Thermodynamically consistent versions of approximations used in modelling moist air

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Abstract
Some existing approaches to modelling the thermodynamics of moist air make approximations that break thermodynamic consistency, such that the resulting thermodynamics does not obey the first and second laws or has other inconsistencies. Recently, an approach to avoid such inconsistency has been suggested: the use of thermodynamic potentials in terms of their natural variables, from which all thermodynamic quantities and relationships (equations of state) are derived. In this article, we develop this approach for unapproximated moist-air thermodynamics and two widely used approximations: the constant-\( \kappa \) approximation and the dry heat capacities approximation. The (consistent) constant-\( \kappa \) approximation is particularly attractive because it leads to, with the appropriate choice of thermodynamic variable, adiabatic dynamics that depend only on total mass and are independent of the breakdown between water forms. Additionally, a wide variety of material from different sources in the literature on thermodynamics in atmospheric modelling is brought together. It is hoped that this article provides a comprehensive reference for the use of thermodynamic potentials in atmospheric modelling, especially for the three systems considered here.

KEYWORDS
constant-kappa approximation, enthalpy, Gibbs potential, Helmholtz free energy, internal energy, moist air, thermodynamic consistency, thermodynamic potential

1 | INTRODUCTION

When considering moist air, it is easy to introduce approximations that break thermodynamic consistency, such that the resulting thermodynamics does not obey the first and second laws or has other inconsistencies. For example, a common approach is to use unapproximated thermodynamics for moist air but define \( \theta_e \) through \( p\alpha = \kappa_d \Pi_d \theta_e \) (with \( \Pi_d = C_{pd} (p/p_e) \) and \( \kappa_d = R_d / C_{pd} \)) and treat it as an advected quantity.\(^1\) This is known as the constant-\( \kappa \) approximation, and applied in this way it is thermodynamically inconsistent: the treatment of \( \theta_e \) as an advected quantity leads to equations that no longer conserve the total energy, since there are missing water-related terms that should appear on the right-hand side of the equation (i.e., \( \theta_e \) is not really an advected quantity).

Remark 1. Although we have referred here to unapproximated thermodynamics for moist air, such a thing does not actually exist. All thermodynamic potentials are empirical: they come from either experiment or derivation from a more fundamental underlying theory.

\(^1\)An advected quantity \( a \) obeys \( Da/ Dt = 0 \) for reversible dynamics.
such as molecular dynamics or statistical mechanics. For example, in this work we assume that heat capacities are temperature-independent, condensates occupy no volume, and each phase of water is an unrelated thermodynamic substance (i.e., there is no equilibrium between water species and Gibbs’ phase rule does not apply). This highlights the fundamental difference between inconsistency error (which is avoidable) and approximation error (which is unavoidable).

A general approach to avoid such inconsistency is through the use of thermodynamic potentials, from which all thermodynamic quantities and relationships can be derived. This approach was advocated in Thuburn, (2017, 2018) and Staniforth and White (2019), although complete sets of thermodynamic potentials in terms of their natural variables are not presented in those works. Internal energy in terms of its natural variables is presented in Bowen and Thuburn (2022a, b). An important usage for potentials is a more rigorous treatment of energetics within a modelling system, as discussed in Lauritzen et al., (2022). In this article, we consider two widely used approximations: the constant-\(\kappa\) approximation and the dry heat capacities approximation. These approximations are used in many existing atmospheric models, often inconsistently. In fact, it is usually difficult to determine exactly what thermodynamic potentials are used for a given model or model component, or even whether there is a single set of thermodynamics. If there is documentation of the thermodynamics, it usually consists of some equations of state such as \(pa = R^* T\) and \(\theta = T(p/p_r)^{R^*/C^*}\), which are possibly approximated independently. However, as demonstrated in this article, equations of this type do not specify the thermodynamics completely. Additionally, approximating these expressions independently can lead to inconsistency. Some consequences of this inconsistency are explored in Section 4.3. By instead starting with thermodynamic potentials and introducing the relevant approximations directly into these, inconsistency can be avoided. We refer to the consistent systems derived from the approximate potentials as the constant-\(\kappa\) system and the dry heat capacities system. In addition to consistency, the constant-\(\kappa\) system also simplifies the dependence on the various water forms (vapour, liquid, and ice) so that, with an appropriate choice of thermodynamic variable (such as the virtual potential temperature \(\theta_v\) discussed below), the adiabatic dynamics depends only on the total mass and the water forms decouple from the rest of the dynamics. This is attractive for numerical modelling, since then water forms can be advanced independently from the dynamics with a larger timestep and/or different numerics.

There are some modelling systems (as of the publication of this article) in which the thermodynamics is articulated explicitly and a thermodynamic system can be identified. These are the following:

- CAM-SE/E3SMv1 (Lauritzen et al., 2018), which uses the dry heat capacities system;
- E3SMv2 (specifically the HOMME-NH dynamical core: Taylor et al., 2020), which uses the constant-\(\kappa\) system;
- CAM-SE-CSLAM (Lauritzen et al., 2018), which uses the unapproximated system.

It is hoped that this article will encourage more groups to articulate the thermodynamics utilized in their models explicitly, and stimulate future research into new consistent thermodynamics with different assumptions.

The main material in this article is complete sets of thermodynamic potentials in their natural variables for the unapproximated, constant-\(\kappa\), and dry heat capacities systems. This work also brings together a lot of material that is scattered around in various sources in the literature, and attempts to provide a comprehensive reference for the use of thermodynamic potentials in atmospheric modelling. It builds on the Gibbs functions introduced in Thuburn, (2017, 2018) and the internal energies introduced in Lauritzen et al., (2018) and Staniforth and White (2019), specifically in making the same fundamental assumptions and obtaining the same thermodynamic potentials up to certain linear functions, which just shift the zeros of entropy and chemical potentials, as discussed in Appendix A. However, Thuburn (2017, 2018), Lauritzen et al. (2018), and Staniforth and White (2019) do not present all thermodynamic potentials and/or do not give them in terms of their natural variables, both of which are done here.

The remainder of this article is structured as follows: Section 2 presents a review of equilibrium thermodynamics in the general case, Section 3 provides the thermodynamic potentials and related quantities for unapproximated (in the sense discussed above) moist air, Section 4 provides the thermodynamic potentials and related quantities for the constant-\(\kappa\) and dry heat capacities systems, and finally Section 5 gives some conclusions. Appendix A derives the unapproximated potentials found in Section 3, Appendix B discusses potential and virtual quantities, Appendix C gives common thermodynamic quantities for all three systems, Appendix D gives latent heats for all

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2Following the usual atmospheric dynamics literature terminology, which differs from the terminology in the thermodynamics literature.

3The four commonly used thermodynamic potentials: internal energy, enthalpy, Gibbs function, and Helmholtz free energy.
three systems, and Appendix E gives chemical potentials for all three systems. It is hoped that the material in Sections 2–4 and the Appendices provides a comprehensive reference for the use of thermodynamic potentials in atmospheric modelling, especially for the three systems considered.

2 | REVIEW OF EQUILIBRIUM THERMODYNAMICS

Consider a multispecies, multiphase fluid composed of \( N \) components. By components, here we refer to constituents with distinct thermodynamic behaviour. In addition to separate substances, this can also include different phases of the same species (e.g., water vapour and liquid water) and/or different allotropes of the same species and phase (e.g., ortho and para forms of hydrogen). In writing the thermodynamics below, we do not assume any equilibrium between different phases of the same species or chemical components undergoing reactions, and instead treat each phase as an independent thermodynamic substance. In particular, this means that each phase has its own independent density, rather than a total density for that species, with proportioning between phases done according to some sort of equilibrium hypothesis or phase rule. This assumption fits with the commonly used splitting in atmospheric modelling between (adiabatic) dynamics and physics. We will also assume that all components of the fluid are at the same temperature \( T \).

A key assumption made in modelling this fluid is that local thermodynamic equilibrium (LTE) holds, in the sense that thermal relaxation times are sufficiently short compared with other dynamical time-scales and therefore large-scale thermodynamic quantities can be defined meaningfully: for example, temperature and entropy. LTE implies that the thermodynamics of this fluid can be described using equilibrium thermodynamics, which is reviewed below. The assumption of LTE is almost universal in atmospheric modelling, especially for the troposphere and stratosphere. More information on equilibrium thermodynamics can be found in standard textbooks on the subject, such as Zdunkowski and Bott (2004).

2.1 | Thermodynamic potentials

Equilibrium thermodynamics tells us that the thermodynamic behaviour of this fluid is completely determined by a thermodynamic potential written in terms of its natural (state) variables. In the thermodynamics literature, the specification of a thermodynamic potential in terms of its natural variables is referred to as the equation of state, while a somewhat different usage occurs in the atmospheric dynamics literature (see below). In the case of the fluid described above, the state variables are one choice from the conjugate pair (volume \( V \), pressure \( p \)), one choice from the conjugate pair (entropy \( S \), temperature \( T \)), and one choice for each component from the conjugate pair (component mass \( M_n \), component chemical potentials \( \mu_n \)).\(^5\) Note that one member of each pair is an extensive quantity, while the other is an intensive quantity.

In atmospheric dynamics, four thermodynamic potentials are commonly used: the internal energy \( U(V,S,M_n) \), the enthalpy \( H(p,S,M_n) \), the Gibbs free energy \( G(p,T,M_n) \), and the Helmholtz free energy \( F(V,T,M_n) \). These are related through

\[
H = U + pV, \quad (1)
\]
\[
G = U + pV - ST, \quad (2)
\]
\[
F = U - ST, \quad (3)
\]

which are known as Legendre transforms.

Associated with each of these thermodynamic potentials are conjugate variables:

\[
p(V,S,M_n) := -\frac{\partial U}{\partial V}, \quad T(V,S,M_n) := \frac{\partial U}{\partial S}, \quad (4)
\]
\[
\mu_n(V,S,M_n) := \frac{\partial U}{\partial M_n}, \quad (5)
\]
\[
V(p,S,M_n) := \frac{\partial H}{\partial p}, \quad T(p,S,M_n) := \frac{\partial H}{\partial S}, \quad (6)
\]
\[
\mu_n(p,S,M_n) := \frac{\partial H}{\partial M_n}, \quad (6)
\]
\[
p(V,T,M_n) := -\frac{\partial G}{\partial V}, \quad S(V,T,M_n) := -\frac{\partial G}{\partial T}, \quad (7)
\]
\[
\mu_n(V,T,M_n) := \frac{\partial G}{\partial M_n}.
\]

\(^5\)This presentation is slightly different from the standard one, which would work in terms of component molar quantities \( N_n \), number of particles \( N_0 \), which are related to mass by \( M_n = m_n N_n = m_n N_0 (N_0)^{1/n} \), through the molar mass \( m_n \) and the Avogadro constant \( N_0 \).

\(^4\)Relaxing the single temperature approximation is possible, but leads to significant increases in complexity. For an example of this in moist atmospheric dynamics, see Bannon (2002).
Note that a given conjugate variable has multiple expressions: for example, we have \( p(V, T, M_n) \) and \( p(V, S, M_n) \). These are not in fact different quantities; they are just alternative ways of expressing the same quantity in terms of different variables.

Using Equations 4–7 plus the total differential, the fundamental thermodynamic identities for \( U(V, S, M_n) \), \( H(p, S, M_n) \), \( G(p, T, M_n) \), and \( F(V, T, M_n) \) are

\[
dU = -pdV + TdS + \sum_n \mu_n dM_n, \tag{8}
\]

\[
dH = Vdp + TdS + \sum_n \mu_n dM_n, \tag{9}
\]

\[
dG = Vdp - SdT + \sum_n \mu_n dM_n, \tag{10}
\]

\[
dF = -pdV - SdT + \sum_n \mu_n dM_n. \tag{11}
\]

Utilizing Equations 8–11 along with Euler’s homogeneous function theorem gives expressions for the thermodynamic potentials (up to a constant) as

\[
U = -pV + TS + \sum_n \mu_n M_n, \tag{12}
\]

\[
H = TS + \sum_n \mu_n M_n, \tag{13}
\]

\[
G = \sum_n \mu_n M_n, \tag{14}
\]

\[
F = -pV + \sum_n \mu_n M_n. \tag{15}
\]

In particular, this shows that the chemical potentials \( \mu_n \) are just the partial Gibbs free energies. Finally, combining Equations 8–11 and 12–15 gives the Gibbs–Duhem relationship,

\[
0 = -Vdp + SdT + \sum_n M_n d\mu_n. \tag{16}
\]

This shows that the intensive quantities are not all independent, and leads to the Gibbs phase rule.

