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A Comparison of the Equivalent Potential Temperature and the Static Energy

R. A. MADDEN AND F. E. ROBITAILLE

National Center for Atmospheric Research,¹ Boulder, Colo.

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Two thermodynamic parameters which are often used in atmospheric analysis are Rossby's equivalent potential temperature and a quantity which has recently been referred to as the static energy (Kreitzberg, 1964). The static energy has also been called the total heat content (Riehl and Malkus, 1958) and the sigma function (Beers, 1945, p. 401). In the following we will refer to the equivalent potential temperature as θ_e given by

$$\theta_e = \theta_d \exp\left(\frac{Lr}{c_p T_s}\right), \quad (1)$$

where θ_d is the partial potential temperature, T_s the temperature at the lifting condensation level (LCL), L the latent heat of vaporization evaluated at T_s , r the mixing ratio of water vapor to dry air, and c_p the specific heat of dry air at constant pressure. The static energy will be referred to as σ given by

$$\sigma = gz + c_p T \cdot Lr, \quad (2)$$

where g is the acceleration of gravity, z the height above the 1000-mb surface, T the Kelvin temperature, and L the latent heat of vaporization evaluated at T .

Though they differ in their units (θ_e is expressed in temperature units and σ in energy units), Riehl and Malkus have pointed to the approximate proportionality between θ_e and σ . This proportionality is expected since the derivation of θ_e presented by Rossby (1932) and that of σ as outlined by Beers begin with the same differential equation. Riehl and Malkus presented a mean vertical distribution of σ for the equatorial trough. With the aid of this vertical profile they postulated a process of selective buoyancy in undiluted cumulonimbus cores, permitting parcel ascent under the condition of constant σ from the subcloud layer to the upper troposphere. Such a process estimates the limit of convection in the equatorial trough. One would expect that vertical profiles of θ_e similarly employed would yield similar results. Fig. 1 shows the vertical profiles of σ and θ_e computed for a mean sounding determined for Palmyra Island (5°53'N, 162°5'W) during the Line

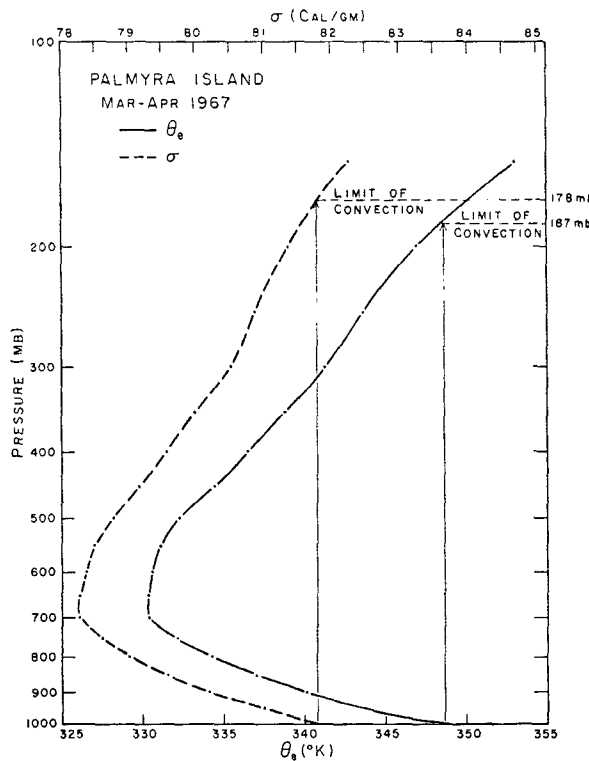


FIG. 1. Mean profiles of θ_e and σ for March-April 1967 at Palmyra showing estimated heights of maximum undiluted cumulus convection assuming conservation of σ and then of θ_e .

Islands Experiment of March and April 1967. The approximate limit of undiluted ascent of a parcel rising from the 1000-mb level is indicated. The σ profile suggests that the limit is 178 mb while the θ_e profile suggests 187 mb. This difference puzzled us and prompted the investigation which is the basis of this note. The following is a summarization of Rossby's derivation of θ_e and an elaboration of the derivation of σ as outlined by Beers.

