Exergy in meteorology: Definition and properties of moist available enthalpy

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SUMMARY

The exergy of the dry atmosphere can be considered as another aspect of the meteorological theories of available energies. The local and global properties of the dry available enthalpy function, also called flow exergy, were investigated in a previous paper.

The concept of exergy is well defined in thermodynamics, and several generalizations to chemically reacting systems have already been made. Similarly, the concept of moist available enthalpy is presented in this paper in order to generalize the dry available enthalpy to the case of a moist atmosphere. It is a local exergy-like function which possesses a simple analytical expression where only two unknown constants are to be determined, a reference temperature and a reference pressure.

The moist available enthalpy, \( a_m \), is defined in terms of a moist potential change in total entropy. The local function \( a_m \) can be separated into temperature, pressure and latent components. The latent component is a new component that is not present in the dry case. The moist terms have been estimated using a representative cumulus vertical profile. It appears that the modifications brought by the moist formulation are important in comparison with the dry case. Other local and global properties are also investigated and comparisons are made with some other available energy functions used in thermodynamics and meteorology.

1. INTRODUCTION

The basis of the modern concept of exergy was introduced by W. Thomson (1853, 1879), later Lord Kelvin. He defined as motivity the amount of work that a system can produce by evolving from an initially heterogeneous distribution of temperature to a constant equilibrium value. Since then the concept of motivity (known as available energy) has been rediscovered and generalized in many articles and monographs dealing with thermodynamics (see the historical review in Haywood (1974) or Kestin (1980)). Nowadays, the available part of the energy is often called the exergy of a system, whereas its untransformable part is sometimes called the anergy, which corresponds to a dead state of the same system.

The terms exergy and anergy are not used in atmospheric science, but several analogous concepts have been introduced in meteorology: (i) the available kinetic energy by Margules (1905); (ii) the available potential energies by Lorenz (1955, 1967), Van Mieghem (1956), Dutton and Johnson (1967), Pearce (1978) and McHall (1990a, 1990b); (iii) the global static entropic energy by Dutton (1973, 1976) and its local version by Pichler (1977); and (iv) the entropic potential energy by Blackburn (1983).

A connection between the thermodynamical concept of exergy and some of these global meteorological approaches (i) to (iv) was proposed in Karlsson (1990) and in Marquet (1990a, 1991 (collectively referred to as MM hereafter)). For instance, it was shown in MM that the local concept of dry available enthalpy \( a_h = (h - h_e) - T_c (s - s_e) \) generalizes some of the results of (i) to (iii). This local function \( a_h(p, T) \) can be used as a Lagrangian energy quantity (see list of symbols in the appendix), yielding a Bernoulli equation verified by \( a_h + e_k + e_G \) and leading to new local non-hydrostatic or hydrostatic energy cycles. It is also easy to take into account an uneven topography and dry static instabilities (i.e. where \( \partial s/\partial z < 0 \)).
It is explained in MM that, for an isobaric layer of a limited space region, the expected hydrostatic conversion term $-R \bar{\omega} T/p$ and two new boundary fluxes appear. These terms cannot be obtained by starting with any local approach of the theory of Lorenz. However, using such a local approach and assuming $\bar{\omega} = 0$, Muench (1965), Brennan and Vincent (1980) and Michaelides (1987) have all mentioned large unbalanced residuals. Pontaud et al. (1990) have shown that these residuals could correspond to the new conversion and flux terms obtained with the available enthalpy formulation where $\bar{\omega} \neq 0$, leading to local energy cycles that are more balanced. All these results show that the introduction of a local exergy-like concept is relevant in meteorology, in agreement with the local approaches of Pichler (1977) and Karlsson (1990).

Nevertheless, the dry available enthalpy only deals with the energetics of the atmosphere when considered as a dry ideal gas with parametrized diabatic heating. This is a crude approximation of the reality, and accordingly Lorenz (1978, 1979) proposed a moist version of the available energy concept. Livezey and Dutton (1976) also generalized on the concept of static entropic energy, $T_0 \Sigma$, to simple-solution fluid systems (cloudy air or salt water). As for thermodynamics, Szargut and Styrlska (1969) proposed a theory of exergetic processes in moist air and Evans (1969, 1980) coined the term essergy (for essential aspect of energy) when he studied the exergy of salt water, the principle of desalination and, more generally, chemically reacting thermodynamic systems. However, the word essergy has not really spread in thermodynamic literature and so the term exergy will be used in this paper. In recent years McHall (1991) derived a moist version of his theory, and Karlsson (1990) investigated the exergy exchanges in the atmosphere when considered as a fluid mixture with chemical reactions, including numerical investigations made at the European Centre for Medium-range Weather Forecasts with a general circulation model.

Similarly, the purpose of this paper is to define an exergy-like local function called moist available enthalpy and denoted by $a_m$. It is expected to be the natural generalization of the dry version, $a_h$.

The differences between the various entropic or available energies introduced in meteorology—see (i) to (iv) above—mainly concern the definition of the reference state of minimum total potential energy. Using another approach, the essergy function introduced by Evans (1969) in thermodynamics, and the exergy function studied by Karlsson (1990) in meteorology, are derived from a fundamental concept of statistical physics: the ‘information gain’, also called ‘Kullback function’ (Kullback 1959) or ‘contrast’. The moist available enthalpy will be introduced differently in this paper, starting from a moist generalization of the concept of potential change in total entropy $(\Delta S = a_m/T)$ which is another approach to the dry available enthalpy (see MM).

To begin with, the general thermodynamic assumptions are set out in section 2. The moist potential change in total entropy is then defined in section 3 together with the analytical expression of the specific moist available enthalpy function $a_m$ and its various components. In section 4 a representative vertical profile of a cumulus cloud is used to estimate the orders of magnitudes of the components of $a_m$. The thermodynamic equations and the equations for the moist energy components are reviewed in section 5. A local moist energy cycle and the local moist Bernoulli equation are then introduced in section 6. Integral properties shown in section 7 lead to possible definitions of $T$ and $p$ (two constants to be determined in $a_m$). In section 8 the moist available enthalpy is expressed in terms of an associated moist potential temperature. Finally, conclusions and remarks are contained in section 9.

It should be mentioned that most of the following results have appeared first in French in Marquet (1990b).
2. MOIST THERMODYNAMICS

The general thermodynamic assumptions that are used throughout this study are based on the thermodynamic local-state theory (De Groot and Mazur 1962; Glansdorff and Prigogine 1971), together with some common meteorological approximations (see Hauf and Höller (1987), referred to as HH hereafter). To enable easy reference these hypotheses are labelled in this paper by $\mathcal{H}_n$. The notations and symbols used in this paper have been chosen according to HH.

$\mathcal{H}_1$ The atmosphere consists of four components at the same temperature $T$ denoted by the subscripts or the superscripts 0 to 3 for dry air, water vapour, liquid water (stable or supercooled) and ice respectively. Precipitation falling at $T_w$ (the so-called wet-bulb temperature) cannot explicitly be taken into account.

$\mathcal{H}_2$ Ideal gas and pure form assumptions are for ideally mixed gases and condensed phases respectively. Salt dissolved in drops or ice crystals is ignored.

$\mathcal{H}_3$ Local-state theory is valid: the local-state functions defined in 'thermostatic' (pressure, temperature, energy, enthalpy, entropy, . . .) remain valid in non-equilibrium thermodynamics; the first-order Chapman–Enskog development is a good enough approximation to the distribution function (otherwise entropy would depend explicitly on gradients of $\rho$ and $T$); variations of $T$ and $\rho$ are 'small enough' between two collisions (mean free path); continuum physics can be applied, leading to the concept of a fluid parcel; gases are not too rarefied (for practical purpose $p > 10^{-1}$ Pa or $z < 100$ km); plasmas or shock waves cannot be investigated. For these assumptions see, for example, Prigogine (1949), Meixner and Reik (1959) and Lebon and Mathieu (1981).

$\mathcal{H}_4$ The specific heats at constant volume and pressure ($c_{v}^j$ and $c_{p}^j$, $j = 0$ to 3) together with the gas constants ($R^i$, $i = 0$ and 1) are temperature-independent. The normal transition between liquid water and ice occurs at the triple point temperature $T_{tr} = 273.16$ K and is pressure-independent. Metastable supercooled water can exist.

$\mathcal{H}_5$ Under- or super-saturation does not exist anywhere. The saturation pressures denoted by $p^i_0(T)$ with $i = 2$ or 3 are those over an infinite and plane surface of liquid (for $i = 2$) or ice (for $i = 3$).

$\mathcal{H}_6$ Thermodynamic and kinematic effects of drop or ice crystal size spectra are not taken into account.

$\mathcal{H}_7$ $\partial h/\partial p = 0$ for the condensed phases. The specific volumes of condensed phases are neglected in the equation of state and in the Clausius–Clapeyron equation: only specific volumes of gases are considered.

$\mathcal{H}_8$ Turbulent fluxes are only molecular ones, although Reynolds terms (the macroscopic parametrized turbulence) could implicitly be included into the source and sink terms of the thermodynamic equations.

$\mathcal{H}_9$ Kinetic energy of diffusion is not taken into account. This is justified if the time derivative of the various components with respect to the barycentric motion may be neglected (see De Groot and Mazur 1962).