### 2.2 Specific thermodynamic potentials

In atmospheric fluid dynamics, it is common to work in terms of specific quantities (quantities per unit mass) rather than extensive quantities. In doing so, we introduce the specific volume \( \alpha = V/M \), specific entropy \( \eta = S/M \), and specific component concentration \( q_n = M_n/M \), where \( M = \sum_n M_n \) is the total mass. Finally, we consider the specific internal energy \( u(\alpha, \eta, q_n) \), specific enthalpy \( h(p, \eta, q_n) \), specific Gibbs free energy \( g(p, T, q_n) \), and specific Helmholtz free energy \( f(\alpha, T, q_n) \). These can be related to \( U(V, S, M_n) \), \( H(p, S, M_n) \), \( G(p, T, M_n) \), and \( F(V, T, M_n) \) through

\[
U = Mu \left( \frac{V}{M}, \frac{S}{M}, M_n \right), \quad H = Mh \left( p, \frac{S}{M}, M_n \right), \tag{17}
\]

\[
G = Mg \left( p, T, \frac{M_n}{M} \right), \quad F = Mf \left( \frac{V}{M}, T, \frac{M_n}{M} \right). \tag{18}
\]

**Remark 2.** Given specific variables \( \alpha, \eta, \) and \( q_n \), it is only possible to determine \( U, H, G, \) and \( F \) up to a constant multiplier, since \( M \) cannot be obtained from these purely specific quantities. However, the partial derivatives of the thermodynamic potentials are what determines the thermodynamics of a system, and therefore this is not an impediment to use of specific thermodynamic potentials \( u, h, g, \) and \( f \) instead of \( U, H, G, \) and \( F \).

Exactly as before, the specific thermodynamic potentials are related through Legendre transforms as

\[
h = u + pa, \tag{18}
\]

\[
g = u + pa - \eta T, \tag{19}
\]

\[
f = u - \eta T. \tag{20}
\]

Using Equations 4–7 and 17 and the chain rule, it is not difficult to show that

\[
p(\alpha, \eta, q_n) = -\frac{\partial u}{\partial \alpha}, \quad T(\alpha, \eta, q_n) = \frac{\partial u}{\partial \eta}, \tag{21}
\]

\[
\alpha(p, \eta, q_n) = \frac{\partial h}{\partial p}, \quad T(p, \eta, q_n) = \frac{\partial h}{\partial \eta}, \tag{22}
\]

\[
\alpha(p, T, q_n) = \frac{\partial g}{\partial p}, \quad \eta(p, T, q_n) = -\frac{\partial g}{\partial T}, \tag{23}
\]

\[
p(\alpha, T, q_n) = -\frac{\partial f}{\partial \alpha}, \quad \eta(\alpha, T, q_n) = -\frac{\partial f}{\partial T}. \tag{24}
\]

However, the dependence on \( M_n \) (through \( M \)) leads to somewhat complicated expressions for \( \mu_n \) in terms of \( \partial x/\partial q_n \), and that \( \mu_n \neq \partial x/\partial q_n \), for any of \( x \in \{u, h, g, f\} \). These expressions are deferred to Appendix E.
Remark 3. In the atmospheric dynamics literature, Equations 21–24 are themselves often referred to as the equation of state. For example, the expression of $p$ in terms of $a$, $T$, and $q_n$ for a single-component perfect ideal gas is $pa = RT$. However, this expression itself does not contain sufficient information to determine the thermodynamics completely: only the thermodynamic potentials written in terms of their natural variables do. As an example, both the constant-$x$ and unapproximated fluids from Sections 3 and 4.1 have $pa = R^*T$, despite being distinct thermodynamic systems with different behaviour. Additionally, just the potentials themselves are not sufficient: for example, the internal energy for a single-component perfect ideal gas can be written as $u = C_vT$, but this is not in terms of natural variables and therefore does not have sufficient information to determine the thermodynamics completely.

Using Equations 4–7 plus 17, analogues of the fundamental thermodynamic identities for $u(a, \eta, q_n)$, $h(p, \eta, q_n)$, $g(p, T, q_n)$, and $f(\alpha, T, q_n)$ are

\[
du = -p\,da + T\,d\eta + \sum_n \mu_n dq_n, \tag{25}
\]

\[
dh = adp + Td\eta + \sum_n \mu_n dq_n, \tag{26}
\]

\[
dg = adp - \eta dT + \sum_n \mu_n dq_n, \tag{27}
\]

\[
df = -p\,da - \eta dT + \sum_n \mu_n dq_n. \tag{28}
\]

Combining Equations 12–15 and 17 gives expressions for the specific thermodynamic potentials (up to a constant) of form

\[
u = -pa + T\eta + \sum_n \mu_n q_n, \tag{29}
\]

\[
h = T\eta + \sum_n \mu_n q_n, \tag{30}
\]

\[
g = \sum_n \mu_n q_n, \tag{31}
\]

\[
f = -pa + \sum_n \mu_n q_n. \tag{32}
\]

As before, the chemical potentials $\mu_n$ are just the partial Gibbs free energies. Combining Equations 25–28 and 29–32 gives the specific form of the Gibbs–Duhem relationship:

\[
0 = -adp + \eta dT + \sum_n q_n d\mu_n, \tag{33}
\]

again showing not all the intensive quantities are independent.

### 2.3 Entropic variables

Instead of using specific entropy $\eta$, it is also possible to use an arbitrary (invertible) function of specific entropy and concentrations: a specific entropic variable $\chi = \chi(\eta, q_n)$. Entropic variables such as potential temperature and potential enthalpy are widely used in atmospheric and oceanic dynamics for two main reasons: in the case of reversible dynamics, they remain advected quantities (since specific entropy and concentrations are advected quantities in this case); and, for certain thermodynamic potentials, a careful choice of entropic variable gives much simpler expressions than specific entropy. Some examples of this are provided in Sections 3 and 4.

We introduce the extensive entropic variable $\Xi = \mathcal{M}_\chi$, and note that $S$ can be written in terms of $\Xi$ and $M_n$ (by inverting $\chi(\eta, q_n)$ to obtain $\eta(\chi, q_n)$) as

\[
S = M\eta \left( \frac{\Xi}{\mathcal{M}} \frac{M_n}{\mathcal{M}} \right). \tag{34}
\]

Now consider $U$ and $H$ as functions of $\Xi$ instead of $S$, denoted with a $\mathcal{V}$ in this section and Appendix E only:

\[
U'(V, \Xi, M_n) = U \left( V, M\eta \left( \frac{\Xi}{\mathcal{M}} \frac{M_n}{\mathcal{M}} \right), M_n \right),
\]

\[
H'(p, \Xi, M_n) = H \left( p, M\eta \left( \frac{\Xi}{\mathcal{M}} \frac{M_n}{\mathcal{M}} \right), M_n \right). \tag{35}
\]

Doing so and using the chain rule on partial derivatives yields

\[
\frac{\partial U'}{\partial V} = \frac{\partial U}{\partial V} = -p, \quad \frac{\partial U'}{\partial \Xi} = \frac{\partial U}{\partial S} \frac{\partial S}{\partial \Xi} = T \frac{\partial \eta}{\partial \Xi} = \lambda, \tag{36}
\]

\[
\frac{\partial H'}{\partial p} = \frac{\partial H}{\partial p} = \alpha, \quad \frac{\partial H'}{\partial \Xi} = \frac{\partial H}{\partial S} \frac{\partial S}{\partial \Xi} = T \frac{\partial \eta}{\partial \Xi} = \lambda, \tag{37}
\]

where $\lambda = T(\partial \eta/\partial \Xi)$ is the generalized temperature, along with complicated expressions for the generalized chemical...
potential,
\[ \xi_n = \frac{\partial U'}{\partial M_n} = \frac{\partial H'}{\partial M_n}, \]
given in Appendix E. The fundamental thermodynamic identities for internal energy \( U'(V, \Xi, M_n) \) and enthalpy \( H'(p, \Xi, M_n) \) can therefore be written as
\[
dU' = -pdV + \lambda d\Xi + \sum_n \xi_n dM_n, \tag{38}
\]
\[
dH' = Vdp + \lambda d\Xi + \sum_n \xi_n dM_n. \tag{39}
\]
In other words, we have replaced the conjugate pairs \((S, T)\) and \((M_n, \mu_n)\) with \((\Xi, \lambda)\) and \((M_n, \xi_n)\). Finally, we have expressions for \( U' \) and \( H' \) (up to a constant):
\[
U' = -pV + \lambda \Xi + \sum_n \xi_n M_n, \tag{40}
\]
\[
H' = \lambda \Xi + \sum_n \xi_n M_n, \tag{41}
\]
and a Gibbs–Duhem type relationship,
\[
0 = -Vdp + \Xi d\lambda + \sum_n M_n d\xi_n. \tag{42}
\]
Using specific thermodynamic potentials \( u(\alpha, \eta, q_n) = u(\alpha, \eta(\chi, q_n), q_n), \) \( q_n = u'(\alpha, \chi, q_n) \) and \( h(p, \eta, q_n) = h(p, \eta(\chi, q_n), q_n) = h'(p, \chi, q_n), \) we have the expressions
\[
U'(V, \Xi, M_n) = Mu' \left( \frac{V}{M}, \frac{\Xi}{M}, \frac{M_n}{M} \right), \tag{43}
\]
\[
H'(p, \Xi, M_n) = Mh' \left( p, \frac{\Xi}{M}, \frac{M_n}{M} \right), \tag{44}
\]
which give
\[
p(\alpha, \chi, q_n) = \frac{\partial u'}{\partial \alpha}(\alpha, \chi, q_n), \tag{44}
\]
\[
\lambda(\alpha, \chi, q_n) = \frac{\partial u'}{\partial \chi}(\alpha, \chi, q_n)
= T(\alpha, \eta(\chi, q_n), q_n) \eta_{\chi}(\chi, q_n), \tag{45}
\]
\[
\alpha(p, \chi, q_n) = \frac{\partial h'}{\partial p}(p, \chi, q_n), \tag{46}
\]
\[
\lambda(p, \chi, q_n) = \frac{\partial h'}{\partial \chi}(p, \chi, q_n)
= T(p, \eta(\chi, q_n), q_n) \eta_{\chi}(\chi, q_n). \tag{47}
\]
for the conjugate variables. However, as is the case for \( \mu_n, \xi_n \neq \partial x'/\partial q_n \) for \( x' \in (u', h'). \) Instead, a complicated relationship between \( \xi_n \) and \( \partial x'/\partial q_n \) holds, discussed in Appendix E. The fundamental thermodynamic identities can be written as
\[
du' = -pd\alpha + \lambda d\chi + \sum_n \xi_n dq_n, \tag{48}
\]
\[
dh' = adp + \lambda d\chi + \sum_n \xi_n dq_n. \tag{49}
\]
Finally, we have expressions for \( u' \) and \( h' \) (up to a constant) of form
\[
u' = -p\alpha + \lambda \chi + \sum_n \xi_n q_n, \tag{50}
\]
\[
\lambda = \lambda \chi + \sum_n \xi_n q_n. \tag{51}
\]
and a specific Gibbs–Duhem type relationship,
\[
0 = -adp + \chi d\lambda + \sum_n q_n d\xi_n. \tag{52}
\]

3 | UNAPPROXIMATED THERMODYNAMICS OF MOIST AIR

We will now specialize from the general development of equilibrium thermodynamics in Section 2 to the case of moist, cloudy air: a mixture of dry air and the three phases of water: water vapour, (cloud) liquid water, and (cloud) ice. The concentrations of these four components are denoted by \( q_d, q_v, q_l, \) and \( q_i, \) respectively. The gaseous components \( q_d \) and \( q_v \) are assumed to be perfect ideal gases with temperature-independent (i.e., constant) heat capacities at constant volume \( C_{vd} \) and \( C_{vv} \) and at constant pressure \( C_{pd} \) and \( C_{pv} \). The condensed components \( q_l \) and \( q_i \) are assumed to be incompressible, with temperature-independent heat capacities \( C_l \) and \( C_i, \) and to appear as pure substances, and we neglect the volume occupied by the condensates.\(^7\) Additionally, we do not assume any equilibrium between phases, so we can capture supersaturation and other out-of-equilibrium situations.

**Remark 4.** Following Thuburn (2017) and Staniforth and White (2019), we could instead predict only total water

\(^7\)Condensate volume can be incorporated without too much additional effort, as done in Pelkowski and Frisius (2011), Thuburn (2017), and Staniforth and White (2019). A more sophisticated treatment of condensates that takes into account the behaviour of droplet and other hydrometeor populations is well beyond the scope of this article, and where the assumption of LTE begins to break down.
where \( C^p = q_d C_{vd} + q_v C_{vv} + q_l C_l + q_i C_i \), \( C^r = q_d C_{pd} + q_v C_{pv} + q_l C_l + q_i C_i \), and \( R^* = q_d R_d + q_v R_v \). A detailed derivation for these is found in Appendix A, where the meaning of all symbols (including the latent heat terms \( L_v \) and \( L_i \)) is explained, and the relationship to the potentials from Thuburn (2017, 2018) and Staniforth and White (2019) is discussed.