The basic equation in the derivation of both θ_e and σ is what Rossby calls the differential equation of the pseudo-adiabatic rain stage. It is given by

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$$c_p \frac{dT}{T} - R_d \left(\frac{dp_a}{p_a} \right) + d \left(\frac{Lr}{T} \right) = 0, \quad (3)$$

where p_a is the partial or dry pressure, and R_d the gas constant for dry air. The units of (3) are those of entropy. The differentials are exact, that is, their integration from one thermodynamic state to another depends only on the initial and final states and not on the process by which the change takes place. We can integrate (3) as a definite integral from one thermodynamic state to another. Let the first state be at the LCL with a temperature, partial pressure, and mixing ratio equal to T_s , p_a and r , respectively. The second state is at a temperature, partial pressure and mixing ratio of θ_e , 1000 mb and zero, respectively. Integration of (3) gives

$$\theta_e = \theta_s \exp \left(\frac{Lr}{c_p T_s} \right).$$

To derive an expression for σ we assume that the local and horizontal pressure changes are zero. If we then multiply the equation for the vertical component of motion by $w dt$ ($w = dz/dt$, the vertical velocity), we can write

$$w dw + \frac{dp}{\rho} + g dz = 0, \quad (4)$$

where ρ is the density of the moist air, and p the total pressure. For saturated air, $dp = dp_a + de_s$, where e_s is the saturation vapor pressure. Assuming that the water vapor behaves as a perfect gas, we have from the Clapeyron-Clausius equation, $de_s = e_s LdT / (R_v T^2)$, where R_v is the gas constant for water vapor. If we assume that the air is at the LCL and therefore saturated, we can make a substitution for dp into (4) giving

$$w dw + \frac{dp_a}{\rho} + \frac{e_s LdT}{R_v \rho T^2} + g dz = 0.$$

Solving for dp_a and substituting from the perfect gas law, we can write

$$dp_a = -\rho_a \left(\frac{\rho w dw}{\rho_a} + \frac{\rho_v LdT}{\rho_a T} + \frac{\rho g dz}{\rho_a} \right), \quad (5)$$

where ρ_a is the density of the dry air and ρ_v the density of the water vapor (i.e., $r = \rho_v / \rho_a$). Now if we expand the last term in (3) and substitute for dp_a from (5), we can write

$$c_p \frac{dT}{T} + \frac{\rho w dw}{\rho_a T} + \frac{\rho g dz}{\rho_a T} + \frac{d(Lr)}{T} = 0,$$

or since $\rho = \rho_a + \rho_v$,

$$c_p dT + (r+1)w dw + (r+1)g dz + d(Lr) = 0.$$

Since $r \ll 1$, we can neglect r in the middle terms, which is in effect neglecting the contribution of water vapor toward the changing kinetic and potential energy of an air parcel. Then we have

$$c_p dT + w dw + g dz + d(Lr) = 0. \quad (6)$$

The units of (6) are those of energy. Unlike (3), the differentials of (6) are not all exact. The differential $d(Lr)$ represents latent heat added to the parcel and $w dw$ represents a change in the kinetic energy of the parcel during some thermodynamic process. Their integration from one thermodynamic state to another depends on the process by which the change takes place. Nevertheless, recognizing that we are only approximating the pseudo-adiabatic process specified by (3), we integrate (6) to give

$$c_p T + w^2/2 + g z + Lr = \text{constant}. \quad (7)$$

Eq. (7) states that, with steady-state conditions, no horizontal pressure changes, neglecting the contribution of water vapor to the changing kinetic and potential energy of the parcel, and approximating the available latent heat by the term Lr , σ plus the vertical kinetic energy per unit mass ($w^2/2$) is a conservative quantity for an air parcel as it moves from one thermodynamic state to another through the pseudo-adiabatic process specified by (3). It is the indefinite integral of (6). If one considers a parcel moving from one thermodynamic state to another by convection in the atmosphere from $z = z_0$ to $z = z$, the change in the vertical kinetic energy is given by

$$\frac{w^2}{2} - \frac{w_0^2}{2} = \int_{z_0}^z g \left(\frac{T_P^* - T_E^*}{T_E^*} \right) dz, \quad (8)$$

where the asterisk signifies virtual temperature and the subscripts P and E represent virtual temperatures of the parcel and of the environment, respectively (Saucier, 1955, p. 65). During undiluted convective ascent from the subcloud layer, the change in vertical kinetic energy in heat units is generally less than 0.5 cal gm^{-1} (Riehl and Malkus), while σ is the order of $70\text{--}85 \text{ cal gm}^{-1}$. On this basis it is usually ignored and σ as stated in (2) is considered a conservative quantity.