Any atmospheric parcel is completely determined by the partial pressures $p^0$ and $p^1$, the temperature $T$ and the concentrations $m^k = \rho^k/\rho$ ($k = 0$ to 3) where $\rho^k$ and $\rho = \sum_k \rho^k$ are the partial and total densities respectively. The mixing ratios of water components are $r^k = m^k/m^0$ ($k = 1$ to 3), the total mixing ratio of water is $r^w = r^1 + r^2 + r^3$ and the total concentration of water is $m^w = m^1 + m^2 + m^3$. All these definitions and notations are chosen according to HH.
In a parcel each component \( k = 0 \) to 3 moves with the uniform partial velocity \( \mathbf{v}^k \), and the barycentric velocity \( \mathbf{v} \) of the parcel is defined by \( \rho \mathbf{v} = \rho^k \mathbf{v}^k \) (Einstein’s summation convention over Latin or Greek letters is used throughout this paper). The material barycentric time-derivative operator is defined by \( \frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \), where the second term is the barycentric advection.

The change in concentration \( \frac{D(m^k)}{Dt} \) can be split into the sum

\[
\frac{D(m^k)}{Dt} = \frac{D_e(m^k)}{Dt} + \frac{D_i(m^k)}{Dt}
\]

(1)

where the external \( \frac{D_e}{Dt} \) and internal \( \frac{D_i}{Dt} \) changes in concentration are

\[
\frac{D_e(m^k)}{Dt} = -(\rho)^{-1} \nabla \cdot \mathbf{J}^k
\]

(2)

\[
\frac{D_i(m^k)}{Dt} = (\rho)^{-1} \mathbf{g}^k.
\]

(3)

The change \( \frac{D_i(m^k)}{Dt} \) is created by a transfer of mass across the boundaries of the open parcel and the change \( \frac{D_e(m^k)}{Dt} \) corresponds to the mass produced within the parcel. They depend, respectively, on the ‘diffusion flux’ \( \mathbf{J}^k = \rho^k (\mathbf{v}^k - \mathbf{v}) \), \( k = 0 \) to 3, and the ‘convergence of the phase fluxes’ \( \mathbf{g}^k \), \( k = 1 \) to 3, due to the chemical changes of state: \( 1 \leftrightarrow 2 \leftrightarrow 3 \).

Various local-state functions are either intensive \((\rho, T)\) or extensive \((e^i, h^i, s^i, \ldots)\). Any extensive function \( \psi = m^k \psi^k \) can be put in the alternative form

\[
\psi = m^k \psi^k = m^0 \psi^0 + m^i \psi^i + m^2 (\psi^2 - \psi^1) + m^3 (\psi^3 - \psi^1)
\]

(4)

where \( m^i \) is associated with the water vapour component \( \psi^1 \), differently to HH where \( m^i \) is associated with the liquid water component \( \psi^2 \). For instance, the specific—namely per unit mass—enthalpy, \( h \), entropy, \( s \) and internal energy, \( e_i \), read

\[
h = m^k h^k = e_i + p/\rho = m^0 h^0 + m^1 h^1 - m^2 I_{21} - m^3 I_{31}
\]

(5)

\[
s = m^k s^k
\]

(6)

\[
e_i = m^k e_i^k
\]

(7)

where \( I_{ij} = h^j - h^i \) are the latent heats.

Using \( \mathcal{K}_5 \) the following identity holds whatever the thermodynamic state of the parcel is, and can help to simplify several formulae (if one of the condensed phases is present the moist air is saturated and the logarithm is zero, on the other hand if the moist air is not saturated there is no condensed phase):

\[
m^2 \ln(p^1/p^{21}) = m^3 \ln(p^1/p^{31}) = 0.
\]

(8)

Using \( \mathcal{K}_7 \) Kirschoff’s law \((i, j = 1, 2, 3)\) and the local Clausius–Clapeyron equation \((i = 2, 3)\) are respectively

\[
\frac{d}{dT}(l_{ij}) = c_p^j - c_p^i, \quad \text{and} \quad T \frac{d}{dT} \ln(p^i) = \frac{l_{ii}}{R^1 T}.
\]

(9)

These equations will often be used in the following integral form with the use of \( \mathcal{K}_4 \):

\[
l_{ij}(T) = l_{ij}(T_i) + (c_p^j - c_p^i)(T - T_i) = (l_{ij})_i + (c_p^j - c_p^i) T_i X
\]

(10)

\[
R^1 T_i \ln\left(\frac{p^{11}(T)}{p^{11}(T_i)}\right) = l_{ii}(T)(1 - T_i/T) - (c_p^j - c_p^i) T_i \mathcal{F}(X)
\]

(11)
where $T_r$ is a constant temperature. Equation (11) holds for $i = 2$ or 3. The function $\mathcal{F}(X) = X - \ln(1 + X)$ is introduced with $X = (T - T_r)/T_r$.

3. The moist available enthalpy

Section 3(a) deals with the dry and moist versions of the 'potential change in total entropy'. The results of the moist version are used in section 3(b) as a starting point to define $a_m$. However, section 3(a) may well be omitted on a first reading of this paper, considering section 3(b) as the mathematical definition of the local function $a_m$.

(a) Introduction

The concept of dry 'potential change in total entropy' is defined in MM. It is denoted by $\Delta_0 S^o = a_b/T_r$ and can be compared with the expression $\Delta S_t = R_{\text{max}}/T_0$ of Landau and Lifchitz (1976, §20).

Landau and Lifchitz have used a geometric approach following the method introduced by Gibbs (1873). The problem is to define the available part of the total energy, namely the part of the energy that a system can release when undergoing a spontaneous process towards an equilibrium state. The system consists of a body surrounded by a medium at constant pressure $p_0$ and temperature $T_0$. The total entropy of the body and medium is $S_t$, and the total energy is $E_t$. Use of an $S_t-E_t$ diagram enables each state of the system to be represented by a point. The equilibrium curve, $(S_t)_{eq}$, is the so-called 'surface of dissipated energy' introduced by Gibbs (1873); it only depends on $E_t$ and is a straight line if the medium is a thermostat (see Fig. 1). The slope of this equilibrium curve is related to the equilibrium temperature by $d(S_t)_{eq}/dE_t = 1/T_0$. If the body is not in equilibrium with the medium and if the point $B$ represents this general state in Fig. 1, the distance $BA$ is the 'capacity for entropy' $\Delta S_t$, whereas the distance $CB$ is the 'available energy' $R_{\text{max}}$ (this terminology was used by Gibbs). According to the second law of thermodynamics any real thermodynamic process results in an increase of the total entropy. Therefore, starting from $B$, the attainable equilibrium points are located above the value $(S_t)_B$, and the maximum variation in total energy is reached when the equilibrium end state is $C$. This special process is the reversible one where the final total entropy has not changed $(S_t)_C = (S_t)_B$. The consequence of the second law is that the distance $CB$ is

![Figure 1. $S_t-E_t$ diagram with the equilibrium curve $(S_t)_{eq}$ and the non-equilibrium state $B$. $\Delta S_t$ is the change in total entropy and $R_{\text{max}}$ is the available energy.](image-url)
a maximum and represents the available energy. The change in total entropy and the available energy are thus simply connected by the slope of the equilibrium curve: \( \Delta S_i = R_{\text{max}}/T_0 \).

The available enthalpy \( a_h \) can also be related to a change in total entropy \( \Delta_a S^o \):

\[
\Delta_a S^o = a_h/T_r = \frac{[h - h_i(T_r)]}{T_r} - [s - s_i(T_r, P_r)]
\]

(12)

where two undefined constants \( T_r \) and \( P_r \) are introduced. It is demonstrated in Marquet (1991) that, for the dry atmosphere case, \( \Delta_a S^o \) is the change in total entropy of a conceptual system undergoing two prescribed processes. This system consists of a unit mass parcel of dry ideal gas \((T, p)\), and a mere conceptual thermostat at \( T_r \). The dry irreversible processes are: first an isobaric change of the parcel from \((T, p)\) to \((T_r, p)\) coming into contact with the thermostat, then a sudden isothermal and adiabatic change from \((T_r, p)\) to \((T_r, P_r)\). In fact the second process involves a work reservoir at \( P_r \), but the change in total entropy \( \Delta_a S^o \) is only related to the unit mass parcel and the thermostat. The work exchanged between the parcel and the work reservoir is not considered as available for the system, the work reservoir is a free source of work. This is the main difference between the concept of available energy and available enthalpy.

For the available energy case one can similarly consider a unit mass parcel associated with a work and heat reservoir at \( T_r \) and \( P_r \). The two new irreversible processes are: first a sudden and adiabatic change from \((T, p)\) to \((T_1, p_1)\) coming into contact with the work reservoir, where \( T_1 \) is the temporary equilibrium value; and then an isobaric change from \((T_1, p_1)\) to \((T_r, P_r)\) coming into contact with the thermostat. The changes in total entropy \( \Delta_1 S_i \) and \( \Delta_2 S_i \) occurring during these two new processes lead to the following available energy formulation: \( a_e = T_r(\Delta_1 S_i + \Delta_2 S_i) = [e_i - (e_i)_1] + p_1(1/\rho - 1/\rho_1) - T_r(s - s_i) \). This is the available energy function used among others by Landau and Lifchitz (1976), Livezey and Dutton (1976) and Karlsson (1990).