From Equations 53–56, the associated conjugate variables \( p, \alpha, T, \) and \( \eta \) are given by

\[
p(\alpha, \eta, q_d, q_v, q_i, q_i) = -\frac{\partial u}{\partial \alpha} = \frac{R^*}{\alpha T_r} \exp \left( \frac{\eta - \eta_0}{C_v^p} \right) \left( \frac{\alpha}{q_d \sigma_{ad}} \right) \left( \frac{\alpha}{q_v \alpha_{av}} \right) \frac{q_{dL}}{T_r}, \tag{57}
\]

\[
T(\alpha, \eta, q_d, q_v, q_i, q_i) = \frac{\partial u}{\partial \eta} = T_r \exp \left( \frac{\eta - \eta_0}{C_v^p} \right) \left( \frac{\alpha}{q_d \sigma_{ad}} \right) \left( \frac{\alpha}{q_v \alpha_{av}} \right) \frac{q_{dL}}{T_r}, \tag{58}
\]

\[
a(\alpha, \eta, q_d, q_v, q_i, q_i) = \frac{\partial h}{\partial p} = \frac{R^* T_r}{p} \exp \left( \frac{\eta - \eta_0}{C_v^p} \right) \left( \frac{q_d R_d p}{R^* p_{vd}} \right) \left( \frac{q_v R_v p}{R^* p_{tv}} \right) \frac{q_{dL}}{T_r}, \tag{59}
\]

Under these assumptions, the full expressions for the various specific thermodynamic potentials are

\[
u(\alpha, \eta, q_d, q_v, q_i, q_i) = C^p T_r \exp \left( \frac{\eta - \eta_0}{C_v^p} \right) \left( \frac{\alpha}{q_d \sigma_{ad}} \right) \left( \frac{\alpha}{q_v \alpha_{av}} \right) \frac{q_{dL}}{T_r} \tag{53}
\]

\[
h(\alpha, \eta, q_d, q_v, q_i, q_i) = C^p T_r \exp \left( \frac{\eta - \eta_0}{C_v^p} \right) \left( \frac{q_d R_d p}{R^* p_{vd}} \right) \left( \frac{q_v R_v p}{R^* p_{tv}} \right) \frac{q_{dL}}{T_r} \tag{54}
\]

\[
g(\alpha, \eta, q_d, q_v, q_i, q_i) = T \left( C^p T_r + q_d R_d \ln \frac{T}{T_r} + q_v \alpha_{av} + q_l \alpha_l + q_i \alpha_i \right) + q_d R_d \ln \frac{q_d R_d}{R^* p_{vd}} + q_v R_v \ln \frac{q_v R_v}{R^* p_{tv}} \tag{55}
\]

\[
f(\alpha, \eta, q_d, q_v, q_i, q_i) = T \left( C^p T_r - q_d R_d \ln \frac{q_d \sigma_{ad}}{\alpha} + q_v R_v \ln \frac{q_v \alpha_{av}}{\alpha} \right) + q_d R_d \ln \frac{q_{dL}}{T_r} + q_v \alpha_{av} \ln \frac{q_v \alpha_{av}}{\alpha} \tag{56}
\]
Note that there are multiple expressions for various conjugate variables, such as \( p(α, η, q_δ, q_v, q_i, q_l) \) and \( p(α, T, q_δ, q_v, q_i, q_l) \), in terms of different variables. From Equations 57–64 the relationship \( pα = R^*T \) is immediately apparent, along with expressions for \( u \) and \( h \) in terms of \( T \):

\[
\begin{align*}
    u &= C^*_v(T - T_i) - q_vR_vT_i + q_v(L_{vr} + L_{ft}) + q_iL_{ft}, \\
    h &= C^*_v(T - T_i) + q_δR_dT_i + q_v(L_{vr} + L_{ft}) + q_iL_{ft}.
\end{align*}
\]  

(65)  

(66)

The expressions for \( μ_ν \) are quite complicated and are given in Appendix E.1.

### 3.1 Potential temperature

The most common entropic variable encountered in atmospheric dynamics is the potential temperature \( θ \), which can be defined in a general way (Zdunkowski and Bott, 2004), independent of the specific thermodynamic potential used, either explicitly using Equation 60 as

\[
\theta(η, q_δ, q_v, q_i, q_l) = T(p_*, η, q_δ, q_v, q_i, q_l)
\]

(67)

or implicitly using Equation 62 as

\[
η(p, T, q_δ, q_v, q_i, q_l) = η(p_*, θ, q_δ, q_v, q_i, q_l).
\]

(68)

In both expressions, we have simply replaced actual pressure \( p \) by some reference pressure \( p_\)\. In other words, potential temperature is the temperature of an air parcel if it is moved adiabatically (at constant entropy and concentrations) from its actual pressure to some reference pressure. This is simply a specific instance of the general approach to a potential quantity discussed in Appendix B. The associated conjugate variable (generalized temperature) for \( θ \) is the Exner pressure \( Π \).

Using Equation 62, this gives

\[
η(θ, q_δ, q_v, q_i, q_l) = C^*_p\eta - R^*\ln\frac{T}{T_i} - R^*\ln\frac{p_i}{p} - q_δR_d\frac{ln\frac{q_dR_d}{P_d}}{\eta} - q_vR_v\frac{ln\frac{q_vR_v}{P_{rv}}}{\eta} + η, 
\]

(69)

and therefore (using Equation 60)

\[
\begin{align*}
    \theta(η, q_δ, q_v, q_i, q_l) &= T_i \exp\left(\frac{η}{C^*_p}\right) \left(\frac{p_i}{R^*}\right)^{R^* \frac{q_dR_d}{P_d}} \left(\frac{q_vR_v}{P_{rv}}\right)^{\frac{R^*}{\eta}} \\
    &= T_i \exp\left(\frac{η - η_i}{C^*_p}\right) \left(\frac{p_i}{R^*}\right)^{R^* \frac{q_dR_d}{P_d}} \left(\frac{q_vR_v}{P_{rv}}\right)^{\frac{R^*}{\eta}},
\end{align*}
\]

(70)

where \( \kappa^* = \frac{R^*}{C^*_p} \).

The internal energy \( u \) (Equation 53) and enthalpy \( h \) (Equation 54) in terms of \( θ \) are given by

\[
\begin{align*}
    u(α, θ, q_δ, q_v, q_i, q_l) &= C^*_v(θ)^{R^* \frac{q_dR_d}{αP_d}} \\
    &= C^*_vT_i - q_vR_vT_i + q_v(L_{vr} + L_{ft}) + q_iL_{ft}, \\
    h(p, θ, q_δ, q_v, q_i, q_l) &= C^*_v\theta \left(\frac{p}{p_i}\right)^{R^* \frac{P_{rv}}{P_d}} - C^*_vT_i + q_dR_dT_i \\
    &+ q_v(L_{vr} + L_{ft}) + q_iL_{ft},
\end{align*}
\]

(71)  

(72)

where \( \gamma^* = C^*_p/R^* \) and \( \delta^* = R^*/C^*_v \) and we have \( \gamma^* - 1 = \delta^* \) and \( \kappa^* \gamma^* = \delta^* \). The expressions in Equations 71 and 72 are significantly simpler than those of Equations 53 and 54, and lead to simpler expressions for the conjugate variables \( p, Π, \) and \( α \) (one motivation for using an entropic variable), which are

\[
\begin{align*}
    p(α, θ, q_δ, q_v, q_i, q_l) &= \frac{∂u}{∂α} = p_i \left(\frac{R^* \theta}{αP_d}\right)^{R^*}, \\
    Π(α, θ, q_δ, q_v, q_i, q_l) &= \frac{∂u}{∂θ} = C^*_p R^* \left\{\frac{p}{P_d}\right\}^{R^*}, \\
    α(α, θ, q_δ, q_v, q_i, q_l) &= \frac{∂h}{∂α} = R^* \left\{\frac{p}{P_d}\right\}^{R^*}.
\end{align*}
\]

(73)  

(74)  

(75)  

(76)

From Equations 73–76, we have \( Πθ = C^*_pT \) and \( pα = \kappa^* Πθ \). The Exner pressure \( Π \) here differs slightly from the form \( Π = (p/p_i)^{\kappa^*} \) often seen in the literature. We prefer the form above, since it is the conjugate variable to \( θ \), defined through \( Π = ∂U/∂θ \) from \( U(α, θ, q_δ) \). We also have expressions for \( u \) and \( h \) in terms of \( θ \) and \( Π \):

\[
\begin{align*}
    u &= C^*_p Πθ - q_vR_vT_i + q_v(L_{vr} + L_{ft}) + q_iL_{ft}, \\
    h &= Π - C^*_pT_i + q_dR_dT_i + q_v(L_{vr} + L_{ft}) + q_iL_{ft}.
\end{align*}
\]

(77)  

(78)

The expressions for generalized chemical potentials \( ξ_n \) are quite complicated, and are given in Appendix E.1.
4 | APPROXIMATED THERMODYNAMICS OF MOIST AIR

We now consider two widely used approximations to the thermodynamic potentials in Equations 53–56. Both involve modifying the heat capacities \( C_v \) and \( C_p \) to remove some of the dependence on water species \( q_v, q_i, q_l \), and therefore simplify the conjugate variables and other expressions.

4.1 | Constant-\( \kappa \) system

To obtain the constant-\( \kappa \) system, we make the substitutions

\[
C_v^* \rightarrow C_{vd} \frac{R^*}{R_d}, \quad C_p^* \rightarrow C_{pd} \frac{R^*}{R_d}
\]

in the thermodynamic potentials (Equations 53–56), but retain \( R^* \). This is equivalent to assuming that \( \kappa^* = \kappa_d \), hence the name “constant \( \kappa \)”. In other words, it amounts to the replacement of \( C_v \) with \( C_{vd}R_c/R_d \) and \( C_p \) with \( C_{pd}R_c/R_d \), along with the neglect of \( C_1 \) and \( C_i \). It is interesting to note that, even with these replacements, we still have relationships between heat capacities at constant pressure and constant volume for both water vapour and moist air, which are given by \( (C_{vd}R_c/R_d) + R_c = C_{pd}R_c/R_d \).

After some algebra, using Equation 79 in Equations 53–56 gives

\[
\begin{align*}
&f(\alpha, T, q_d, q_v, q_i, q_l) \\
&= T \left( -C_{vd} \frac{R^*}{R_d} \ln \frac{T}{T_i} + q_d R_d \ln \frac{q_d R_d}{\alpha} + q_v R_v \ln \frac{q_v R_v}{\alpha} - \eta_i \right) \\
&\quad - C_{vd} \frac{R^*}{R_d} (T - T_i) - q_v R_v T_i + q_v (L_v + L_i) + q_i L_i.
\end{align*}
\]

The associated conjugate variables \( p, \alpha, T \) and \( \eta \) for Equations 80–83 are given by

\[
\begin{align*}
p(\alpha, \eta, q_d, q_v, q_i, q_l) &= \frac{\partial u}{\partial \alpha} \\
 &= \frac{R^*}{\alpha} T \exp \left( \frac{\eta - \eta_i}{C_{vd} \frac{R^*}{R_d}} \left( \frac{\alpha}{q_d R_d} \right) \frac{q_d R_d}{C_{vd} R_d} \left( \frac{\alpha}{q_v R_v} \right) \frac{q_v R_v}{C_{vd} R_d} \right),
\end{align*}
\]

\[
\begin{align*}
T(\alpha, \eta, q_d, q_v, q_i, q_l) &= \frac{\partial u}{\partial \eta} \\
 &= T \exp \left( \frac{\eta - \eta_i}{C_{vd} \frac{R^*}{R_d}} \left( \frac{\alpha}{q_d R_d} \right) \frac{q_d R_d}{C_{vd} R_d} \left( \frac{\alpha}{q_v R_v} \right) \frac{q_v R_v}{C_{vd} R_d} \right),
\end{align*}
\]

\[
\begin{align*}
\alpha(p, \eta, q_d, q_v, q_i, q_l) &= \frac{\partial h}{\partial p} \\
 &= \frac{R^*}{p} T \exp \left( \frac{\eta - \eta_i}{C_{pd} \frac{R^*}{R_d}} \left( \frac{q_d R_d p}{R^* p_d} \right) \frac{q_d R_d p}{C_{pd} R_d} \left( \frac{q_v R_v p}{R^* p_v} \right) \frac{q_v R_v p}{C_{pd} R_d} \right),
\end{align*}
\]

\[
\begin{align*}
T(p, \eta, q_d, q_v, q_i, q_l) &= \frac{\partial h}{\partial \eta} \\
 &= T \exp \left( \frac{\eta - \eta_i}{C_{pd} \frac{R^*}{R_d}} \left( \frac{q_d R_d p}{R^* p_d} \right) \frac{q_d R_d p}{C_{pd} R_d} \left( \frac{q_v R_v p}{R^* p_v} \right) \frac{q_v R_v p}{C_{pd} R_d} \right),
\end{align*}
\]

\[
\begin{align*}
\alpha(p, T, q_d, q_v, q_i, q_l) &= \frac{\partial g}{\partial p} = \frac{R^* T}{p}, \\
\eta(p, T, q_d, q_v, q_i, q_l) &= -\frac{\partial g}{\partial T}.
\end{align*}
\]
Potential temperature of obliquity is defined as $p(a, T, q\alpha, q_v, q_i, q_l) = \frac{\partial f}{\partial \alpha} = R^* T \ln \frac{R^*}{\alpha}$, by replacing $R^* T$ according to $\alpha$.

