $\delta \Phi_j = \int \phi \delta \rho_j \, dV_t$.

For a moist atmosphere consisting of dry air and water vapor, the availability (2.1) is, using (2.2)–(2.5),

$$\delta A = \delta U_d + \delta U_v + \delta \Phi_d + \delta \Phi_v - T_r \delta S_d - T_r \delta S_v$$
$$- (h_{rd} - T_r s_{rd0}) \delta M_d - (h_{rv} - T_r s_{rv0}) \delta M_v, \quad (2.6)$$

where $h = u + p\alpha$ is the specific enthalpy. If the mass of dry air and water vapor is conserved, $\delta M_d = \delta M_v = 0$ and (2.6) reduces to (1.1) with $\text{TE} = U + \Phi$. If the equilibrium atmosphere were to be supersaturated at the temperature T_r, then a portion of the vapor is assumed (Bannon 2012) to reside in an ice (liquid if T_r is above freezing) reservoir at the surface. In this case, the vapor entropy is that at saturation with respect to ice (denoted with an asterisk) $s_{rv0} = s_{v0}^*(T_r)$ and the loss of vapor is compensated by a gain in ice $\delta M_v = -\delta M_i > 0$ so that the total water content $\delta M_w = 0$ is conserved. Then the last term in (2.6) becomes

$$(h_{rv} - T_r s_{v0}^*) \delta M_v + (h_{ri} - T_r s_{ri0}) \delta M_i. \quad (2.7)$$

Equality of the chemical potentials at equilibrium between phases implies that $h_{rv} - T_r s_{v0}^* = h_{ri} - T_r s_{ri}$. Then the relation (1.1) again holds but with the inclusion of the ice contributions to the differences in total energy and entropy. It is noted that, by similar arguments, the relation (1.1) holds for an atmosphere initially containing water and ice hydrometeors.

The fundamental relation (1.1) provides an unambiguous determination of the available energy of a system. An atmospheric example (Fig. 1) is that for a 25-km-deep moist standard atmosphere with a surface temperature and pressure of 288.15 K and 1013.25 hPa.
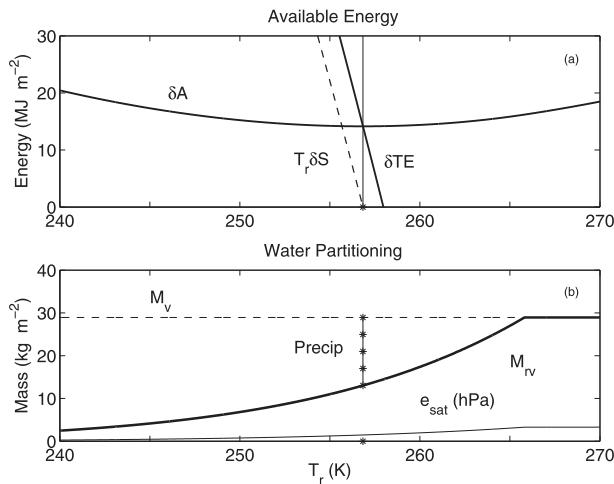
FIG. 1. (a) The atmospheric availability δA (thick solid curve) for a 25-km-deep moist standard atmosphere as a function of the reference temperature T_r. The tilted solid line is the difference in total potential energy $\delta \mathrm{TE}$ between the atmosphere and the reference atmosphere; the dashed line is that for the reference temperature times the difference in entropy $T_r \delta S$. The thin vertical line corresponds to the equilibrium temperature T_0 where the availability is a minimum. (b) The thick solid curve denotes the mass of water vapor M_{rv} in the reference atmosphere as a function of reference temperature. The horizontal dashed line is the mass of water vapor M_v in the atmosphere. Their difference, $\delta M_v = M_v - M_{rv}$, denotes the amount of water in the atmosphere precipitated into the surface ice reservoir in the reference state. The reference surface vapor pressure e_*, denoted by the thin solid curve, increases following the Clausius–Clapeyron relation for water vapor and ice with T_r until the reference atmosphere is sufficiently warm to contain all the atmosphere's water in a subsaturated state. The asterisks on the abscissas denote $T_0 = 256.83 \pm 0.01$ K.