The moist generalization that is considered in this paper is made of a unit mass moist parcel verifying \( \delta e_{1, \ldots, n} \) assumptions, a conceptual thermostat at \( T_r = T_u = 273.16 \) K, a moist dead state (at temperature \( T_r \) and total pressure \( p_r \)) and finally four thermochemical processes. The moist potential change in total entropy is denoted by \( \Delta_m S^o \).

The dead state is a saturated moist air parcel at \( T_r \), in possible chemical equilibrium with an infinite and plane surface of ice, thus \( p_i = p^{3i}(T_r) \) according to \( \delta e_i \). There is no condensed phase: \( r^2 = r^3 = 0 \) and \( r^1 = r^{31} \) (the saturation mixing ratio over ice). The total pressure \( p_r \) and \( T_r \) are supposed to be two constants. From \( \delta e_i \) the partial pressure of the dry-air component in the dead state only depends on \( T_r \) and \( p_r \): \( p^{0i}(T_r, p_r) = p_i - p^{3i}(T_r) \).

The dead state is a passive environment in that the chemical potential of water vapour, \( \mu_i \), and the chemical potential of ice, \( \mu_3 \), are the same (ice is the stable condensed phase at \( T_r \)). The partial chemical potential is defined in thermodynamics as \( \mu^k(T, p) = h^k(T) - T s^k(T, p) \), for each component \( k = 0 \) to \( 3 \).

Let us define the following sequence of thermochemical processes undergone by the unit mass parcel and involving the thermostat:

(i) an isothermal \((T)\) and adiabatic reversible separation of the parcel into its different parts. The separation of the gases is realized via semi-permeable membranes. The condensed phases are in equilibrium with the respective gas partial pressures. The final state can be called the separate component state. This can be summarized by:

\[
(p^0, p^1; m^k, k = 0 \text{ to } 3) \leftrightarrow (p^0, m^0) + (p^1, m^1) + (p^{21}, m^2) + (p^{31}, m^3);
\]
(ii) if metastable phases are present (e.g. supercooled water) they are transformed (at T and p) into the more stable form at T, using heat exchanges with the thermostat if needed;

(iii) an irreversible and isobaric change from T to T_r coming into contact with the thermostat, the final phase being the more stable one at T_r; and

(iv) a sudden and isothermal irreversible change of pressure at T_r, to reach \((p_r^0, T_r)\) conditions for dry air and \((p_r^31, T_r)\) for all components 1 to 3 (the final phase being the more stable one at T_r). The work reservoir involved in this adiabatic process is supposed to be a free source of work.

The change in total entropy is zero for all components during the adiabatic and irreversible process (i). Introducing the notation \(b^k = (h^k - h^k_r) - T_r (s^k - s^k_r)\) where the subscript \(r\) denotes the dead state, the value of the moist change in total entropy for the dry-air component \((\Delta_m S^0)_0\) along the path (i) to (iv) can be computed according to Marquet (1991): \((\Delta_m S^0)_0 = b^0 / T_r\). Indeed, (iii) and (iv) correspond in this case to the dry processes of MM recalled at the beginning of this section, and the processes (i) and (ii) are ineffective for the dry-air component.

It is more difficult to carry out the computation of \((\Delta_m S^0)_k\) for the water components \((k = 1, 2, 3)\) because numerous cases must be investigated depending on the various changes of phase that can occur along the path (i) to (iv). There are in fact eight different cases. Each of them is depicted in the p–T diagram of Fig. 2 by possible initial points \(E_1, \ldots, E_8\) and the common final state \(E_r\) (the gaseous saturated dead state). If \(p_r^1 = p_r^31(T_r)\) and \(p_0 = p^31(T_0) = p^{21}(T_0)\), where \(T_0 = T_{tr}\), these states can be briefly defined as:

![Figure 2. p–T diagram with a representation of the different paths for each water component between the real states \(E_k (k = 1\) to \(8)\) and the fixed thermodynamic reference state \(E_r\).](image-url)
\( E_1: \) water vapour at \( p^1 \leq p_1^1 \) (always gaseous)

\( E_2: \) water vapour at \( p^1, p_1^1 \leq p_0 \) (gas \( \leftrightarrow \) solid \( \rightarrow \) gas)

\( E_3: \) water vapour at \( p^1 \geq p_0 \) (gas \( \leftrightarrow \) liquid \( \rightarrow \) solid \( \rightarrow \) gas)

\( E_4: \) supercooled liquid water at \( T \leq T_r \) (liquid \( \rightarrow \) solid \( \rightarrow \) gas)

\( E_5: \) supercooled liquid water at \( T, T_1 \leq T \leq T_0 \) (liquid \( \rightarrow \) solid \( \rightarrow \) gas)

\( E_6: \) normal liquid water at \( T \geq T_0 \) (liquid \( \rightarrow \) solid \( \rightarrow \) gas)

\( E_7: \) ice at \( T \leq T_r \) (solid \( \rightarrow \) gas)

\( E_8: \) ice at \( T, T_1 \leq T \leq T_0 \) (solid \( \rightarrow \) gas).

The computations of \((\Delta_m S)^k\) are somewhat long, but they are consistent since the cases \( E_{1,2,3}, E_{4,5,6} \) and \( E_{7,8} \) respectively lead to the following expressions \( a^k_m, a^1_m \) and \( a^3_m \) for the partial moist available enthalpies:

\[
a^0_m = T_r (\Delta_m S^0)^0 = b^0 \tag{13}
\]

\[
a^1_m = T_r (\Delta_m S^0)^1 = b^1 + (\mu^1_r - \mu_r) = b^1 \tag{14}
\]

\[
a^2_m = T_r (\Delta_m S^0)^2 = b^2 + (\mu^2_r - \mu_r) \tag{15}
\]

\[
a^3_m = T_r (\Delta_m S^0)^3 = b^3 + (\mu^3_r - \mu_r) = b^3. \tag{16}
\]

The result \( a^0_m \) for \( k = 0 \) is recalled and \( \mu_r = \mu^0_r = \mu^1_r \) denotes the reference chemical potential of water elements in the dead state \((\mu^k_r = h^k_r - T_r s^k_r)\). The hypotheses \( 3_{1,2,4,5,6,7} \) together with the integral forms (10) and (11) of Eq. (9) have all been used to work out Eqs. (13) to (16).

\[ (b) \text{ Definition of } a_m \]

Let us assume that \( a_m = m^k a^k_m \). The subscript \( r \) denotes the moist dead state described in section 3(a). It is a passive environment represented by a saturated moist parcel at \( T_r \leq T_0 = 273.16 \text{ K} \) and without a condensed phase. The partial available enthalpies \( a^k_m \) are defined by Eqs. (13) to (16) where \( b^k = (h^k - h^k_r) - T_r (s^k - s^k_r) \). Using these definitions the analytical expression of the local moist available enthalpy is

\[
a_m = m^k (h^k - h^k_r) - T_r m^k (s^k - s^k_r) + m^2 (\mu^2_r - \mu^2_r). \tag{17}
\]

At first sight one could note a dissymmetry, with an arbitrary importance given to liquid water through \( m^2 \); but this equation really is symmetric with respect to water components \((i = 1 \text{ to } 3)\). The two terms \( m^1 (\mu^1_r - \mu^2_r) \) and \( m^3 (\mu^3_r - \mu^2_r) \) coming from Eqs. (14) and (16) could be included in Eq. (17), but they are zero because \( \mu^1_r = \mu^2_r \). The only dissymmetry is the fact that ice is a more stable component than liquid water at \( T_r \).

An alternative form can be derived using Eqs. (5) and (6) with \( \mu^k_r = h^k_r - T s^k_r \) to give

\[
a_m = h - T_r s - m^k \mu^k_r + m^2 (\mu^2_r - \mu^2_r) \tag{18}
\]

where the last term \( \mu^3_r \) can be replaced by \( \mu^1_r \). The transformation (4) is then applied to \( -m^k \mu^k_r \) with \( \mu^3_r = \mu^1_r \), yielding

\[
a_m = h - T_r s - m^0 \mu^0_r - m^k \mu^1_r. \tag{18}
\]

From Eq. (17) one can verify that \( a_m \) is independent of any arbitrary choice for the absolute values of energy, enthalpy or entropy. Indeed the enthalpies \( h^k - h^k_r \) and the entropies \( s^k - s^k_r \) can be expressed in terms of \( T - T_r \) and \( p^k/p^k_r \). They are respectively, \( c^k_p (T - T_r) \) and \( c^k_p \ln (T/T_r) - R^k \ln (p^k/p^k_r) \), except for the entropy of the condensed
phases which is \( c^k \ln(T/T_i), k = 2 \) and \( 3 \). The last term \( \mu_i^2 - \mu_i^1 \) in Eq. (17) corresponds to the chemical affinities related to the water vapour: \( \dot{s}_i^1 = \mu_i^1 - \mu_i^i = R^1 T \ln(p_i^1/p_i^i), \)
\( i = 2 \) or \( 3 \). And \( \dot{s}_i^2 - \dot{s}_i^1 \) yields \( \mu_i^2 - \mu_i^1 = R^1 T_i \ln(p_i^2(T_i)/p_i^3(T_i)) \) which only depends on \( T_i \).