Remark 6. As discussed in Section 2, we see that $p\alpha = R^* T$ still holds. This is a good demonstration that these sorts of expression (often referred to as equations of state in the atmospheric dynamics literature) do not contain a complete description of the thermodynamics, since both unapproximated and constant-$\kappa$ systems give the same expression, despite having different thermodynamics.

Additionally, we have expressions for $u$ and $h$ in terms of $T$:

$$u = C_{vd} R^* \frac{T}{T_r} - q_v R_v T_r + q_v (L_{vr} + L_{fr}) + q_i L_{fr},$$

$$h = C_{pd} R^* \frac{T}{T_r} + q_d R_d T_r + q_v (L_{vr} + L_{fr}) + q_i L_{fr}.$$  

The expressions for $\mu_n$ are quite complicated, and are given in Appendix E.2.

### 4.1.1 Potential temperature

As for the unapproximated system, we define potential temperature $\theta$ either explicitly using Equation 87 or implicitly using Equation 89 by replacing $p$ with $p_i$, to obtain

$$\eta(\theta, q\alpha, q_v, q_i, q_l) = C_{pd} R^* \frac{R^*}{R_d} \theta \ln \frac{R^*}{T_r} - R^* \ln \frac{R^*}{P} - q_d R_d \ln \frac{q_d R_d}{p_{vd}} - q_v R_v \ln \frac{q_v R_v}{p_{vd}} + \eta,$$

$$= T_r \exp \left( \frac{\eta - \eta_T}{C_{pd} R^* / R_d} \right) \left( \frac{p_i}{p_{vd}} \right)^{\delta_d} \left( \frac{q_d R_d}{p_{vd}} \right)^{\delta_d} \left( \frac{q_v R_v}{p_{vd}} \right)^{\delta_d}.$$  

Now, writing $u$ (Equation 80) and $h$ (Equation 81) in terms of $\theta$, we obtain

$$u(\theta, q\alpha, q_v, q_i, q_l) = C_{vd} R^* \theta \left( \frac{P}{p} \right)^{k_d} \left( \frac{R^* \theta}{\alpha p} \right)^{\delta_d} - C_{vd} R^* T_r - q_v R_v T_r + q_v (L_{vr} + L_{fr}) + q_i L_{fr},$$

$$h(\theta, q\alpha, q_v, q_i, q_l) = C_{pd} R^* \theta \left( \frac{P}{p} \right)^{k_d} - C_{pd} R^* T_r + q_d R_d T_r + q_v (L_{vr} + L_{fr}) + q_i L_{fr}.$$  

The conjugate variables $p$, $\Pi$, and $\alpha$ for Equations 96 and 97 are

$$p(\alpha, \theta, q\alpha, q_v, q_i, q_l) = -\frac{\partial u}{\partial \alpha} = p_i \left( \frac{R^* \theta}{\alpha p} \right)^{\gamma_d},$$

$$\Pi(\alpha, \theta, q\alpha, q_v, q_i, q_l) = \frac{\partial u}{\partial \theta} = C_{pd} R^* \left( \frac{R^* \theta}{\alpha p} \right)^{\delta_d},$$

$$\alpha(p, \theta, q\alpha, q_v, q_i, q_l) = \frac{\partial h}{\partial p} = R^* \theta \left( \frac{P}{p} \right)^{k_d},$$

$$\Pi(p, \theta, q\alpha, q_v, q_i, q_l) = \frac{\partial h}{\partial \theta} = C_{pd} R^* \left( \frac{P}{p} \right)^{k_d}.$$  

Although reduced compared with using $\eta$, there is still a nontrivial dependence on $q_v$, $q_i$, and $q_l$ in both the thermodynamic potentials and the conjugate variables, through the $R^*$ terms. From Equations 98–101, we have $p\alpha = k_d \Pi \theta$ and $\Pi \theta = (R^*/k_d) T$. These two expressions also yield $\theta = T(p_i/p)^{k_d}$. Expressions for $u$ and $h$ in terms of $\theta$ and $\Pi$ are

$$u = C_{vd} \Pi \theta - C_{vd} R^* T_r - q_v R_v T_r + q_v (L_{vr} + L_{fr}) + q_i L_{fr},$$

$$h = \theta \Pi - C_{pd} R^* T_r + q_d R_d T_r + q_v (L_{vr} + L_{fr}) + q_i L_{fr}.$$  

The expressions for \( \xi_n \) are quite complicated, and are given in Appendix E.2.

4.1.2 Virtual potential temperature

Although using potential temperature simplifies the expressions for the thermodynamic potentials and conjugate variables, there is still a nontrivial dependence on the moisture variables \( q_v, q_i, \) and \( q_l \). However, it is known from previous work (Taylor et al., 2020) that for the constant-\( \kappa \) approximation there must exist a choice of entropic variable that removes this dependence. This turns out to be the virtual potential temperature \( \theta_v \) (see Appendix B for more discussion of virtual quantities), defined through

\[
\theta_v(\eta, q_d, q_v, q_i, q_l) = T_i \exp \left( \frac{\eta - \eta_0}{\gamma_d} \right) \left( \frac{q_d}{p_i} \right) \left( \frac{q_v}{p_i} \right) \left( \frac{q_i}{p_i} \right) \left( \frac{q_l}{p_i} \right) \tag{104} \]

\[
\eta(\theta_v, q_d, q_v, q_i, q_l) = C_{pd} \frac{R}{\gamma_d} \ln \frac{\theta_v}{T_i} R^* \ln p_T - q_d R_d \ln \frac{q_d}{p_i} + q_v \frac{R}{\gamma_d} (C_{pd} \ln R_d - C_{vd} \ln R^*) \tag{105} \]

This is simply the expression for \( \theta_v \) in terms of \( p, \eta, \) and \( q_n \), which is independent of \( p \) for the constant-\( \kappa \) system (i.e., Equation B18), and therefore an entropic variable. The associated conjugate variable turns out to be, as might be expected, the virtual Exner pressure \( \Pi_v \).

Now writing \( u \) (Equation 80) and \( h \) (Equation 81) in terms of \( \theta_v \), we obtain

\[
u(\alpha, \theta_v, q_d, q_v, q_i, q_l) = C_{vd} (\theta_v)^\xi \left( \frac{R_d}{\alpha p_i} \right) \delta_d - C_{vd} \frac{R^*}{R_d} T_T - q_v R_v T_T + q_v (L_{vT} + L_{iT}) + q_i L_{iT}, \tag{106} \]

\[
h(p, \theta_v, q_d, q_v, q_i, q_l) = C_{pd} \theta_v \left( \frac{p}{p_i} \right) \kappa_i - C_{pd} \frac{R^*}{R_d} T_T + q_d R_d T_T + q_v (L_{vT} + L_{iT}) + q_i L_{iT} \tag{107} \]

Crucially, almost all of the dependence of \( U \) and \( H \) on \( q_d, q_v, q_i, q_l \) has been absorbed into \( \theta_v \), other than a trivial linear dependence that will affect only \( \xi_n \).

The conjugate variables \( p, \Pi_v, \) and \( \alpha \) for Equations 106 and 107 are

\[
p(\alpha, \theta_v, q_d, q_v, q_i, q_l) = -\frac{\partial u}{\partial \alpha} = p_t \left( \frac{R_d \theta_v}{\alpha p_t} \right)^\gamma_d \tag{108} \]

\[
\Pi_v(\alpha, \theta_v, q_d, q_v, q_i, q_l) = \frac{\partial u}{\partial \Pi_v} = C_{pd} \left( \frac{R_d \theta_v}{\alpha p_t} \right) \delta_d \tag{109} \]

\[
\alpha(p, \theta_v, q_d, q_v, q_i, q_l) = \frac{\partial h}{\partial p} = \frac{R_d \theta_v}{p_t} \left( \frac{p}{p_t} \right)^\kappa_d \tag{110} \]

\[
\Pi_v(p, \theta_v, q_d, q_v, q_i, q_l) = \frac{\partial h}{\partial \Pi_v} = C_{pd} \left( \frac{p}{p_t} \right)^\kappa_d \tag{111} \]

Due to the absorption of most of the dependence on \( q_d, q_v, q_i, q_l \) into \( \theta_v \), the expressions for \( p, \Pi_v, \) and \( \alpha \) are independent of \( q_d, q_v, q_i, q_l \). This is extremely useful, because, with an appropriate choice of predicted variables, this means that the adiabatic (i.e., reversible) dynamics of the water species will decouple from the rest of the dynamics. This permits utilization of different spatial and temporal numerics for the two sets of variables. An example of this for the HOMME-NH dynamical core is found in Taylor et al. (2020).

From Equations 108–111, we have \( p \alpha = \kappa_d \Pi_v \theta_v \) and \( \Pi_v \theta_v = (R^*/\kappa_d) T \). The former is usually taken as the starting point for the definition of \( \theta_v \). These two expressions also yield \( \theta_v = (R^*/R_d) T(p_t/p)^{\xi_d} = T_v(p_t/p)^{\xi_d} \) for virtual temperature \( T_v = T(R^*/R_d) \), which is slightly different from the naively expected \( \theta_v = T(p_t/p)^{\xi_d} \). Expressions for \( u \) and \( h \) in terms of \( \theta_v \) and \( \Pi_v \) are

\[
u = \frac{C_{vd}}{C_{pd}} \Pi_v \theta_v - C_{vd} \frac{R^*}{R_d} T_T - q_v R_v T_T + q_v (L_{vT} + L_{iT}) + q_i L_{iT}, \tag{112} \]

\[
h = \theta_v \Pi_v - C_{pd} \frac{R^*}{R_d} T_T + q_d R_d T_T + q_v (L_{vT} + L_{iT}) + q_i L_{iT} \tag{113} \]

The expressions for \( \xi_n \) are quite complicated, and are given in Appendix E.2.

4.2 Dry heat capacities system

Another approximation often used is to assume that all of the heat capacities of the various species are the same (see Appendix C for a general definition of heat capacity), such as in Boville and Bretherton (2003). Usually
these are taken to be the heat capacity of dry air, although this is not required. We will retain the notation $C_{q_{vd}}$ and $C_{pd}$. To accomplish this, in the thermodynamic potentials (Equations 53–56), we make the substitution

$$C_{q_{vd}} \to C_{vd}, \quad C_{pd} \to C_{pd},$$

but retain $R^*$. In this case, we no longer have the relationship $C_v + R^* = C_p$, which leads to interesting artifacts when using potential temperature as an entropic variable.