The lapse rates are 6.5, 0, and -1.0 K km^{-1} for $z > 0, 11$, and 20 km, respectively. The water vapor distribution is that of a surface relative humidity of 70% with an e-folding height of 3 km. The thermodynamic parameters are standard (Bohren and Albrecht 1998). Figure 1 and Table 1 provide visual and quantitative evidence of the relation (1.1). Evaluation of the variables requires definition of reference values. The potential energy is defined to be zero at the surface of the atmosphere. The

enthalpies of dry air and ice are defined to be zero at a temperature 100°C below the triple point. The entropy is defined relative to a zero entropy at the triple point temperature $T_{tp} = 273.16$ K with vapor pressure $e_{tp} = 6.11$ hPa and dry air pressure $p_{oo} = 1000$ hPa. Inspection of Table 1 indicates that the equilibrium atmosphere has, relative to the moist atmosphere, (i) a decrease in potential energy despite a slight increase in that of the water, (ii) a decrease in total internal energy despite an increase in that of the dry air, and (iii) a decrease in total energy despite an increase in that of the dry air. The total energy difference is equal to the available energy. The AE contributions of the dry air and water vapor are both positive with that of the dry air dominating the two.

3. Oceanic available energy

The reference state of the ocean is taken to be isothermal, isohaline, and hydrostatic. The reference salinity $S_{A0} = M_S/(M_W + M_S)$ is the same regardless of the temperature. Here, the subscripts S and W refer to the salt and water, respectively, and S_A is the absolute salinity. Treating the seawater as a binary fluid, we have $\mu_j \delta \chi_j = \mu \delta \chi$ where the relative chemical potential is $\mu = \mu_{salt} - \mu_{water}$ and $\chi = S_A$. Then the specific availability (1.2) may be written as

$$\delta a = \delta h - T_r \delta s - \alpha \delta p - \mu_r \delta \chi. \qquad (3.1)$$

Gibbs (1873) has shown that the total chemical potential (i.e., the sum of the intrinsic chemical potential μ_j and the geopotential) is a constant for each component in a system in equilibrium. Then the relative chemical potential in the reference state μ_r is a constant.

The differences in internal and potential energy for the ocean are

$$\delta U = \int \rho \delta u \, dV_t + \int u_r \delta \rho \, dV_t, \qquad (3.2)$$

$$\delta \Phi = \int \phi \delta \rho \, dV_t. \qquad (3.3)$$

TABLE 1. Budget of the moist standard atmosphere for the mass M, potential energy Φ, internal energy U, total energy (TE $= U + \Phi$), entropy S, and available energy (AE). Values for the equilibrium atmosphere with temperature $T_0 = 256.83$ K are in parentheses.

	Dry air	Water vapor/ice	Total
M (Mg m^{-2})	10.061 (10.061)	0.029 (0.013/0.016)	10.090 (10.090)
Φ (MJ m^{-2})	661.66 (649.78)	0.91 (1.08/0)	662.57 (650.86)
U (MJ m^{-2})	62.48 (103.58)	84.06 (37.69/2.79)	146.54 (144.06)
TE (MJ m^{-2})	724.14 (753.36)	84.97 (38.77/2.79)	809.11 (794.92)
S (TJ K^{-1} m^{-2})	1.7182 (1.8774)	0.3038 (0.1464/−0.0021)	2.0219 (2.0217)
AE (MJ m^{-2})	11.679	2.449	14.128