On the contrary, the values of zero-entropies are used in HH to derive the entropy temperature. Standard chemical values for enthalpy and entropy are also introduced in many technical papers in order to derive the 'standard chemical exergy' for each chemical element (see, for example, Szargut (1980); Ahrendts (1980); Morris and Szargut (1986)).

Equation (18) gives the more general definition of \( a_m \) in terms of \( h \) and \( s \). It must be remarked that each term of this expression (i.e. \( h, s, \mu_i^0 \) and \( \mu_i^1 \)) cannot be separately determined without assuming unnecessary agreed reference values for \( h \) and \( s \). Indeed, even if \( h^1, h^2 \) and \( h^3 \) are linked through the latent heats \( l_i = h^i - h^1 \), \( h^0 \) cannot be connected with the others for lack of chemical reaction between dry air and water elements. Nevertheless, Eq. (18) is interesting in that it reveals that \( a_m \) exactly varies as \( h - T_i s \) for a closed parcel (i.e. if \( m^0 \) and \( m^1 \) are two constants). Moreover \( a_m \) simply varies as \( h \) for a closed parcel with adiabatic and reversible motion ( \( s \) is also a constant in that case). This last property will be investigated in section 8, yielding the definition of a conservative potential temperature.

The moist available enthalpy defined by Eqs. (17) and (18) is different from the flow exergy function \( e_i + p_0 v - T_0 s - m^k \mu_0^k \) (Evans 1969 or 1980; Landau and Lifchitz 1976 §96; Livezey and Dutton 1976; Karlsson 1990). The local approach of Karlsson and the global approach of Livezey and Dutton are different from the present one because in their papers the reference state is defined with a reference pressure \( p_0^k(z) \) which varies as \( \exp(-z/H^k) \). The reference entropy \( s_0^k(T_0, p_0^k(z)) \) is not a constant, and the reference chemical potential \( \mu_0^k(z) \) is equal to \( h_0^k - T_0 s_0^k(z) \). Equation (18) is more similar to the definition of the stationary flow availability function \( h - T_0 s - m^k \mu_0^k \) given by Evans and quoted in Ahrendts (1980), or the flow exergy \( h - T_0 s - m^k \mu_0^k(z) \) defined in Karlsson (1990), except for the term \( m^1 \mu_1^1 \) in place of \( \Sigma_{k=1}^3 m^k \mu_0^k \).

(c) The components of \( a_m \)

In order to show in what sense \( a_m \) is a generalization of the dry function \( a_t \) (MM), \( a_m \) must be further transformed. Starting from Eq. (17) the first two terms \( m^k(h^k - h^1) = c^k (T - T_i) \) and \( m^k T_i (s^k - s^1) \) can be transformed with (4) to give respectively

\[
\begin{align*}
&m^0 c_p^s - m^2 (c_p^1 - c^2) - m^3 (c_p^1 - c^3) \right) T_i X, \\
&m^0 c_p^s - m^2 (c_p^1 - c^2) - m^3 (c_p^1 - c^3) \right) T_i \ln(1 + X) - m^0 R^0 T_i \ln(p_0^0/p_0^i) - \\
&\quad - m^1 R^1 T_i \ln(p_0^1/p_0^i).
\end{align*}
\]

The specific heats \( c_p = m^k c_p^k \) and \( c_p^1 = c_p^0 + r c_p^1 \) have been introduced as well as the variable \( X = (T - T_i)/T_i \). The last term of Eq. (17) is computed as \( \mu_i^2 - \mu_i^1 = R^1 T_i \ln(p_i^2/p_i^3) \). A new form is then obtained for \( a_m \) using the function \( \Phi(X) = X - \ln(1 + X) \):

\[
a_m = m^0 c_p^s T_i \Phi(X) - \left[ m^2 (c_p^1 - c^2) + m^3 (c_p^1 - c^3) \right] T_i \Phi(X) + \\
\quad + m^0 R^0 T_i \ln(p_0^0/p_0^i) + m^1 R^1 T_i \ln(p_0^1/p_0^i) + m^2 R^1 T_i \ln(p_i^2/p_i^3).
\]

The last step is to use the property \( p_i^2 = p_i^1 \) together with Eq. (11) to transform the last term and the terms between square brackets into an expression involving pressures and
latent heats
\[- (m^2 l_{21} + m^3 l_{31}) (1 - T_i/T) + (m^2 + m^3) R^1 T_i \ln(p^1/p^3) -
- [m^2 R^1 T_i \ln(p^1/p^2) + m^3 R^1 T_i \ln(p^1/p^3)]\]

where the last term between square brackets is zero according to Eq. (8).

After these manipulations one obtains the separation of \(a_m\) into three moist energy components:
\[
a_m = a_T + a_i + a_p, \text{ with:} \tag{19}
\]
\[
a_T = m^0 c_r^0 T_i \mathcal{F}(X) \geq 0 \tag{20}
\]
where \(\mathcal{F}(X) \geq 0\)
\[
a_i = - (m^2 l_{21} + m^3 l_{31}) \left(1 - \frac{T_i}{T} \right) \tag{22}
\]
\[
a_p = m^0 R^0 T_i \ln(p^0/p^9) + m^0 R^1 T_i \ln(p^1/p^3) \tag{23}
\]

The dry case is defined by \(m^1 = m^2 = m^3 = m^1_i = 0, m^0 = 1, p^0 = p,\) and \(p^0 = P,\) where \(P\) is the reference pressure introduced in the dry available enthalpy approach (see the beginning of section 3(a)). In the dry case \(a_m\) reduces to \(a_h = c_h^0 = b^0,\) and both \(a_T\) and \(a_p\) are the same as the temperature and pressure components already defined in MM \((c_p^0 \rightarrow c_p^0 \text{ in Eq. (20)})\). The functions \(a_T, a_p\) in Eqs. (20) and (23) are called the moist temperature and pressure components of \(a_m\).

The latent component \(a_i\) is a new one. It is different from zero only if there is a condensed phase inside the parcel (i.e. \(m^2 \neq 0\) or \(m^3 \neq 0\)). Since \(l_{21} \geq 0\) and \(l_{31} \geq 0,\) the sign of \(a_i\) is the same as \(-(T - T_i)\). One can recognize in Eq. (22) the so-called efficiency factor \(\eta_T = 1 - T_i/T\) introduced in the available and static entropic energy theories and also used in the dry available enthalpy approach. But in the present moist theory \(\eta_T\) appears directly in the formulation of the latent-energy component, whereas it was involved in the previous studies only at the stage of the prognostic equations for the energy components. It should be noticed that, from Eqs. (20) to (22), \(a_T\) and \(a_i\) vanish if \(T = T_i \Leftrightarrow \mathcal{F}(X) = 0 \Leftrightarrow \eta_T = 0.\)

4. Numerical evaluations

The local available enthalpy function \(a_m\) was separated in section 3(c) into the three components \(a_T, a_i\) and \(a_p.\) They are natural generalizations of the temperature and pressure components derived for the dry case, namely \((a_T)_d = c_p^0 T_i \mathcal{F}(X)\) and \((a_p)_d = R^0 T_i \ln(p^0/P_i).\) The latent heat part \(a_i\) does not exist in the dry case.

In this section an attempt is made to estimate the orders of magnitudes of these moist components. A representative vertical profile of a cumulus cloud with liquid cloud water is used (see Fig. 3). There is neither ice nor precipitable liquid water. Air is saturated above the 850 hPa level. The profiles of the mixing ratios of water vapour \(r^1,\) cloud liquid water \(r^2,\) as well as the total mixing ratio of water \(r = r^1 = r^2\) are shown in Fig. 4. Values of \(r^1\) and \(r^2\) are about 10 g kg\(^{-1}\), and values of \(r^2\) are about 1.5 g kg\(^{-1}\).

The impact of moisture on the definition of available enthalpy is firstly the appearance of a new term \(a_i,\) secondly the modification of the dry components by terms depending on \(r\) \((a_T\) and \(a_p).\) The moist components can be rewritten as \(a_T = m^0 ((a_T)^0 + (a_T)^I)\) and
Figure 3. A representative vertical profile of a cumulus (dew points and state curve on a Skew-entrogram for \( p \approx 500 \) hPa).

Figure 4. Profiles of the mixing ratios of water vapour, \( r^1 \), and cloud liquid water, \( r^2 \), with the corresponding profile of total mixing ratio of water, \( r^t = r^1 + r^2 \). Note that different scales are used for \( r^2 \) and \( r^1 \) and \( r^t \).
\( a_p = m^0[(a_p)^0 + (a_p)^1] \), with
\[
(a_T)^0 = c_p^0 T_r \mathcal{T}(X), \quad (a_T)^1 = r c_p^1 T_r \mathcal{T}(X), \\
(a_p)^0 = R^0 T_r \ln(p^0/p_r^0), \quad (a_p)^1 = r R^1 T_r \ln(p^1/p_r^1).
\]
The dead state is defined by the constants \( T_r = 251 \) K, \( p_r^1 = 0.85 \) hPa and \( p_r^0 = 369.15 \) hPa.