This gives (after some algebra)

$$u(a, \eta, q_d, q_v, q_l, q_l) = C_{q_{vd}} T_r \exp \left( \frac{\eta - \eta_l}{C_{vd}} \left( \frac{\alpha}{q_d \alpha_{vd}} \right) - \frac{q_{vd}}{C_{vd}} \frac{\alpha}{q_v \alpha_{vd}} \right) - C_{vd} T_r - q_v R_v T_r + q_v (L_{vr} + L_{lf}) + q_l L_{lf},$$

$$h(p, \eta, q_d, q_v, q_l, q_l) = C_{pd} T_r \exp \left( \frac{\eta - \eta_l}{C_{pd}} \left( \frac{q_d R_d p}{R^* P_{pd}} \right) \frac{q_{vd}}{C_{vd}} \frac{q_v R_v p}{R^* P_{pd}} \right) - C_{pd} T_r + q_d R_d T_r + q_v (L_{vr} + L_{lf}) + q_l L_{lf},$$

$$g(p, T, q_d, q_v, q_l, q_l) = T \left( C_{pd} - C_{pd} \ln \frac{T}{T_r} + q_d R_d \ln \frac{q_d R_d p}{R^* P_{pd}} \right) + q_v R_v \ln \frac{q_v R_v p}{R^* P_{pd}} - \eta_l - C_{pd} T_r + q_d R_d T_r + q_v (L_{vr} + L_{lf}) + q_l L_{lf},$$

$$f(a, T, q_d, q_v, q_l, q_l) = T \left( C_{vd} - C_{vd} \ln \frac{T}{T_r} + q_d R_d \ln \frac{q_d \alpha_{vd}}{\alpha} \right) + q_v R_v \ln \frac{q_v \alpha_{vd}}{\alpha} - \eta_l - C_{vd} T_r - q_v R_v T_r + q_v (L_{vr} + L_{lf}) + q_l L_{lf}.$$ 

The associated conjugate variables $p, \alpha, T,$ and $\eta$ for Equations 115–118 are given by

$$p(a, \eta, q_d, q_v, q_l, q_l) = -\frac{\partial u}{\partial \alpha} = \frac{R^*}{T_r} \exp \left( \frac{\eta - \eta_l}{C_{vd}} \left( \frac{\alpha}{q_d \alpha_{vd}} \right) - \frac{q_{vd}}{C_{vd}} \frac{\alpha}{q_v \alpha_{vd}} \right),$$

$$T(a, \eta, q_d, q_v, q_l, q_l) = \frac{\partial u}{\partial \eta} = \frac{T_r}{T} \exp \left( \frac{\eta - \eta_l}{C_{vd}} \left( \frac{\alpha}{q_d \alpha_{vd}} \right) - \frac{q_{vd}}{C_{vd}} \frac{\alpha}{q_v \alpha_{vd}} \right),$$

$$a(p, \eta, q_d, q_v, q_l, q_l) = \frac{\partial h}{\partial p} = \frac{R^*}{T_r} \exp \left( \frac{\eta - \eta_l}{C_{pd}} \left( \frac{q_d R_d p}{R^* P_{pd}} \right) \frac{q_{vd}}{C_{vd}} \frac{q_v R_v p}{R^* P_{pd}} \right),$$

$$\eta(p, T, q_d, q_v, q_l, q_l) = -\frac{\partial g}{\partial T} = \frac{C_{pd} \ln \frac{T}{T_r} - R^* \ln \frac{p}{R^*} - q_d R_d \ln \frac{q_d R_d}{P_{pd}} - q_v R_v \ln \frac{q_v R_v}{P_{pd}} - \eta_l}{T_r},$$

$$p(a, T, q_d, q_v, q_l, q_l) = -\frac{\partial f}{\partial a} = R^* \frac{T}{\alpha},$$

$$\eta(a, T, q_d, q_v, q_l, q_l) = -\frac{\partial f}{\partial T} = C_{vd} \ln \frac{T}{T_r} - q_d R_d \ln \frac{q_d \alpha_{vd}}{\alpha} - q_v R_v \ln \frac{q_v \alpha_{vd}}{\alpha} + \eta_l.$$ 

Again, from Equations 119–126 the relationship $pa = R^* T$ still holds, along with expressions for $u$ and $h$ in terms of $T$:

$$u = C_{vd} (T - T_r) - q_v R_v T_r + q_v (L_{vr} + L_{lf}) + q_l L_{lf},$$

$$h = C_{pd} (T - T_r) + q_d R_d T_r + q_v (L_{vr} + L_{lf}) + q_l L_{lf}.$$ 

The expressions for $\mu_\eta$ are quite complicated, and are given in Appendix E.4.
4.2.1 Potential temperature

As done for the previous two systems, we define potential temperature $\theta$ either explicitly using Equation 122 or implicitly using Equation 124 by replacing $p$ with $p_t$ to obtain

$$
\eta(\theta, q_d, q_v, q_l, q_i) = C_{pd} \ln \frac{\theta}{T_t} - R^* \ln \frac{P_t}{R^*} - q_d R_d \ln \frac{q_d R_d}{P_{pd}} - q_v R_v \ln \frac{q_v R_v}{P_{pv}} + \eta_i.
$$

$$
\theta(\eta, q_d, q_v, q_l, q_i) = T_t \exp \left( \frac{\eta - \eta_i}{C_{pd}} \right) \left( \frac{P_t}{R^*} \right)^{\frac{\eta_i}{C_{pd}}} \left( \frac{P_{pd}}{C_{pd}} \right)^{\frac{\eta - \eta_i}{C_{pd}}}.
$$

(129)

Now, writing $u$ (Equation 115) and $h$ (Equation 116) in terms of $\theta$, we obtain

$$
u(\alpha, \theta, q_d, q_v, q_l, q_i) = C_{vd} (\theta) \gamma_d \left( \frac{R^*}{\alpha p_t} \right)^{\frac{R^*}{\alpha p_t}} (T_t)^{\frac{R^* - R_d}{\alpha p_t}}

- C_{vd} T_t - q_v R_v T_t + q_v (L_{vt} + L_{fl}) + q_l L_{fl},
$$

(131)

$$
h(p, \theta, q_d, q_v, q_l, q_i) = C_{pd} \theta \left( \frac{p}{P_t} \right)^{\frac{R^*}{\alpha p_t}} - C_{pd} T_t

+ q_d R_d T_t + q_v (L_{vt} + L_{fl}) + q_l L_{fl}.
$$

(132)

The strange term $(T_t)^{R^* - R_d}/C_{vd}$ that appears in the $u$ equation is a consequence of the fact $C_v + R^* \neq C_p$.

The conjugate variables $p$, $\Pi$, and $\alpha$ for Equations 131 and 132 are

$$
p(\alpha, \theta, q_d, q_v, q_l, q_i) = -\frac{\partial u}{\partial \alpha} = \frac{R^*}{\alpha} (\theta) \gamma_d \left( \frac{R^* \theta}{\alpha p_t} \right)^{\frac{R^*}{\alpha p_t}} (T_t)^{\frac{R^* - R_d}{\alpha p_t}},
$$

(133)

$$
\Pi(\alpha, \theta, q_d, q_v, q_l, q_i) = \frac{\partial u}{\partial \theta} = C_{pd} (\theta) \gamma_d \left( \frac{R^* \theta}{\alpha p_t} \right)^{\frac{R^*}{\alpha p_t}} (T_t)^{\frac{R^* - R_d}{\alpha p_t}},
$$

(134)

$$
\alpha(p, \theta, q_d, q_v, q_l, q_i) = \frac{\partial h}{\partial p} = \frac{R^* \theta}{p} \left( \frac{p}{P_t} \right)^{\frac{R^*}{\alpha p_t}},
$$

(135)

$$
\Pi(p, \theta, q_d, q_v, q_l, q_i) = \frac{\partial h}{\partial \theta} = C_{pd} \left( \frac{p}{P_t} \right)^{\frac{R^*}{\alpha p_t}}.
$$

(136)

There is some simplification and reduction of the dependence on moisture variables, but $u$, $h$, and the associated conjugate variables still have nontrivial dependence through $R^*$. From Equations 133–136, we have $pa = (R^*/C_{pd}) \Pi \theta$ and $\Pi \theta = C_{pd} T_t$. These two expressions also yield $\theta = T(p_t/p)^{R^*/C_{pd}}$. Expressions for $u$ and $h$ in terms of $\theta$ and $\Pi$ are

$$
u = \frac{C_{vd}}{C_{pd}} \Pi \theta - C_{vd} T_t - q_d R_d T_t + q_v (L_{vt} + L_{fl}) + q_l L_{fl},
$$

(137)

$$
h = \theta \Pi - C_{pd} T_t + q_d R_d T_t + q_v (L_{vt} + L_{fl}) + q_l L_{fl}.
$$

(138)

The expressions for $\xi_a$ are quite complicated, and are given in Appendix E.4.

4.3 Quantifying errors

Detailed discussion about both inconsistency and approximation errors in thermodynamics for coupled climate models can be found in Lauritzen et al. (2022). In this section we provide only a few small examples. Specifically, we estimate discrepancies between the dry heat capacities, constant-$\kappa$, and unapproximated systems using a typical value for water-vapour concentration in the Tropics, $q_v = 0.01$ (Vallis, 2017). For thermodynamic constants, we take approximate values $C_{vd} = 1.006$, $C_{pv} = 1.872$, $C_{vd} = 719$, $C_v = 1.410$, $R_d = 287$, and $R_v = 462$, all in units of $\text{J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}$ (Emanuel, 1994). In what follows, for simplicity we will also assume that there is only one water form in the atmosphere, water vapour, since it is the most dominant form; therefore $q_l = q_i = 0$.

Let us start by considering the change in internal energy $\Delta u$ due to a change $\Delta T$ in temperature:

$$
\Delta u_{\text{unapprox}} = C_v^* \Delta T,
\Delta u_{\text{constant-$\kappa$}} = C_{vd} \frac{R^*}{R_d} \Delta T,
\Delta u_{\text{dry}} = C_{vd} \Delta T.
$$

(139)

With $q_v = 0.01$, we have

$$
C_v^* \approx 725.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1},
C_{vd} \frac{R^*}{R_d} \approx 723.84 \text{ J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1},
C_{vd} \approx 719 \text{ J} \cdot \text{K}^{-1} \cdot \text{kg}^{-1}.
$$

(140)
The constant-\(\kappa\) system will therefore underestimate the change in \(u\) by 0.35\%, while the dry heat capacities system will underestimate the change by 0.95\%. This error is almost three times larger, although still quite small numerically.

However, such computations may not be too informative in applications like global climate system modelling. Instead, we consider global climatological means of water enthalpy fluxes for precipitation and evaporation at the atmosphere–ocean interface for the Energy Exascale Earth System Model (E3SM) (Golaz et al., 2019) or the Community Earth System Model (CESM) (Danabasoglu et al., 2020), both currently using the dry heat capacities approach. The enthalpy fluxes for evaporation and precipitation are computed using the specific heat capacity of dry air, \(C_{pd} \approx 1,006\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}\), equal approximately \(10\text{W}\cdot\text{m}^{-2}\) each as a global mean average, and are largely based on fluctuations of water vapour. In the unapproximated system, the same fluxes would be computed with \(C_{pv} \approx 1,872\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}\). Therefore, the dry heat capacities system underestimates water energy fluxes in the global model by almost a factor of 2. For global climate simulations, it is a significant difference. On the other hand, in the constant-\(\kappa\) system the enthalpy fluxes would be computed with the specific heat capacity of water vapour corresponding to this system, \(C_{pv}(R_v/R_d) \approx 1,618\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{-1}\), and enthalpy fluxes in this system would differ from the fluxes in the unapproximated system only by 16%.

5 | CONCLUSIONS

This article has presented complete sets of thermodynamic potentials in terms of their natural variables for three systems describing moist air: unapproximated, constant-\(\kappa\), and dry heat capacities, along with the associated thermodynamic quantities and relationships derived consistently from them. It is intended as a comprehensive reference for the use of thermodynamic potentials in atmospheric modelling, especially for the three systems considered here. An interesting future research topic would be going in the other direction and relaxing some of the approximations made here: for example, introducing temperature-dependent heat capacities, condensates with volume, mixed (non-pure) condensates (including treatment of hydrometeor populations), and some type of equilibrium between water phases. This would be useful for more sophisticated atmospheric models, such as high-resolution large eddy simulations (LES) or models for exoplanetary atmospheres, and in advanced physics parameterizations.

AUTHOR CONTRIBUTIONS

Christopher Eldred: conceptualization; formal analysis; investigation; writing – original draft; writing – review and editing. Mark Taylor: formal analysis; investigation; writing – review and editing. Oksana Guba: formal analysis; investigation; writing – review and editing.

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APPENDIX A. DERIVING UNAPPROXIMATED THERMODYNAMIC POTENTIALS

Recall that we are considering a mixture of dry air and the three phases of water: water vapour, (cloud) liquid water, and (cloud) ice; with concentrations denoted by $q_d$, $q_l$, and $q_i$. The gaseous components $q_d$ and $q_i$ are assumed to be perfect ideal gases with temperature-independent heat capacities at constant volume $C_{vd}$ and $C_{vi}$, heat capacities at constant pressure $C_{pd}$ and $C_{pi}$, and gas constants $R_d$ and $R_v$. The condensed components $q_l$ and $q_i$ are assumed to be incompressible with temperature-independent heat
capacities \( C_i \) and \( C_l \) and to appear as pure substances, and we neglect the volume occupied by the condensates. We additionally assume that the different water phases behave as separate thermodynamic substances, and therefore there is no equilibrium between phases, so we can capture supersaturation and other out-of-equilibrium situations. This means that the Gibbs phase rule does not have to be satisfied.

The assumption of zero-volume, incompressible condensates along with ideal gas behaviour for dry air and water vapour means that the partial pressures for the gaseous components are determined by Dalton’s law:

\[
p_{i,a} = (p_d + p_v)\alpha = q_d R_d T + q_v R_v T = R^* T, \tag{A1}
\]

with \( R^* = q_d R_d + q_v R_v \), where \( p_d = (q_d R_d / R^*) p \) and \( p_v = (q_v R_v) / R^* p \) are the partial pressures of dry air and water vapour.

Under the assumption of a single temperature \( T \) for all components, along with zero-volume, incompressible condensates, the total Gibbs function can be written as the concentration-weighted sum of the Gibbs function for each component (Zdunkowski and Bott, 2004) plus some additional terms related to the latent heat of the vapour and liquid phases of water, using the common \( T \) and the relevant partial pressures from Equation A1.