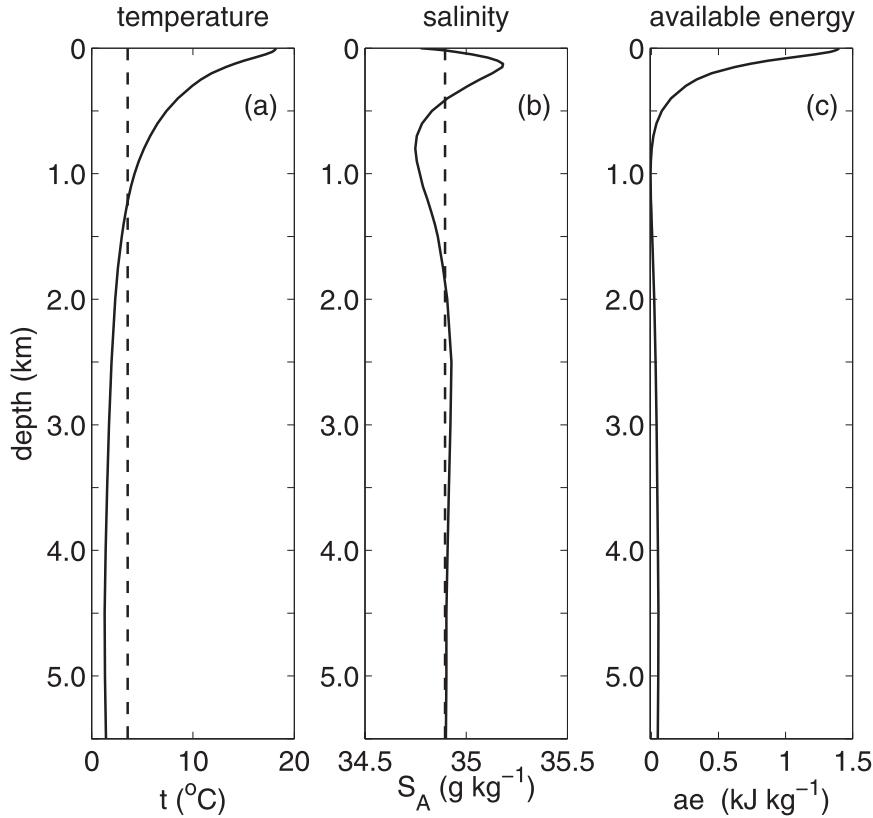temperature   salinity   available energy

FIG. 2. Vertical profiles of the horizontal mean *WOA05* (a) temperature, (b) absolute salinity, and (c) specific available energy as a function of depth. The dashed curves correspond to the equilibrium values $T_0 = 3.56°C$ and $S_{A0} = 34.90\,\text{g kg}^{-1}$.

Expressions for the differences in enthalpy and entropy are similar in form to (3.2). We also note that the chemical potential contribution to the availability vanishes:

$$\int \mu_r \rho \delta\chi \, dV_t = \mu_r \delta M_S = 0, \qquad (3.4)$$

because the reference relative chemical potential μ_r is a constant and the salinity is conserved.

Then, one finds

$$\delta A = \delta H - \int \delta p \, dV_t - \int g_r \delta\rho \, dV_t - T_r \delta S, \quad (3.5)$$

where $g = h - Ts$ is the specific Gibbs function. It is readily shown that the first two terms on the right-hand side combine to yield the difference in internal energy $\delta U = \delta H - \int \delta p \, dV_t$. The general thermodynamic relation for the specific Gibbs function $dg = -s \, dT + v \, dp + \mu \, d\chi$ (e.g., Reif 1965) applied to the isothermal, isohaline, hydrostatic reference state implies that $dg_r = -d\phi$. Then the reference specific Gibbs function is $g_r = g_{r0} - \phi$,

where g_{r0} is a constant surface value. Using this result, the third term in (3.5) yields the difference in potential energy

$$-\int g_r \delta\rho \, dV_t = -g_{r0} \delta M + \int \phi \delta\rho \, dV_t = \delta\Phi, \quad (3.6)$$

where we have assumed mass conservation. Thus, the proof of (1.1) is demonstrated. It is noted that the proof is readily extended to the case of an ocean containing ice.

An ocean example of (1.1) is that for the horizontal mean temperature and salinity of the *World Ocean Atlas 2005* (*WOA05*) (Locarnini et al. 2006; Antonov et al. 2006) (Fig. 2) and is presented in Fig. 3. The required thermodynamic variables are evaluated with the Gibbs SeaWater (GSW) Oceanographic Toolbox of Thermodynamic Equation of Seawater-2010 (TEOS-10) (McDougall and Barker 2011). The zero point for the entropy and enthalpy of seawater is defined as that at standard atmospheric surface pressure with a temperature of 0°C and an absolute salinity of $S_A = 35.165\,04$ (Feistel 2008). The potential energy zero is defined as
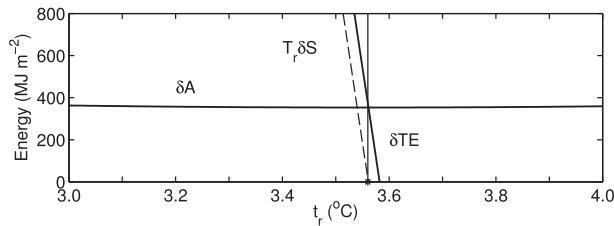
FIG. 3. The oceanic availability δA (thick solid curve) for the horizontal mean WOA05 as a function of the reference temperature. The tilted solid line is the difference in total potential energy δTE between the ocean and the reference ocean; the dashed line is that for the reference temperature times the difference in entropy $T_r \delta S$. The thin vertical line with asterisk corresponds to the equilibrium temperature $T_0 = 3.56°C$ where the availability is a minimum.