The vertical profiles of \((a_T)^0\) is depicted on Fig. 5. (It is similar to the lower part, \( p \approx 500 \) hPa, of Fig. 6(a) in MM.) The profile of the water pressure component \((a_p)^1\) is also shown in Fig. 5. The values of \((a_p)^1(p)\) are greater than the values of the dry-air temperature component \((a_T)^0(p)\). The moist correction to \(a_p\) is thus an important one. It can be as high as 5 kJ kg\(^{-1}\) and the ratio \((a_p)^1/(a_p)^0\) (not shown) is about 7\% for \( p \approx 700 \) hPa.

![Figure 5. Vertical profiles of \((a_T)^0\) and \((a_p)^1\).](image)

The vertical profiles of \(a_l\) and \((a_T)^1\) are depicted on Fig. 6. The values of \(a_l(p)\) are about \(-0.4\) kJ kg\(^{-1}\), one order of magnitude less than \((a_T)^0(p)\) or \((a_p)^1(p)\), but in fact it is an important contribution to the available enthalpy budget because 0.4 kJ kg\(^{-1}\) is a typical value for the dry baroclinicity component (see Fig. 6(b) of Marquet (1991)). This result still holds with the isobaric average of the latent component \(a_l\) is always negative and the average value is close to the order of magnitude.

As for the values of \((a_T)^1(p)\), they do not exceed 0.1 kJ kg\(^{-1}\)—which is small in comparison with all other components—but the ratio \((a_T)^1/(a_T)^0\) is greater than 2\% for \( p \approx 700 \) hPa and it could be important to take \((a_T)^1\) into account in a fine exergetic budget.

These evaluations are not thorough however. The impacts of the ice cloud component and the precipitable liquid water (or ice) should have been investigated. The precipitable mixing ratio can indeed be as high as 8 g kg\(^{-1}\), a value which is five times the liquid cloud water content \(r^2\). However, as explained in section 2, liquid precipitation cannot be taken into account in the present exergetic analysis (\(\mathcal{H}_l\)). The effects of the presence of ice, either the cloud or the precipitable part, are not studied in the present paper. From \(\mathcal{H}_l\), solid precipitation is indeed outside the scope of this exergy approach, although a profile of cloud ice crystals could have been considered.
The preliminary conclusion from these results is that the use of the moist available enthalpy concept could prove to be useful in analyses of mesoscale systems where conversions involving the terms \(a_i\), \((a_T)^i\) or \((a_p)^i\) could be of the same magnitude as the other main conversions.

5. THERMODYNAMIC EQUATIONS

To study the conversions that occur in local, mesoscale or global systems, the local budget of \(a_m\) must be related to the local budgets of the other forms of energy (potential, kinetic). The objective of this section is thus to derive an analytical expression for \(\frac{D(a_m)}{Dt}\), with \(\frac{D}{Dt}\) obtained from section 2 and \(a_m\) from section 3(b) in terms of \(h\) and \(s\). The knowledge of the first (for \(h\)) and second (for \(s\)) laws of thermodynamics can thus serve this purpose.

Using \(\mathcal{H}_{1,...,9}\), and following De Groot and Mazur (1962), these laws can be rewritten as

\[
\frac{Dh}{Dt} = \frac{1}{\rho} \frac{Dp}{Dt} + (\varepsilon + q) - \frac{1}{\rho} \mathbf{J}^k \cdot \nabla (h^k) + h^k \frac{D \varepsilon}{Dt} (m^k) \tag{24}
\]

\[
T \frac{Ds}{Dt} = (\varepsilon + q) - \frac{1}{\rho} \mathbf{J}^k \cdot \nabla (h^k) + T \frac{D \varepsilon}{Dt} (m^k) - \mu^k \frac{D \sigma}{Dt} (m^k) \tag{25}
\]

where the positive Rayleigh function \(\varepsilon = (\rho)^{-1} (\sigma, \nabla)\cdot v\) is the specific dissipation of mechanical energy (\(\sigma\) is the viscous stress tensor), and where \(q\) is the specific heating rate: \(q = -\rho^{-1} \nabla \cdot J_{iq}\). The inner heat flux, \(J_{iq}\), is caused by conduction and radiation, but not by changes of phase which are explicitly taken into account by internal changes in enthalpy: \(D_h(h^k)/Dt\).

The prognostic equations for the barycentric velocity \(v\), the specific kinetic energy of the barycentric motion \((e_K = \mathbf{v} \cdot \mathbf{v}/2)\) and the specific gravitational energy \((e_G = \Phi = \)
gz) are

\[
\frac{Dv}{Dt} = -\frac{1}{\rho} \nabla(\rho) + \frac{1}{\rho} \nabla(\sigma) + g - f k \times v + F_t
\]

(26)

\[
\frac{De_k}{Dt} = g \cdot v - \frac{1}{\rho} v \cdot \nabla(p) - \varepsilon + \frac{1}{\rho} \nabla(\sigma) + v \cdot F_r
\]

(27)

\[
\frac{De_G}{Dt} = -g \cdot v
\]

(28)

where \( F_t \) represents external forces like friction and where \( f \) is the Coriolis parameter.

The local-budget equation for \( a_m \) can then be obtained using Eq. (18) with

\[
\frac{D(\mu^0)}{Dt} - \frac{D(h)}{Dt} - \mu \frac{D(m^0)}{Dt} - \mu^1 \frac{D(m^1)}{Dt} = 0
\]

With the use of Eqs. (24) and (25), one obtains

\[
\frac{D(a_m)}{Dt} = (\rho)^{-1} \frac{D(p)}{Dt} + \eta \veps + q - \eta \psi(\rho)^{-1} J_k \cdot \nabla(h_k) +
\]

\[
+ (h_k - T_k s_k) \frac{Dc}{Dt} + (T_k/T) \mu_k \frac{D(m^k)}{Dt} - \left[ \mu^0 \frac{D(m^0)}{Dt} + \mu^1 \frac{D(m^1)}{Dt} \right].
\]

The first term of the second line of Eq. (29) is the sum \((h_k - T_k s_k)\frac{D(m^k)}{Dt} - D_i(m^k) / Dt\). The second term is the sum \((T_k/T)(h_k - T_k s_k)\frac{D(m^k)}{Dt}\). The terms between the square brackets can also be transformed using Eq. (4) applied to \( \mu_k = h_k - T_k s_k \) to give the sum \(-(h_k - T_k s_k)\frac{D(m^k)}{Dt} + (\mu^0_k - \mu^1_k)\frac{D(m^0)}{Dt}\), where the property \( \mu^3_k = \mu^1_k \) is used to cancel the term containing \( D(m^3) / Dt \). Adding these three terms leads to the budget equation for \( a_m \).

\[
\frac{Da_m}{Dt} = \frac{1}{\rho} \frac{Dp}{Dt} + \frac{1}{\rho} v \cdot \nabla(p) + \eta \veps + q - \frac{1}{\rho} \nabla(h_k) +
\]

\[
+ (h_k - h_k) \frac{D(m^k)}{Dt} - \eta h_k \frac{D(m^k)}{Dt} + (\mu^0_k - \mu^1_k) \frac{D(m^0)}{Dt}.
\]

The first term of the second line of Eq. (30) is the sum \((h_k - T_k s_k)\frac{D(m^k)}{Dt} - D_i(m^k) / Dt\). The second term is the sum \((T_k/T)(h_k - T_k s_k)\frac{D(m^k)}{Dt}\). The terms between the square brackets can also be transformed using Eq. (4) applied to \( \mu_k = h_k - T_k s_k \) to give the sum \(-(h_k - T_k s_k)\frac{D(m^k)}{Dt} + (\mu^0_k - \mu^1_k)\frac{D(m^0)}{Dt}\), where the property \( \mu^3_k = \mu^1_k \) is used to cancel the term containing \( D(m^3) / Dt \). Adding these three terms leads to the budget equation for \( a_m \).

\[
h_k \frac{D(m^k)}{Dt} = \frac{1}{2} l_{\alpha \beta} \frac{D(m^\beta)}{Dt} = l_{21} \frac{D(m^1)}{Dt} + l_{22} \frac{D(m^2)}{Dt} + l_{31} \frac{D(m^3)}{Dt}
\]

(31)

where more precisely

\[
\frac{D(m^0)}{Dt} = \left[ \frac{D(m^1)}{Dt} + \frac{D(m^2)}{Dt} \right]
\]

(32)
It must be remarked that Eq. (30) is a symmetric equation with respect to the water components \( k = 1 \) to 3. The only dissymmetry lies in the choice of a dead state saturated with respect to ice (\( \mu^3_i = \mu^1_i \)). The consequence is the missing of the term \((\mu^3_i - \mu^1_i)D(m^3_i)/Dt\).

Equation (24) is the equation for the enthalpy; but neither enthalpy nor energy can be computed numerically for lack of knowledge of their absolute values, contrary to the temperature which is the physical associated concept and which is easy to measure. After some manipulations, using Eqs. (1) to (3) and the property \( \nabla(h^k) = c^k_p \nabla(T) \), an equation for the temperature can be derived from Eq. (24), yielding

\[
\frac{c_p}{\rho} \frac{DT}{Dt} = \frac{1}{\rho} \frac{DP}{Dt} + (\varepsilon + q) - \frac{1}{\rho} c^k_p J^k \cdot \nabla(T) - h^k \frac{D(m^k)}{Dt}. \tag{33}
\]

According to Eq. (31) the last term of this equation can be computed and, as expected, Eq. (33) is a well-founded prognostic equation for \( T \).