Specifically, we start with the well-known Gibbs function for a single-component perfect ideal gas with heat capacities \( C_p \) and \( C_v \) and gas constant \( R \) (Zdunkowski and Bott, 2004):

\[
g_p(p, T) = C_p(T - T_r) + T \left( -C_p \ln \frac{T}{T_r} + R ln \frac{p}{p_r} - \eta_0 \right), \tag{A2}
\]

where \( \eta_0 \) is the specific entropy at \( T_r \) and \( p_r \) (with \( p_r \alpha_r = RT_r \)). The pressure here will become the partial pressure for the component in the full expression. Note that this differs from the Gibbs function for an ideal gas found in Thuburn (2017) by a function of the form \( A + BT \). This is acceptable, since this changes only the zero of entropy \( \eta = -\partial g / \partial T \). Here we have normalized \( g \) such that \( g = -T_r \eta_0 \) at \( T = T_r \) and \( p = p_r \), and therefore \( \eta = \eta_0 \) at \( T = T_r \) and \( p = p_r \).

For a pure, incompressible, zero-volume condensate with heat capacity \( C \), the Gibbs function is (Zdunkowski and Bott, 2004)

\[
g_c(p, T) = C(T - T_r) + T \left( -C \ln \frac{T}{T_r} - \eta_0 \right), \tag{A3}
\]

where \( \eta_0 \) is the specific entropy at \( T_r \). There is no dependence on \( p_r \), since we have assumed incompressibility, and \( g \) is normalized such that \( g = -T_r \eta_0 \) at \( T = T_r \) and again therefore \( \eta = \eta_0 \) at \( T = T_r \) and \( p = p_r \). As before, this differs from the Gibbs function for a condensate found in Thuburn (2017) by a function of the form \( A + BT \).

Using Equations A2 and A3, we can write the partial Gibbs functions for each component as

\[
g_{d}(p, T, q_d) = C_{pd}(T - T_r)
\]

\[+ T \left( -C_{pd} \ln \frac{T}{T_r} + R_d \ln \frac{p_d}{p_{rd}} - \eta_d \right) + R_d T_r, \tag{A4}\]

\[
g_{v}(p, T, q_v) = C_{pv}(T - T_r)
\]

\[+ T \left( -C_{pv} \ln \frac{T}{T_r} + R_v \ln \frac{p_v}{p_{rv}} - \eta_v \right) + L_{ft} + L_{vr}, \tag{A5}\]

\[
g_{i}(p, T, q_i) = C_{i}(T - T_r)
\]

\[+ T \left( -C_i \ln \frac{T}{T_r} - \eta_{ri} \right) + L_{ft}, \tag{A6}\]

\[
g_{(p, T, q_i)} = C_{i}(T - T_r) + T \left( -C_i \ln \frac{T}{T_r} - \eta_{ri} \right), \tag{A7}\]

where \( p_{rd} \alpha_{rd} = R_d T_r, p_{rv} \alpha_{rv} = R_v T_r, L_{ft} \) is the latent heat of freezing at \( T_r \), and \( L_{vr} \) is the latent heat of vaporization at \( T_r \), recalling \( p_d = (q_d R_d / R^*) p \) and \( p_v = (q_v R_v) / R^* p \). Note that some care must be taken in the choice of \( p_{rd} \) and \( p_{rv} \) in order to obtain the correct saturation vapour pressure. The latent heat terms are required in order to obtain correct expressions for the equilibrium between phases of water, although this is not treated here. They are also dependent on the choice of reference state, as discussed in Lauritzen et al. (2022). The last term \( (R_d T_r) \) in the \( g_d \) equation simply shifts the zero of the partial Gibbs function for dry air, and amounts only to a change in the zero of chemical potential \( \mu_d \). Now the total Gibbs function is just the concentration-weighted sum of the partial Gibbs functions in Equations A4–A7:

\[
g = q_d g_{d} + q_v g_{v} + q_i g_{i} + q_i g_{i}. \tag{A8}\]

Putting this all together gives

\[
g(p, T, q_d, q_v, q_i, q_i)
\]

\[= T \left( C_p^* - C_p^* \ln \frac{T}{T_r} + q_d R_d \ln \frac{q_d R_d p}{R^* p_{rd}}
\]

\[+ q_v R_v \ln \frac{q_v R_v p}{R^* p_{rv}} - \eta_v \right)
\]

\[- C_p^* T_r + q_v (L_{ft} + L_{vr}) + q_d R_d T_r, \tag{A9}\]

where \( C_p^* = q_d C_{pd} + q_v C_{pv} + q_i C_i + q_i C_i, \ C_v^* = q_d C_{vd} + q_v C_{vv} + q_i C_i + q_i C_i \), and \( \eta_v = q_d \eta_{vd} + q_v \eta_{rv} + q_i \eta_{ri} + q_i \eta_{ri} \), with \( C_p^* = C_v^* + R^* \). This is Equation 55. As in the partial
Gibbs function cases, this (assuming $q_l = 0$) differs from the moist air Gibbs function found in Thuburn (2017) by a function of the form $A + BT + \sum_n C_n q_n$, where the last two terms just shift the zeros of entropy $\eta$ and chemical potentials $\mu_n$, respectively.

From Equation A9 along with the expressions for the conjugate variables $\alpha(p, T, q_n)$ and $\eta(p, T, q_n)$, it is possible to derive all the other thermodynamic potentials. For example, $\eta(p, T, q_n)$ can be solved to yield $T(p, \eta, q_n)$, and then $h(p, \eta, q_n) = g(p, T(p, \eta, q_n), q_n) + \eta T(p, \eta, q_n)$, that is, Equation 54. Similar manipulations give $u(a, \eta, q_n)$ (Equation 53) and $f(a, T, q_n)$ (Equation 56), and are left as an exercise for the interested reader.

APPENDIX B. POTENTIAL AND VIRTUAL QUANTITIES

B.1 Potential quantities

A potential quantity (denoted here with $X_{\alpha}$) is the value a thermodynamic quantity would have if pressure $p$ changed to some reference pressure $p_r$ holding specific entropy $\eta$ and concentrations $q_n$ fixed (an adiabatic process). In other words, such quantities are defined through a relationship of the form

$$X_{\alpha}(p, \eta, q_n) = X(p_r, \eta, q_n), \quad (B1)$$

where $X(p, \eta, q_n)$ is the original variable. Note that this definition implies that potential variables are also entropic variables. For example, potential temperature $\theta$ is defined through

$$\theta(\eta, q_n) = T(p_r, \eta, q_n). \quad (B2)$$

In other words, it is the temperature $T$ if $p \rightarrow p_r$ while holding $\eta$ and $q_n$ fixed.

B.2 Virtual quantities

A virtual quantity (denoted here with $X_v$) is the value a thermodynamic quantity would have if the concentration of a given component $q_d$ changed to 1 while all other concentrations $q_s$ went to zero, holding pressure $p$ and specific volume $\alpha$ fixed. In other words, such quantities are defined through a relationship of the form

$$X_v(p, \alpha) = X(p, \alpha, q_d = 1, q_s = 0), \quad (B3)$$

where $X(p, \alpha, q_d, q_s)$ is the original quantity. Note that these are not entropic variables, in general. For atmospheric dynamics, the usual case has $q_d$ as dry air and $q_s$ as water substances, and so a virtual quantity represents the value of a quantity a dry parcel with the same pressure and specific volume as a moist sample would have. For example, virtual temperature is defined (implicitly) through

$$p(\alpha, T, q_d, q_s) = p(\alpha, T_v, 1, 0). \quad (B4)$$

B.2.1 Examples

To make this more concrete, let us consider virtual temperature $T_v$, virtual potential temperature $\theta_v$, and virtual Exner pressure $\Pi_v$.

B.2.1.1 Unapproximated system

We start by considering the unapproximated system introduced in Section 3. In this case, we have

$$p(\alpha, T, q_d, q_v, q_l, q_i) = \frac{R^* T}{\alpha}, \quad (B5)$$

$$p(\alpha, \theta, q_d, q_v, q_l, q_i) = p_r \left( \frac{R^* \theta}{\alpha \rho_v} \right)^{\eta_v}, \quad (B6)$$

$$p(\alpha, \Pi, q_d, q_v, q_l, q_i) = p_r \left( \frac{\Pi}{C_{pd}} \right)^{\kappa_d}, \quad (B7)$$

and therefore

$$T_v(\alpha, p) = \frac{p \rho}{R_d}, \quad (B8)$$

$$\theta_v(\alpha, p) = \left( \frac{p_r}{p} \right)^{\eta_d} \frac{p \rho}{R_d}, \quad (B9)$$

$$\Pi_v(\alpha, p) = C_{pd} \left( \frac{p}{p_r} \right)^{\kappa_d}. \quad (B10)$$

An interesting question is whether $\theta_v$ is an entropic variable. This can be investigated by using the expression for $\alpha = \alpha(p, \eta, q_n)$ to obtain $\theta_v(p, \eta, q_n)$. Doing so gives

$$\theta_v(p, \eta, q_n) = \left( \frac{p_r}{p} \right)^{\eta_d} \left( \frac{p}{R^*} \right)^{\kappa_v} R^* T_r \frac{\rho_v}{\rho} \frac{R_v}{R_d} \frac{q_d R_d}{p v_d} \left( \frac{q_l R_v}{p v_v} \right)^{\frac{\kappa_v}{\kappa_d}}, \quad (B11)$$

and therefore we see that $\theta_v$ is not an entropic variable for the unapproximated system.

B.2.1.2 Constant-\(\kappa\) system

Next we consider the constant-\(\kappa\) system introduced in Section 4.1. In this case, we have
and therefore
\[ T_v(\alpha, p) = \frac{pa}{R_d}, \tag{B22} \]

\[ \theta_v(\alpha, p) = \left( \frac{p_T}{p} \right)^{\kappa_d} \frac{pa}{R_d}, \tag{B23} \]

\[ \Pi_v(\alpha, p) = C_{pd} \left( \frac{p}{p_T} \right)^{\kappa_d}. \tag{B24} \]

Using the expression for \( \alpha = \alpha(p, \eta, q_n) \) to obtain \( \theta_v(p, \eta, q_n) \) gives
\[ \theta_v(p, \eta, q_n) = \left( \frac{p_T}{p} \right)^{\kappa_d} \frac{R_s}{R_d} T_T \times \exp \frac{\eta}{\gamma_{pd} R_d} \left( \frac{q_d R_d}{p_{rd}} \right) \left( \frac{q_r R_v}{P_v} \right)^{\frac{\gamma_{pd}-\kappa_d}{\gamma_{pd}}} \tag{B25} \]

which is independent of \( p \), and therefore we see that \( \theta_v \) is an entropic variable for the constant-\( \kappa \) system. In fact, Equation B18 is just another way of writing Equation 104.

**APPENDIX C. COMMONLY USED THERMODYNAMIC QUANTITIES**

Following classical equilibrium thermodynamics, a variety of commonly used thermodynamic quantities can be defined using the general thermodynamic potentials from Section 2: heat capacities at constant volume \( C_v \) and pressure \( C_p \), sound speed (squared) \( c_s^2 \), adiabatic temperature gradient \( \Gamma \), 8 coefficient of thermal expansion \( \alpha_T \), isochoric thermal pressure coefficient \( \beta_v \), isothermal compressibility \( \beta_T \), and isentropic compressibility \( \beta_s \).
along with adiabatic index $\gamma = C_v / C_p$.

The quantities in Equations C1–C4 can be used to rewrite the fundamental thermodynamic identities for $u$ (Equation 25) and $h$ (Equation 26) in terms of $dT$ instead of $d\eta$, as

\[
du = C_v dT + p(\beta_v T - 1) \, d\alpha + \sum_n \left( \mu_n + T \frac{\partial \eta}{\partial q_n} \right) \, dq_n. \tag{C5}\]

\[
dh = C_p dT + \alpha(1 - \alpha_p T) \, dp + \sum_n \left( \mu_n + T \frac{\partial \eta}{\partial q_n} \right) \, dq_n. \tag{C6}\]

This requires expressing $d\eta$ in terms of $dT$, $dq_n$, either $d\alpha$ or $dp$, and appropriate partial derivatives of $\eta$ by using $\eta(\alpha, T, q_n)$ or $\eta(p, T, q_n)$, and then using Equations C1–C4 to simplify. Note that we have $d\eta/\partial q_n(\alpha, T, q_n)$ in Equation C5 and $d\eta/\partial q_n(p, T, q_n)$ in Equation C6.