Two major differences between θ_e and σ are now evident. First, by neglecting the specific process by which latent heat is realized, the integration of $d(Lr)$ to Lr in the derivation of σ somewhat underestimates the effect of the available latent heat. Second, θ_e is related to the 1000-mb level through a definite integration from the LCL to a partial pressure of 1000 mb, while σ is based on an indefinite integration and is related to 1000 mb only by the arbitrary choice of z as the height above it. If (6) were integrated as a definite integral

the 1000-mb level, the change in kinetic energy specified by (8) would result primarily from a dry adiabatic descent to 1000 mb and, depending on atmospheric stability, exceed the 0.5 cal gm^{-1} suggested for convective ascent.

In summary, θ_e is exactly conserved during thermodynamic processes specified by the differential equation of the pseudo-adiabatic rainstage (3), while σ is only approximately conserved. Estimates of the vertical limit of convection using both profiles are nearly the same although neither estimate is necessarily the equilibrium pressure where the parcel density is the same as the environmental density. The fact that the two estimates are nearly the same is somewhat fortuitous in that it so happens that the differences, $\theta_e - \sigma c_p^{-1}$, in the subcloud layer and in the upper troposphere are nearly equal; the difference in the low levels is due to the process by which latent heat is realized and the difference in the upper levels (where moisture content tends to zero) to the degree of stability of the underlying atmosphere. Estimates of convective penetration using θ_e profiles better approximate those obtained using the parcel method on a suitable thermodynamic chart. However, since both θ_e and σ are derived from a dif-

ferential equation that is an approximation to real cloud ascent and since both parameters yield estimates of undilute convection differing by only a few millibars, judging one parameter more suitable than the other in this type of analysis is not practical.

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On the Free Energy of Formation of Droplets from the Vapor

FARID F. ABRAHAM

IBM Scientific Center, Palo Alto, Calif.

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We recently presented a thermodynamic discussion of homogeneous nucleation (Abraham, 1968). The thermodynamic argument viewed the surface of the drop as a two-dimensional membrane having no thickness and the transition in density between liquid and vapor as discontinuous. It was further assumed that the total spherical surface area A of the drop was the only additional extensive parameter of the "drop-system." If a third system, the surface of the drop, is defined [as suggested in Sec. 8 of Abraham (1968)], we conclude that this model is consistent only if the intensive parameter, $\sigma = [\partial F^{(s)}(T, A) / \partial A]$, is size-independent (i.e., $d\sigma = 0$). In any case, the $A d\sigma$ term in Eq. (26) should not be included in the Gibbs-Duhem relation for the intensive parameters of the liquid state. This does not invalidate the analysis of this paper since it was explicitly assumed that σ was size-independent, i.e., Eq. (27b).

The purpose of this note is to draw attention to a very general and rigorous analysis of the thermodynamics of the spherical interface presented by Ono and Kondo (1960). One of the most familiar examples of a spherical interface is the drop of liquid with its

surrounding vapor. It is of particular interest to find the valid form of the free energy of formation $\Delta F(r^*)$ of a critical size droplet of radius r^* if σ is size-dependent. We will present a non-rigorous derivation of $\Delta F(r^*)$ for $\sigma = \sigma(r)$ and conclude the derivation by giving Ono and Kondo's (1960) interpretation of the result based on their rigorous thermodynamic study.

The elevation of the total Helmholtz free energy of the system as the transition is made from vapor only to a drop of radius r plus vapor is (e.g., Ono and Kondo, 1960)

$$\Delta F(r) = -\left(\frac{4\pi}{3v_l} kT \ln S\right) r^3 + 4\pi\sigma(r)r^2, \quad (1)$$

where v_l is the volume per molecule in the bulk liquid state, k the Boltzmann constant, T temperature and S the supersaturation ratio. The extremum equation

$$\frac{\partial}{\partial r} [\Delta F(r)] = 0$$