6. LOCAL PROPERTIES

(a) A local energy cycle

The local energy cycle will not be investigated in its more general form. Some hypotheses will be made in order to simplify the formulae. The aim in this first study is to forget the contributions due to various irreversibilities.

After some manipulation the three terms on the second line of Eq. (29) can be put in the form

\[
(h^k - T_e s^k) \frac{D_e(m^k)}{Dt} + (\mu^0_i - \mu^1_i) \frac{D_e(m^i)}{Dt} + \frac{T_e}{T} \left\{ (\mu^2_i - \mu^1_i) \frac{D_i(m^2)}{Dt} + (\mu^1_i - \mu^1_i) \frac{D_i(m^3)}{Dt} \right\}.
\]

This last expression is obtained without approximation. Indeed, there is no chemical reaction between dry air and the water element, and from Eq. (1) \( D_i(m^0)/Dt = D_e(m^i)/Dt = 0 \). Another consequence is \( D_i(m^0)/Dt = -D_e(m^2)/Dt = -D_e(m^3)/Dt \). Then the terms between square brackets of the second line of Eq. (29) can be rewritten as

\( (\mu^0_i - \mu^1_i) D_e(m^i)/Dt \). As for the term \( (T_e/T) \mu^k D_e(m^k)/Dt \), it can be transformed using \( D_e(m^1)/Dt = -D_i(m^2)/Dt - D_i(m^3)/Dt \).

The parcel is now supposed to be closed and inviscid \( \sigma = 0, \varepsilon = 0, J^k = 0 \Rightarrow \forall k: D_i(m^k)/Dt = 0 \). The first and second terms of the last expression cancel because \( D_e(m^k)/Dt = 0 \). The last terms also cancel out as far as changes of phase are reversible (i.e. if \( \mu \) is the same in each phase of the chemical reaction). Indeed, using Eqs. (32), these last terms can be rewritten as

\[
\frac{T_e}{T} \left\{ (\mu^1_i - \mu^2_i) \frac{D_i(m^2)}{Dt} + (\mu^2_i - \mu^3_i) \frac{D_i(m^3)}{Dt} + (\mu^1_i - \mu^3_i) \frac{D_i(m^3)}{Dt} \right\}
\]

and if one of the \( D_i(m^3)/Dt \) is not zero, the corresponding \( (\mu^a_i - \mu^b_i) \) is zero. Therefore Eq. (30) reduces to the simplified form \( D_i(a_m)/Dt = \rho^{-1} D(p)/Dt + \eta \tau q \).

Under all these assumptions Eqs. (27), (28) and the simplified form of Eq. (30) yield the local energy cycle for an inviscid and closed parcel:

\[
\begin{align*}
D/\Dt(a_m) &= \rho^{-1} \partial p/\partial t + \rho^{-1} v \cdot \nabla(p) + \eta \tau q \\
D/\Dt(e_K) &= + g v - \rho^{-1} v \cdot \nabla(p) + v \cdot F_t \\
D/\Dt(e_G) &= - g v.
\end{align*}
\tag{34}
\]
The terms $-\varepsilon$ and $\rho^{-1} \nabla (\sigma \mathbf{v})$ are zero in the kinetic equation according to the hypotheses of a closed and inviscid parcel. The local cycle (34) is a moist generalization of the dry available enthalpy cycle investigated in MM and, like $a_h$ and $a_m$, can be considered as a moist Lagrangian energy-like quantity.

If the previous assumptions were not verified, some other terms would appear in $D(a_m)/Dt$ and in $D(e_k)/Dt$. These terms would take account of irreversibilities caused by change of phase, diffusion fluxes or viscosity. Non-equilibrium thermodynamics deals with these irreversibility terms (see, for example, De Groot and Mazur 1962). A full local cycle with the five components \{$e_G, e_K; a_T, a_p, a_i$\} can also be obtained, separating $a_m$ into \{$a_T, a_p, a_i$\} in (34).

(b) The Bernoulli equation

Adding the three equations of (34) gives:

$$\frac{D}{Dt}(a_m + e_k + e_G) = \rho^{-1} \partial p/\partial t + \eta_T q + \mathbf{v} \cdot \mathbf{F}_c. \tag{35}$$

Equation (35) shows that $a_m + e_k + e_G$ is a constant along any particular streamline of an adiabatic frictionless and reversible steady flow if the parcels are assumed to be inviscid and closed with, however, possible reversible internal changes of phase of water components inside them. Equation (35) is the moist generalization of the dry Bernoulli equation of Marquet (1991).

This moist Bernoulli equation demonstrates that, if the required assumptions are verified, $a_m$ exactly varies as $-(e_k + e_G)$ during the motion of the parcel. Therefore energy conversions really occur between the various forms $a_m$, $e_k$ and $e_G$.

According to the local cycle (34) a set of conversion terms is given by $C_{(e_k, k)} = +g \cdot \mathbf{v}$ and $C_{(a_m, k)} = -\rho^{-1} \mathbf{v} \cdot \nabla (p)$, insofar as the other terms are interpreted as sources and sinks. As usual, however, this interpretation of physical conversions is not unambiguous (Johnson and Downey 1982). Other sets of conversion or source/sink terms can be defined in (34) provided the Bernoulli equation (35) remains unchanged.

7. Integral properties

The objectives of this section are to derive a global conservation law verified by the total moist available enthalpy $A_m$ and to give definitions for the two undetermined quantities $T_c$ and $p_r^0$.

The local moist property $\rho^{-1} \partial p/\partial t = D(RT)/Dt - \rho^{-1} \nabla (p \mathbf{v})$ holds true, provided that $R = m^{E_0} R^0 + m^{E_1} R^1$ and $p = p^0 + p^1$. Starting with the integral form of this moist property together with the integral form of Eq. (35), it can be demonstrated that for an adiabatic frictionless and reversible motion of inviscid and closed atmospheric parcels:

$$\frac{d}{dt}(A_m + E_k) = \frac{d}{dt}(H - (E_i + E_G)). \tag{36}$$

The velocity component normal to the earth's surface is supposed to be zero.

For a hydrostatic atmosphere and if there is no topography $H = E_i + E_G$, but in that case $E_k$ must be replaced in (36) by the kinetic energy of horizontal motion $E_k^h$:

$$\frac{d}{dt}(A_m + E_{k}^h) = 0. \tag{37}$$
Under these assumptions the global hydrostatic conservation law (37) is equivalent to the one derived by Lorenz (1955, 1967). It is a moist generalization of the dry conservation law \( d(A_h + E_k) / dt \) derived in Marquet (1991).

Similarly to MM the temperature \( T_r \) can be defined so that \( 1/T_r \) is the space–time average over the whole moist atmosphere of \( 1/T \). This choice implies that a uniform— in space and time—heating rate does not generate moist available enthalpy in space–time average. All terms in Eq. (27) which possess \( \eta_T = 1 - T_r/T \) as a multiplicative factor are subject to this property, in particular \( (\varepsilon + q) \). The value of \( T_r \) can be estimated as 250 K.

If \( T_r \) is known, the saturating pressure \( p^* = p^* (T_r) \) and the two energy components \( a_T \) and \( a_l \) are determined completely at each point of the atmosphere. Following MM the pressure \( p^0 = p_r - p^* (T_r) \) can then be defined so that the third energy component, \( a_p \), cancels out by space–time averaging. In this problem the known variables are \( m^0, m^1, T_r, p^0 \) and \( p^* \), and \( p^0 \) is the unknown quantity. The value of \( p^0 \) can be estimated as \( p_0/e = 368 \) hPa.

Using Eq. (23), and the notations of the appendix, these definitions can be summarized by:

\[
\frac{1}{T_r} = \frac{1}{\Delta t} \int_{t_i}^{t_f} dt \int \int \int \frac{1}{M} \frac{dm}{d \tau} \frac{\ell}{T} \frac{dM}{d \tau} \frac{dm}{d \tau} \frac{\ell}{T} \frac{dM}{d \tau}
\]

(38)

and

\[
\ln(p^0) = \frac{1}{\Delta t} \int_{t_i}^{t_f} dt \int \int \int \left( \frac{m^0}{M^0} \ln(p^0) + \frac{m^1}{M^0} \frac{R^1}{R^0} \ln(p^1/p^0) \right) \frac{dm}{d \tau} \frac{\ell}{T} \frac{dM}{d \tau}
\]

(39)

where \( M^0 \) is the space–time average of the water vapour concentration \( m^0 \).