### C.1 Maxwell relationships

Using the equality of mixed partial derivatives, a set of relationships between the derivatives of $p$, $\alpha$, $\eta$, and $T$ can be established:

\[
\frac{\partial^2 u}{\partial \alpha \partial \eta} = -\frac{dp}{\partial \eta} = \frac{\partial T}{\partial \alpha}, \quad \frac{\partial^2 h}{\partial \rho \partial T} = \frac{\partial \alpha}{\partial \eta} = \frac{\partial T}{\partial \rho}, \quad \frac{\partial^2 g}{\partial \rho \partial T} = \frac{\partial \alpha}{\partial \eta} = \frac{\partial \rho}{\partial \alpha} = \frac{\partial T}{\partial \rho}. \tag{C7}\]

Similarly, for an arbitrary entropic variable $\chi$, a set of relationships between the derivatives of $p$, $\alpha$, $\chi$, and $\lambda$ can be established:

\[
\frac{\partial^2 u}{\partial \alpha \partial \chi} = -\frac{dp}{\partial \chi} = \frac{\partial T}{\partial \alpha}, \quad \frac{\partial^2 h}{\partial \rho \partial \chi} = \frac{\partial \alpha}{\partial \chi} = \frac{\partial T}{\partial \rho}, \quad \frac{\partial^2 g}{\partial \rho \partial \chi} = \frac{\partial \alpha}{\partial \chi} = \frac{\partial \rho}{\partial \alpha} = \frac{\partial \chi}{\partial \rho}. \tag{C8}\]

These are known as Maxwell relationships and are quite useful in determining commonly used thermodynamic quantities and relating partial derivatives.

### C.2 Unapproximated system

Now, based on the unapproximated thermodynamic potentials from Section 3, the commonly used thermodynamic quantities are

\[
C_v(\alpha, T, q_\alpha, q_v, q_i) = T \frac{C_v}{T} = C_v, \tag{C10}\]

\[
C_p(\alpha, T, q_\alpha, q_v, q_i) = T \frac{C_p}{T} = C_p, \tag{C11}\]

\[
\Gamma(p, \eta, q_\alpha, q_v, q_i) \quad \frac{\partial^2 u}{\partial \alpha \partial \chi} = -\frac{dp}{\partial \chi} = \frac{\partial T}{\partial \alpha}, \quad \frac{\partial^2 h}{\partial \rho \partial \chi} = \frac{\partial \alpha}{\partial \chi} = \frac{\partial T}{\partial \rho}, \quad \frac{\partial^2 g}{\partial \rho \partial \chi} = \frac{\partial \alpha}{\partial \chi} = \frac{\partial \rho}{\partial \alpha} = \frac{\partial \chi}{\partial \rho}. \tag{C12}\]

As expected, $C_v = C_r$ and $C_p = C_p$. Note that these together give $\frac{1}{\alpha^2} C_v^2 \Gamma = \frac{1}{\alpha^2} C_p^2 C_T \Gamma = p$. Additionally, we have

\[
du = C_v^2 dT + C_v dT + C_v dT + C_v(T - T_i) dT = C_v dT, \tag{C18}\]
\[ dh = C_p \, dT + C_{pd}(T - T_i) \, dq_d + C_{pv}(T - T_v) \, dq_v + C_i(T - T_i) \, dq_i + R_d T_i \, dq_d + (L_vr + L_l) \, dq_v + L_l \, dq_l, \]  
\[ \alpha \] along with \[ C_v + R^* = C_p. \]  

C.3 Constant-\( \kappa \) system

Based on the constant-\( \kappa \) thermodynamic potentials from Section 4.1, the commonly used thermodynamic quantities are

\[ C_v(\alpha, T, q_d, q_v, q_l, q_i) = \frac{C_{vd} R^*}{R_d}, \]  
\[ C_p(p, T, q_d, q_v, q_l, q_i) = \frac{C_{pd} R^*}{R_d}, \]  
\[ \Gamma(p, \eta, q_d, q_v, q_l, q_i) = \frac{R_d}{pC_{pd}} \, T_i \, \exp \left( \frac{\eta - \eta_l}{C_{pd} R_d} \right) \left( \frac{p}{R^*} \right)^{\frac{\alpha \eta}{R_d}} \]  
\[ \left( \frac{q_d R_d}{p_d} \right)^{\frac{\alpha \eta}{R_d}} \left( \frac{q_v R_v}{p_v} \right)^{\frac{\alpha \eta}{R_v}} = \frac{R_d T}{pC_{pd}} = \frac{R_d C_v}{R^* C_{vd}}, \]  
\[ \gamma \]  
\[ \alpha_p(p, T, q_d, q_v, q_l, q_i) = \frac{1}{T}, \]  
\[ \beta_o(a, T, q_d, q_v, q_l, q_i) = \frac{1}{T}, \]  
\[ \beta_T(p, T, q_d, q_v, q_l, q_i) = \frac{1}{p}, \]  
\[ \beta_v(p, \eta, q_d, q_v, q_l, q_i) = \frac{C_{vd}}{C_{pd} p^2}. \]  

As expected, \( C_v = C_{vd} R^*/R_d \) and \( C_p = C_{pd} R^*/R_d \). Note that these together give \((1/\alpha^2) c_v^2 C_v \Gamma = (1/\alpha^2) c_v^2 (C_{vd} R^*/R_d) \Gamma = p\). Additionally, we have

\[ du = \frac{C_{pd} R^*}{R_d} \, dT + C_{pd}(T - T_i) \, dq_d + C_{vd} \frac{R_v}{R_d} (T - T_v) \, dq_v - R_v T_v \, dq_v + (L_vr + L_l) \, dq_v + L_l \, dq_l, \]  
\[ dh = \frac{C_{pd} R^*}{R_d} \, dT + C_{pd}(T - T_i) \, dq_d + C_{pd} \frac{R_v}{R_d} (T - T_v) \, dq_v + R_d T_i \, dq_d + (L_vr + L_l) \, dq_v + L_l \, dq_l. \]  
\[ \text{along with } C_v + R^* = C_p. \]  

C.4 Dry heat capacities system

Based on the dry heat capacities thermodynamic potentials from Section 4.2, the commonly used thermodynamic quantities are

\[ C_v(\alpha, T, q_d, q_v, q_l, q_i) = T \frac{C_{vd}}{T} = C_{vd}, \]  
\[ C_p(p, T, q_d, q_v, q_l, q_i) = T \frac{C_{pd}}{T} = C_{pd}, \]  
\[ \gamma \]  
\[ \alpha_p(p, T, q_d, q_v, q_l, q_i) = \frac{1}{T}, \]  
\[ \beta_o(a, T, q_d, q_v, q_l, q_i) = \frac{1}{T}, \]  
\[ \beta_T(p, T, q_d, q_v, q_l, q_i) = \frac{1}{p}, \]  
\[ \beta_v(p, \eta, q_d, q_v, q_l, q_i) = \frac{C_{vd}}{C_{pd} p^2}. \]
$\beta(p, \eta, q_d, q_v, q_l) = \frac{C_{vd}}{C_{pd}p}$. \hfill (C37)

As expected, $C_v = C_{vd}$ and $C_p = C_{pd}$. Note that these together give $(1/a^2)c_v^2C_{vd}\Gamma = p$. Additionally, we have

$$\begin{aligned}
du &= C_{vd}dT - R_vdTdq_v + (L_{vt} + L_{ft})dq_v + L_{ft}dq_l, \hfill (C38)
dh &= C_{pd}dT + R_dTdq_d + (L_{vt} + L_{ft})dq_v + L_{ft}dq_l. \hfill (C39)
\end{aligned}$$

However, we have $C_v + R^* \neq C_p$, in contrast to the unapproximated and constant-$\kappa$ approximation cases.

**APPENDIX D. LATENT HEATS**

To determine the latent heats (which are simply the partial enthalpy differences between phases), we split $h$ into contributions due to dry air, water vapour, liquid, and ice through

$$h = q_dh_d + q vh_v + q lh_l + q qh_l.$$ \hfill (D1)

In general, we have $h_k(p, \eta, q_d, q_v, q_l)$ in this definition, not $h_k(p, \eta, q_k)$. Then the latent heat of vaporization $L_v$ and latent heat of melting $L_f$ are defined as

$$L_v = h_v - h_l,$$ \hfill (D2)

$$L_f = h_l - h_i.$$ \hfill (D3)

These are worked out for the various thermodynamic potentials below, using the form $h = h(T, q_d, q_v, q_l)$. \hfill (C38)

**D.1 Unapproximated system**

Based on the unapproximated thermodynamic potentials from Section 3, the partial enthalpies are

$$\begin{aligned}
h_v &= C_{pv}(T - T_r) + L_{vt} + L_{ft}, \hfill (D4)
h_l &= C_l(T - T_i) + L_{ft}, \hfill (D5)
h_i &= C_l(T - T_i), \hfill (D6)
\end{aligned}$$

which gives

$$L_v = (C_{pv} - C_l)T + L_{vt} - (C_{pv} - C_l)T_r.$$ \hfill (D7)

At $T = T_r$, we have $L_v = L_{vt}$ and $L_f = L_{ft}$, as expected. This fits with the definitions in Thuburn (2017) if we define

$$\begin{aligned}
L^0_v &= L_{vt} - (C_{pv} - C_l)T_r, \hfill (D9)
L^0_f &= L_{ft} - (C_l - C_i)T_r, \hfill (D10)
\end{aligned}$$

to finally obtain

$$\begin{aligned}
L_v &= (C_{pv} - C_l)T + L^0_f, \hfill (D11)
L_f &= (C_l - C_i)T + L^0_f. \hfill (D12)
\end{aligned}$$

**D.2 Constant-$\kappa$ system**

Based on the constant-$\kappa$ thermodynamic potentials from Section 4.1, the partial enthalpies are

$$\begin{aligned}
h_v &= \frac{C_{pd}R_v}{R_d}(T - T_r) + L_{vt} + L_{ft}, \hfill (D13)
h_l &= L_{ft}, \hfill (D14)
h_i &= 0, \hfill (D15)
\end{aligned}$$

which gives

$$\begin{aligned}
L_v &= \frac{C_{pd}R_v}{R_d}T + L_{vt} - \frac{C_{pd}R_v}{R_d}T_r, \hfill (D16)
L_f &= L_{ft} \hfill (D17)
\end{aligned}$$

At $T = T_r$, we have $L_v = L_{vt}$ and $L_f = L_{ft}$, as expected. This fits with the definitions in Thuburn (2017) if we define

$$\begin{aligned}
L^0_v &= L_{vt} - \frac{C_{pd}R_v}{R_d}T_r, \hfill (D18)
L^0_f &= L_{ft} \hfill (D19)
\end{aligned}$$

to finally obtain

$$\begin{aligned}
L_v &= \frac{C_{pd}R_v}{R_d}T + L^0_v, \hfill (D20)
L_f &= L_{ft} \hfill (D17)
\end{aligned}$$
\[ L_f = L_f^0. \] (D21)

From the perspective of latent heats, the constant-\(\kappa\) approximation consists of dropping the partial enthalpies associated with liquid/ice (other than the \(L_f^0\) term in \(h_l\)) and modifying \(C_{pd}\) to \(C_{pd}R_v/R_d\). This eliminates the temperature dependence of the latent heat of melting and changes the coefficient of temperature dependence for the latent heat of vaporization.

### D.3 Dry heat capacities system

Based on the dry heat capacities thermodynamic potentials from Section 4.2, the partial enthalpies are

\[ h_v = C_{pd}(T - T_v) + L_{vT} + L_{fT}, \] (D22)

\[ h_l = C_{pd}(T - T_l) + L_{lT}, \] (D23)

\[ h_l = C_{pd}(T - T_l), \] (D24)

where we have used \(\sum q_n = 1\), which gives

\[ L_v = L_{vT}, \] (D25)

\[ L_l = L_{lT}. \] (D26)

This fits with the definitions in Thuburn (2017) if we define

\[ L_v^0 = L_{vT}, \] (D27)

\[ L_l^0 = L_{lT}, \] (D28)

to finally obtain

\[ L_v = L_v^0, \] (D29)

\[ L_l = L_l^0. \] (D30)

As expected, all temperature dependence in the latent heats has disappeared.

### APPENDIX E. CHEMICAL POTENTIALS \(\mu_n\) AND GENERALIZED CHEMICAL POTENTIALS \(\xi_n\)

The expressions for chemical potential \(\mu_n\) and generalized chemical potentials \(\xi_n\) are quite complicated, and are given here to avoid disrupting the flow of the main text.

We start by considering the expression of generalized chemical potentials,

\[ \xi_n := \frac{\partial X'}{\partial M_n} \]

for \(X' \in \{U', H'\}\). By using Equations 34 and 35 and the chain rule, these are given as

\[ \xi_n = \mu_n - \lambda \chi + \eta T + T \frac{\partial \eta}{\partial q_n} - \sum_{n'} T \frac{\partial \eta}{\partial q_{n'}} q_{n'}. \] (E1)

where we have used \(\mu_n := \partial X/\partial M_n\).