that at a depth of 5.5 km. The equilibrium temperature and salinity are found to be $T_0 = 3.56° \pm 0.01°C$ and $S_{A0} = 34.90 \, g \, kg^{-1}$. The specific available energy resides mainly in the upper ocean and thermocline (Fig. 2c) and its profile predominantly reflects the temperature difference from the equilibrium temperature. The mean available energy of 353 MJ m^{-2} is large compared to the available potential energy estimates of Oort et al. (1989, 1994) and Huang (2005) that lie in the range of 0.4–2.3 MJ m^{-2}. This difference is partially due to the restriction of the available potential energy (APE) estimates to baroclinic energy sources that exclude the available energy inherent in the stable stratification associated with the oceanic thermocline. It is noted that knowledge of T_0 and S_{A0} is particularly useful for the oceanographer who may assess the available energy from a limited regional field program. Inspection of the ocean budget (Table 2) indicates that the equilibrium ocean has a greater potential energy but less internal energy than the ocean. The difference in total energy is again equal to the available energy. The slight disparity in mass may be rectified by an 8.6-cm increase in the sea surface height of the equilibrium ocean. This volume increase implies, in the theory of Huang (2005), a pressure work contribution $p_{atm} \delta V$ against the standard atmospheric surface pressure of -8.9×10^{-3} MJ m^{-2}.

4. Conclusions

The fundamental energy relation (1.1) provides a unique method for the determination of the equilibrium temperature T_0 that, as noted by Karlsson (1990), is a state variable of a thermodynamic system. An advantage of the availability (1.2) is that it is independent of any arbitrary constants employed in the definitions of internal energy, potential energy, and entropy. The examples provided here for a constant-volume atmosphere and for an ocean bounded by a constant-pressure atmosphere imply interpretation as Helmholtz or Gibbs

TABLE 2. Budget of the WOA05 mean ocean for the mass M, potential energy Φ, internal energy U, total energy (TE = $U + \Phi$), and entropy S. The ocean's equilibrium temperature is 3.56°C.

	Ocean	Equilibrium
M (Gg m^{-2})	4.3292	4.3291
Φ (GJ m^{-2})	133.84	133.86
U (GJ m^{-2})	58.498	58.102
TE (GJ m^{-2})	192.34	191.96
S (MJ K^{-1} m^{-2})	210.79	210.73

functions, respectively. The derivations presented here further suggest that the function is valid for a solid such as Earth's crust. The methodology is readily applicable to other geophysical systems. An equilibrium temperature for the Earth system consisting of the atmosphere, ocean, and pedosphere will be close to that of the ocean because of its greater mass. Applications to three-dimensional global datasets of the atmosphere and ocean are in progress and will be presented in other forums.

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CORRIGENDUM

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Two corrections are noted in Bannon (2013).

In the second and third sentences of the first paragraph starting on page 2651, the sign of the entropy difference is incorrectly stated. The sentences should read ''If the entropy difference is positive $\delta S(T_r) > 0$, then it is impossible for the system to attain its reference state. If the difference is negative $\delta S(T_r) < 0$, then the availability is less than the difference in total potential energy $\delta A < \delta \mathrm{TE}(T_r)$.''

The analysis of the *World Ocean Atlas 2005* (*WOA05*) mean ocean assumed that the reference ocean has a uniform salinity. This assumption does not account for barodiffusion. A correct analysis for the global ocean is contained in Bannon and Najjar (2014).

These corrections do not alter the main result of the paper that proved the relation (1.1) between the availability function and the departures in energy and entropy between a geophysical system and its isothermal reference state.

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