8. THE MOIST POTENTIAL TEMPERATURE

The function \( a_m \) defined by Eq. (18) can be written in an alternative way in order to introduce a moist potential temperature denoted by \( \theta^* \). Using a method initiated in HH the sum \( s - m^0 s^0 - m^1 s^1 \), which is the entropy part of \( a_m \) can be expressed in terms of \( m^0 c_p^* \ln(\theta^*/\theta^* \) ), where \( c_p^* = c_p^0 + r^1 c_p^1 \) and \( p_0 = 10^5 \) Pa:

\[
a_m = h - m^0 h^0 - m^1 h^1 - m^0 c_p^* T_r \ln(\theta^*/\theta^* \)
\]

(40)

with

\[
\theta^* = \frac{T(p^0/p_0)}{T_r(p^0/p_0)} \frac{m^1}{m^0} \frac{R^1}{R^0} \frac{c_p^0}{c_p^*} \left( \frac{p^0}{p_0} \right)^{R^1/c_p^0} \left( \frac{p^1}{p_0} \right)^{R^1/c_p^0} \exp \left( - \frac{R^2 I_{21} + R^3 I_{31}}{C_p^* T_r} \right).
\]

(41)

This result is obtained starting from Eq. (18) of section 3(a) written in the form

\[
a_m = (h - m^0 h^0 - m^1 h^1) - T_r (m^k s^k - m^0 s^0 s^0 - m^1 s^1) \)

The enthalpy parts will not be changed. The entropy parts can be transformed using Eq. (4) applied to \( m^k s^k \), yielding \( m^0 (s^0 - s^0) + m^1 (s^1 - s^0) + m^2 (s^2 - s^0) + m^3 (s^3 - s^1) \). The next step is to express the various differences of entropy, with the introduction of the chemical potentials and the
latent heats for \( s^2 - s^1 \) and \( s^3 - s^1 \)
\[
\begin{align*}
s^0 - s^i &= c_p^0 \ln(T/T_i) - R^0 \ln(p^0/p^i) \\
s^1 - s^i &= c_p^1 \ln(T/T_i) - R^1 \ln(p^1/p^i) \\
s^2 - s^1 &= (\mu^1 - \mu^2)/T - (h^1 - h^2)/T = R^1 \ln(p^1/p^{21}) - l_{21}/T \\
s^3 - s^1 &= (\mu^1 - \mu^3)/T - (h^1 - h^3)/T = R^1 \ln(p^1/p^{31}) - l_{31}/T. 
\end{align*}
\]

The moist available enthalpy becomes
\[
\begin{align*}
a_m &= h - m^0 h_i^0 - m^i h_i^1 - m^0 c_p^* \ln(T/T_i) - m^0 R^0 \ln(p^0/p^i) - m^0 r R^1 \ln(p^1/p^i) \\
&\quad - m^0 (r^2 l_{21} + r^3 l_{31})/T + R^1 [m^2 \ln(p^1/p^{21}) + m^3 \ln(p^1/p^{31})].
\end{align*}
\]
The terms between the square brackets are zero according to Eq. (8) and the result is then obtained because Eqs. (40) and (41) are just another way of writing it using logarithms and exponentials.

The quantity \( \theta^* \) is analogous from (41) to the entropic temperature \( \theta_s \) of HH, while \( \theta^* \) seems to generalize the ice liquid potential temperature \( \theta_i \) of Tripoli and Cotton (1981), provided that \( \theta^* \) is associated with the denominator of (41) and if \( \theta^* \) is the product of the numerator and the exponential term.

Using the present notations, \( \theta_s \) is defined in HH by \( s = m^0 s_i^0 + m^i s_i^1 + m^0 (c_p^0 + r c_p^2) \ln(T/T_i) \). In this study, \( \theta^* \) is similarly related to the entropy by \( s = m^0 s_i^0 + m^i s_i^1 + m^0 (c_p^0 + r c_p^2) \ln(\theta^*/\theta_i^*) \). As noted in HH, conceptual problems could arise with the \( \theta_s \) formulation if liquid water is not present in the moist parcel (i.e. if \( r^2 = r^1 + r^3 \neq 0 \)). Indeed it could be difficult to interpret the terms \( m^i s_i^1 \) and \( r c_p^2 \) in this case, whereas in the various terms of (40) and (41) only the water vapour element which is always present is involved through \( m^i s_i^1 \) and \( r c_p^2 \). This is more consistent.

The advantage of introducing \( \theta^* \) by (40) lies in a property already mentioned in section 3(b). For an adiabatic (\( q = 0 \)) and reversible ((\( \mu^x - \mu^y \))D_1(m^y)/Dt = 0) motion of an inviscid (\( \epsilon = 0 \)) and closed (D_1(m^y)/Dt = 0 and \( J^k = 0 \)) parcel: D_1(a_m - h)/Dt = -T_i D_1(s)/Dt = 0. This property can be derived from Eqs. (24) and (30) together with the remarks made at the beginning of section 6(a):
\[
0 = \frac{T}{T_i} \frac{D(a_m - h)}{Dt} = - (\epsilon + q) + \frac{1}{\rho} J^k \nabla(h^k) - T \left[ m^0 \frac{D c_p^0}{Dt} + \frac{T}{T_i} \left( \mu^0 - \mu_i^1 \right) \right] + \frac{D c_p^2}{Dt} + \left( \mu^1 - \mu^2 \right) \frac{D c_p^1}{Dt} + \left( \mu^3 - \mu^1 \right) \frac{D c_p^3}{Dt}. 
\]

For such a motion, \( a_m - h, m^0 h_i^0 + m^i h_i^1, m^0 c_p^* T_i \) and \( \theta_i^* \) are all constants and one can deduce from Eqs. (40) to (42) the conservation of
\[
\theta^* = T \left( \frac{p^0}{p_{00}} \right)^{-R_0/c_p^*} \left( \frac{p^1}{p_{00}} \right)^{-R_1/c_p^*} \exp \left( - \frac{r^2 l_{21} + r^3 l_{31}}{c_p^* T} \right). 
\]
during the motion of the parcel. This conservative property holds whatever the state of the parcel or its evolution with time (saturated or not, with liquid water or ice). The quantity \( \theta^* \) can be called the moist potential temperature associated with the moist entropy, \( s \), and with the moist available enthalpy, \( a_m \).

9. CONCLUDING REMARKS

In this paper the moist available enthalpy \( a_m \) is defined as a local exergy-like function. The concept of potential change in total entropy has been used to generalize the dry
available enthalpy $a_n$ to the moist atmosphere case, different from the real exergy approach where a Kullback function can be used. A moist reference dead state is introduced to define $a_m$, but the name ‘reference’ does not here have the same meaning as it is understood in the meteorological approach of available energy. It is not a reference state which could be constructed from a given state of the atmosphere neither to minimize the total moist enthalpy (Lorenz), nor to maximize the total entropy with some constraints (Dutton). It is a chemically stable local state, a passive environment, and any parcel of the real atmosphere can reach this reference dead state separately from each other.

The mathematical expression of $a_m$ is simple and analytical, this corresponds to Lorenz’s (1978, 1979) demand. In fact it is possible to put $a_m$ into various synonymous forms, such as Eqs. (17), (18), (19) and (40). Each of these forms yields a special property satisfied by $a_m$. Equation (17) means that $a_m$ is independent of any arbitrary choice for the absolute values of energy, enthalpy or entropy functions. Equation (18) shows that $a_m$ is similar to what is called flow-exergy in thermodynamics. Equation (19) is the separation of $a_m$ into the three components $a_T$, $a_i$ and $a_r$. These components are the generalizations of the same components already defined with the dry available enthalpy, except for the latent part, $a_i$, which is a new one. Eq. (40) serves as an introduction for the moist potential temperature, $\theta^*$, which satisfies conservative properties.

Moreover, using the local-state theory as moist thermodynamics, the local function $a_m$ leads to:

(i) a moist Bernoulli law satisfied by $a_m + e_G + e_K$;
(ii) a moist local energy cycle involving $a_m$, $e_G$ and $e_K$; and
(iii) a moist integral hydrostatic conservative property satisfied by $A_m + E_K$.

Another property is that $a_m$, like $a_n$ in the dry study (Marquet 1991), is only partially convex. Indeed, only $\mathcal{F}(X)$ and $a_T$ are positive and convex in $X$. On the contrary, for an ideal gas, the exergy function $e = (e_1 - (e_i)_1) + p_T((\rho)^{-1} - (\rho_i)^{-1}) - T_i(s - s_i)$ is convex since it can be rewritten as the sum of two terms depending on the function $\mathcal{F}(X) = X - \ln(1 + X) - c_v T_i \mathcal{F}((T/T_r - 1) + RT_r \mathcal{F}(\rho/r - 1)$. The possibility of cancelling out the integral of $a_i$ is used in this study to define the value of $p_i$, it is not possible to have this result with a convex function.

The purpose of the present paper is to show that the exergy-like function $a_m$ verifies at the same time all the properties recalled in this section. It is a general thermodynamic quantity which was not easy to guess from the two laws of thermodynamics, although the moist version (Eqs. (19) to (23)) requires only modest modification of the expression for the dry case.

The author is aware of the theoretical nature of the present paper. At this point numerical evaluations of the various concepts and functions introduced in this study must still be realized with case studies, for instance for an open moist synoptic-scale system. It is a knowledge of the conversion terms which would be the more revealing of the interest of this exergetic analysis. An attempt is, however, made in section 4 to estimate the orders of magnitude of the moist available enthalpy components with a vertical profile that simulates a cumulus cloud. It is found that the moist contributions are important in comparison with the dry version. The results of a synoptic-scale study using dry and moist versions of the available enthalpy concept will be presented in a future paper. The dry and moist exergy cycles will be applied with the hydrostatic assumption, stressing the problem of the various energy conversions between isobaric layers of an open limited atmospheric domain, including the study of boundary fluxes.

The various results derived in this paper can, however, be applied from now on. The first step is to determine the two constants $T_r$ and $p_r$ according to the definitions (38).
and (39). It is also possible to use prescribed realistic values such as 251 K and 370 hPa. The moist available enthalpy components can then be computed from Eqs. (19) to (23). The budget equation for \( a_m \) can be studied starting from Eq. (30), or with the suitable assumptions from the simplified Eq. (34). The simplified moist available enthalpy cycle is not very different from other enthalpy cycles and it is not very interesting in this form, except it was necessary to demonstrate that this cycle exists with the moist formulation. On the contrary the Bernoulli equation (35) can be useful in order to develop some qualitative or quantitative arguments such as Convective Available Potential Energy considerations or Carnot heat-engine analogy applied to convection or cyclone problems for instance. Finally, the conservative properties of the moist potential temperature defined by Eqs. (40), (41) and (43), which solely come from the second law of thermodynamics, can serve as accurate air-mass analysis.

On a more general point of view, it could be interesting to find a function of statistical physics similar to the Kullback function in order to provide another consistent physical meaning to \( a_m \). It would also be worth taking into account precipitation which falls at \( T_v \neq T \) in unsaturated air. This implies generalizing \( a_m \) using, for instance, thermodynamics of a thermally heterogeneous medium. Finally, we may ask whether these moist functions could be used as moist prognostic variables in numerical models dealing with liquid water or ice.

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APPENDIX

General

The subscript \( r \) denotes the values in the reference dead state (like in \( p_r \) and \( T_r \)). The subscripts or superscripts \( i, j, k, \alpha \) and \( \beta \) are used to denote partial values: 0 for dry air, 1 for water vapour, 2 for liquid water (stable or supercooled) and 3 for ice. When they are repeated twice in two different terms, these subscripts or superscripts represent an implicit sum over the values 0 to 3 (for example, \( a_m = m^k a_m^k = \Sigma_{k=0}^3 m^k a_m^k \)).

Basic thermodynamics

- \( T, p, \theta \)  
  Temperature, total pressure, potential temperature
- \( h, e_i, s \)  
  Specific enthalpy, internal energy, entropy
- \( H, E_i, S \)  
  Integrated forms of \( h, e_i, s \)
- \( \rho^k, \rho = \Sigma_{k=0}^3 \rho^k \)  
  Partial and total densities
- \( \nu = 1/\rho \)  
  Specific volume
- \( m^k = \rho^k/\rho \ (k = 0 \to 3) \)  
  Concentrations
- \( m^i = m^1 + m^2 + m^3 \)  
  Total concentration of the water element
- \( r^k = m^k/m^0 \ (k = 1 \to 3) \)  
  Mixing ratios
- \( r^i = r^1 + r^2 + r^3 \)  
  Total mixing ratio of the water element
- \( p^0, p^1 \)  
  Partial pressures for dry air and water vapour (\( p = p^0 + p^1 \))
MOIST AVAILABLE ENTHALPY

\[ R^i (i = 0 \text{ and } 1) \]
\[ c_{p^i}, c_{v^i} \text{ (} j = 0 \text{ to } 3 \text{)} \]
\[ c_p = m^k c_p^k \]
\[ c_{p*} = c_{p^0} + r c_{p^1} \]
\[ T_{tr} = 273.16 \text{ K} \]
\[ l_i = h_i - h_i^p \]
\[ T_w \]
\[ p_i^l(T) \]
\[ \mu^k = h^k - T s^k \]
\[ \delta k = \mu^1 - \mu^i \]

Gas constants: \( R = m^0 R^0 + m^1 R^1 \)
Specific heats at constant pressure and volume.
For condensed phases \( j = 2 \) and \( j = 3 \): \( c_p^i = c_{v^i} = c_l \)
Total specific heats at constant pressure
A notation used in section 7 (and in section 3(c))
Latent heat (\( i \) to \( j \) transformation)
Wet-bulb temperature
Saturating pressure over liquid water (\( i = 2 \)) and ice (\( i = 3 \))
Chemical potentials of the elements \( k = 0 \) to \( 3 \)
Chemical affinities related to \( i \) form (\( i = 2 \) and 3) and water vapour

Basic kinematics

\[ e_K, e_G \]
\[ E_K, E_G \]
\[ e_{K*} \]
\[ z, \omega \]
\[ \bar{\omega}, \bar{T} \]
\[ \partial / \partial t, D / D t \]
\[ \delta / \delta t, D / D t \]
\[ D_e / D t, D_U / D t \]
\[ D_k / D t \]
\[ v = \rho^k v^k / \rho \]
\[ v^k \]
\[ J^k \]
\[ \beta^k \]
\[ q = - (\rho)^{-1} \nabla \cdot J_{eq} \]
\[ \sigma \]
\[ \varepsilon = (\rho)^{-1} (\sigma \cdot \nabla) \cdot v \]
\[ \Phi \]
\[ g \]
\[ k \]
\[ g = g_k \]
\[ F_r \]
\[ C_{(G,K)}, C_{(m,K)} \]

Specific kinetic and potential energy
Integrated forms of \( e_K, e_G \)
Integrated kinetic energy of the horizontal wind
Upward distance, vertical wind component in isobaric coordinate
Isobaric average of \( \omega \) and \( T \)
Eulerian and Lagrangian derivative
Natural time derivative (function of \( t \) only)
External and internal Lagrangian change in time
Chemical Lagrangian rate of change of \( \alpha \) into \( \beta \) element
Barycentric velocity of the parcel
Partial velocity of the element \( k \) in the parcel
Diffusion flux of the element \( k \)
Phase flux of the element \( k \)
The inner heat flux
The specific heating rate
Viscous stress tensor
Positive Rayleigh function
Geopotential
The gravity force
The unit upward vertical vector
Magnitude of gravity
External forces
Conversion terms between \( e_G \) and \( e_K \), and \( a_m \) and \( e_K \) respectively

Exergy theory

\[ p_r = p_r^0 + p_r^1, T_r \]
\[ P_r \]
\[ a_r, a_m \]
\[ a_m^k = T_r (\Delta m^w S^w)^k, k = 0 \text{ to } 3 \]
\[ b^k = (h^k - h_i^k) - T_r (s^k - s_i^k) \]
\[ a_e \]
Reference dead state pressures and temperature (moist case)
Reference pressure for the dry enthalpy case
Specific dry and moist available enthalpy
Partial moist available enthalpy (\( a_m = m^k e_m^k \))
Notation used in section 3(a)
Specific available energy
a_T, a_l, a_p

A_h, A_m, A_T, A_l, A_p

\( T_0 \Sigma \)

\( \theta^*; \theta^*_r \)

\( \theta_S \)

\( \mathcal{F}(X) = X - \ln(1 + X) \)

\( \eta_T = 1 - T_i/T = (T - T_i)/T \)

\( R_{\text{max}} \)

\( T_0 \)

\( T_1 \)

\( \Delta_1 S_t \) and \( \Delta_2 S_t \)

\( \Delta S_t = R_{\text{max}}/T_0 \)

\( (E_i) \)

\( (S_i) \)

\( \Delta S \)

\( (S)_{\text{eq}} \)

\( \Delta_o S^o \)

\( \Delta_m S^o = m^k (\Delta_m S^o)^k \)

\( p_{00} = 10^5 \text{ Pa} \)

\( \mathcal{H}_n \)

\( H^k \)

\( t_2, t_1, \Delta t = t_2 - t_1 \)

\( M^0 \)

\( \Delta m, M \)

\( \mathcal{M} \)

\( \psi \)

Specific temperature, latent and pressure components of \( a_m \)

Integrated forms of \( a_h, a_m, a_T, a_l, a_p \)

Static entropic energy

Moist potential temperatures (real and reference values)

Entropic temperature (Hauf and Höller 1987)

The positive function used in the temperature moist component \( a_T \) (section 3(c)): \( X = T/T_r - 1 = (T - T_r)/T_r \)

Efficiency factor

Maximum delivered work or available energy (Landau and Lifchitz 1976, §20, except they use \( R_{\text{min}} \) to denote the maximum delivered work as a minimum received work)

Temperature of the thermostat

Equilibrium temperature used in the definition of \( a_c \) see section 3(a)

Two changes in total entropy used in the definition of \( a_c \), see section 3(a)

Difference in total entropy between the real state and the associated equilibrium state of temperature \( T_0 \) (Landau and Lifchitz 1976, §20)

Total energy (for a unit mass parcel plus a thermostat)

Total entropy (for a unit mass parcel plus a thermostat)

Change in total entropy (for any process involving the system 'unit mass parcel plus thermostat')

Equilibrium curve

Dry potential change in total entropy

Moist (total, partial for \( k = 0 \) to 3) potential change in total entropy.

Other quantities

Conventional pressure

Label for the hypothesis number \( n \)

Equivalent height

Times, a time interval

Space–time average of \( m^0 \)

Element of mass, mass of the atmosphere

Mass integrating domain of the atmosphere

Dummy specific function.
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