Next, using Equation 17, the chain rule, and some algebra, it is not too difficult to obtain an expression for the chemical potential \(\mu_n\) (which is \(\partial X/\partial M_n\) for \(X \in \{U, H, G, F\}\)) in terms of \(\partial x/\partial q_n\) for \(x \in \{u, h, g, f\}\):

\[ \mu_n := \frac{\partial X}{\partial M_n} = g + \frac{\partial x}{\partial q_n} - \sum_{n'} q_n \frac{\partial x}{\partial q_{n'}}. \] (E2)

Similarly, using Equation 43 we can obtain an expression for the generalized chemical potential \(\xi_n\) in terms of \(\partial x'/\partial q_n\) for \(x' \in \{u', h'\}\):

\[ \xi_n := \frac{\partial X'}{\partial M_n} = g_x + \frac{\partial x'}{\partial q_n} - \sum_{n'} q_{n'} \frac{\partial x'}{\partial q_{n'}}. \] (E3)

where \(g_x = u' + \lambda \chi\). Note that

\[ \sum q_n \mu_n = g, \quad \sum q_n \xi_n = g_x. \] (E4)

To close these expressions, we need \(\partial x/\partial q_n\) for \(x \in \{u, h, g, f\}\) and \(\partial x'/\partial q_n\) for \(x' \in \{u', h'\}\) in terms of the relevant state variables. These are provided in the following sections.

**Remark 7.** An important point is that not all component specific concentrations are independent, since \(\sum q_k = 1\), so there are actually only \(N - 1\) independent concentrations. However, the component masses \(M_n\) are independent, and since the chemical potentials are fundamentally defined in terms of \(M_n\), this interdependence between the \(q_n\) values does not matter and we can treat all \(q_n\) as independent when taking derivatives.

### E.1 Unapproximated system

#### E.1.1 \(\frac{\partial x}{\partial q_n}\) for \(x \in \{u, h, g, f\}\)

Based on the unapproximated thermodynamic potentials from Section 3, \(\partial x/\partial q_n\) for \(x \in \{u, h, g, f\}\) are
\[
\frac{\partial u}{\partial q_d}(\alpha, \eta, q_d, q_v, q_t, q_i) = A \left[ C_{vd} - \frac{C_{vd}}{C_v} \left( \eta - \eta_t - q_d R_d \ln \frac{\alpha}{q_d a_{rd}} \right) - q_v R_v \ln \frac{\alpha}{q_v a_{rv}} \right] + R_d \ln \frac{q_d a_{rd}}{\alpha} + R_d - \eta_d \right] - C_{vd} T_r, \\
\frac{\partial h}{\partial q_d}(p, \eta, q_d, q_v, q_t, q_i) = A \left[ C_i - \frac{C_i}{C_p} \left( \eta - \eta_t + q_d R_d \ln \frac{q_d R_d p}{R^2 p_{rd}} \right) + q_v R_v \ln \frac{q_v R_v p}{R^2 p_{rv}} \right] - C_i T_r + L_{fr}, \\
\frac{\partial u}{\partial q_v}(\alpha, \eta, q_d, q_v, q_t, q_i) = A \left[ C_{vv} - \frac{C_{vv}}{C_v} \left( \eta - \eta_t - q_d R_d \ln \frac{\alpha}{q_d a_{rd}} \right) - q_v R_v \ln \frac{\alpha}{q_v a_{rv}} \right] + R_v \ln \frac{q_v a_{rv}}{\alpha} + R_v - \eta_v \right] - C_{vv} T_r + L_{vr} + L_{fr} - R_v T_r, \\
\frac{\partial h}{\partial q_v}(p, \eta, q_d, q_v, q_t, q_i) = A \left[ C_i - \frac{C_i}{C_p} \left( \eta - \eta_t + q_d R_d \ln \frac{q_d R_d p}{R^2 p_{rd}} \right) + q_v R_v \ln \frac{q_v R_v p}{R^2 p_{rv}} \right] - C_i T_r, \tag{E6}
\]

with \( A = T_r \exp \left( \frac{\eta - \eta_t}{C_p} \right) \left( \frac{q_d R_d p}{R^2 p_{rd}} \right) \frac{\alpha}{q_d a_{rd}} \frac{\alpha}{q_v a_{rv}} \) = \( T(\alpha, \eta, \eta_t) \).

\[
\frac{\partial u}{\partial q_t}(\alpha, \eta, q_d, q_v, q_t, q_i) = A \left[ C_{vt} - \frac{C_{vt}}{C_v} \left( \eta - \eta_t - q_d R_d \ln \frac{\alpha}{q_d a_{rd}} \right) - q_v R_v \ln \frac{\alpha}{q_v a_{rv}} \right] - C_{vt} T_r, \tag{E7}
\]

\[
\frac{\partial h}{\partial q_t}(p, \eta, q_d, q_v, q_t, q_i) = T \left( \frac{C_{pt} - C_{pt} \ln \frac{T}{T_r} + R_d \ln \frac{q_d R_d p}{R^2 p_{rd}} - \eta_d}{C_{vt} T_r + R_d T_r} \right) - C_{pt} T_r + R_d T_r, \tag{E8}
\]

with \( A = T_t \exp \left( \frac{\eta - \eta_t}{C_p} \right) \left( \frac{q_v R_v p}{R^2 p_{rv}} \right) \frac{\alpha}{q_v a_{rv}} \) = \( T(\alpha, \eta, \eta_t) \).

\[
\frac{\partial h}{\partial q_i}(p, \eta, q_d, q_v, q_t, q_i) = A \left[ C_i - \frac{C_i}{C_p} \left( \eta - \eta_t + q_d R_d \ln \frac{q_d R_d p}{R^2 p_{rd}} \right) + q_v R_v \ln \frac{q_v R_v p}{R^2 p_{rv}} \right] - C_i T_r, \tag{E9}
\]

\[
\frac{\partial h}{\partial q_i}(p, \eta, q_d, q_v, q_t, q_i) = T \left( \frac{C_{pt} - C_{rt} \ln \frac{T}{T_r} + R_d \ln \frac{q_d R_d p}{R^2 p_{rd}} - \eta_d}{C_i T_r + R_d T_r} \right) - C_{pt} T_r + R_d T_r, \tag{E10}
\]

\[
\frac{\partial g}{\partial q_d}(p, T, q_d, q_v, q_t, q_i) = T \left( C_{pd} - C_{pd} \ln \frac{T}{T_r} + R_d \ln \frac{q_d R_d p}{R^2 p_{rd}} - \eta_d \right) - C_{pd} T_r + R_d T_r, \tag{E11}
\]

\[
\frac{\partial g}{\partial q_v}(p, T, q_d, q_v, q_t, q_i) = T \left( C_{pv} - C_{pv} \ln \frac{T}{T_r} + R_v \ln \frac{q_v R_v p}{R^2 p_{rv}} - \eta_v \right) - C_{pv} T_r + L_{vr} + L_{fr}, \tag{E12}
\]

\[
\frac{\partial g}{\partial q_t}(p, T, q_d, q_v, q_t, q_i) = T \left( C_{pt} - C_{pt} \ln \frac{T}{T_r} - \eta_t \right) - C_{pt} T_r, \tag{E13}
\]

\[
\frac{\partial f}{\partial q_d}(\alpha, T, q_d, q_v, q_t, q_i) = T \left( C_{vd} - C_{vd} \ln \frac{T}{T_r} + R_d \ln \frac{q_d a_{rd}}{\alpha} \right) + R_d - \eta_d \right] - C_{vd} T_r, \tag{E14}
\]

\[
\frac{\partial f}{\partial q_v}(\alpha, T, q_d, q_v, q_t, q_i) = T \left( C_{vd} - C_{vd} \ln \frac{T}{T_r} + R_d \ln \frac{q_d a_{rd}}{\alpha} \right) + R_d - \eta_d \right] - C_{vd} T_r, \tag{E15}
\]

\[
\frac{\partial f}{\partial q_t}(\alpha, T, q_d, q_v, q_t, q_i) = T \left( C_{vt} - C_{vt} \ln \frac{T}{T_r} - \eta_t \right) - C_{vt} T_r, \tag{E16}
\]

\[
\frac{\partial f}{\partial q_i}(\alpha, T, q_d, q_v, q_t, q_i) = T \left( C_{vi} - C_{vi} \ln \frac{T}{T_r} \right) - C_{vi} T_r, \tag{E17}
\]
\[
\frac{\partial f}{\partial q_v}(\alpha, T, q_d, q_v, q_i, q_l)
= T \left( C_{vv} - C_{v\alpha} \ln \frac{T}{T_r} + R_v \ln \frac{q_v \alpha_v}{\alpha} + R_v - \eta_v \right) - C_v T_r + L_v + L_{fr} - R_v T_r,
\]
\text{(E18)}

\[
\frac{\partial f}{\partial q_l}(\alpha, T, q_d, q_v, q_i, q_l)
= T \left( C_l - C_i \ln \frac{T}{T_r} - \eta_l \right) - C_i T_r,
\]
\text{(E19)}

\[
\frac{\partial f}{\partial q_i}(\alpha, T, q_d, q_v, q_i, q_l)
= T \left( C_i - C_l \ln \frac{T}{T_r} - \eta_l \right) - C_i T_r.
\]
\text{(E20)}

### E.1.2 \( \frac{\partial x'}{\partial q_a} \) for potential temperature \( \theta \)

Based on the thermodynamic potentials from Section 3, \( \frac{\partial x'}{\partial q_a} \) for \( x' \in \{u', h'\} \) for potential temperature \( \theta \) are

\[
\frac{\partial u'}{\partial q_d}(\alpha, \theta, q_d, q_v, q_i, q_l)
= A \left[ C_{vd} + \ln(\theta) \left( C_{pd} - \frac{C_{vd} C_{pd}}{C_{pd}^*} \right) + \ln \left( \frac{R^*}{\alpha P_r} \right) \left( \frac{R_d - \frac{C_{vd} R^*}{C_{pd}^*}}{C_{pd}^*} \right) \right] - C_v T_r,
\]
\text{(E21)}

\[
\frac{\partial u'}{\partial q_v}(\alpha, \theta, q_d, q_v, q_i, q_l)
= A \left[ C_{vv} + \ln(\theta) \left( C_{v\alpha} - \frac{C_{vv} C_{v\alpha}^*}{C_{v\alpha}^*} \right) + \ln \left( \frac{R^*}{\alpha P_r} \right) \left( \frac{R_v - \frac{C_{vv} R^*}{C_{v\alpha}^*}}{C_{v\alpha}^*} \right) \right] - C_v T_r + L_v + L_{fr} - R_v T_r,
\]
\text{(E22)}

\[
\frac{\partial u'}{\partial q_i}(\alpha, \theta, q_d, q_v, q_i, q_l)
= A \left[ C_l + \ln(\theta) \left( C_i - \frac{C_{l\alpha} C_{pd}}{C_{pd}^*} \right) + \ln \left( \frac{R^*}{\alpha P_r} \right) \left( \frac{C_{l\alpha} R^*}{C_{pd}^*} \right) \right] - C_i T_r + L_i,
\]
\text{(E23)}

\[
\frac{\partial u'}{\partial q_l}(\alpha, \theta, q_d, q_v, q_i, q_l)
= A \left[ C_i + \ln(\theta) \left( C_l - \frac{C_{l\alpha} C_{pd}}{C_{pd}^*} \right) + \ln \left( \frac{R^*}{\alpha P_r} \right) \left( \frac{C_{l\alpha} R^*}{C_{pd}^*} \right) \right] - C_i T_r,
\]
\text{(E24)}

with \( A = (\theta)^{\gamma^*} \left( \frac{R^*}{\alpha P_r} \right)^{\delta^*} = T(\alpha, \theta, q_n). \)

\[
\frac{\partial h'}{\partial q_d}(p, \theta, q_d, q_v, q_i, q_l)
= \theta \left( \frac{P}{P_r} \right)^{\kappa^*} \left[ C_{pd} + \ln \left( \frac{P}{P_r} \right) \left( \frac{R_d - \frac{C_{pd} R^*}{C_{pd}^*}}{C_{pd}^*} \right) \right] - C_v T_r,
\]
\text{(E25)}

\[
\frac{\partial h'}{\partial q_v}(p, \theta, q_d, q_v, q_i, q_l)
= \theta \left( \frac{P}{P_r} \right)^{\kappa^*} \left[ C_{v\alpha} + \ln \left( \frac{P}{P_r} \right) \left( \frac{R_v - \frac{C_{v\alpha} R^*}{C_{v\alpha}^*}}{C_{v\alpha}^*} \right) \right] - C_v T_r + L_v + L_{fr} - R_v T_r,
\]
\text{(E26)}

\[
\frac{\partial h'}{\partial q_i}(p, \theta, q_d, q_v, q_i, q_l)
= \theta \left( \frac{P}{P_r} \right)^{\kappa^*} \left[ C_i + \ln \left( \frac{P}{P_r} \right) \left( \frac{R^* C_i}{C_{pd}^*} \right) \right] - C_i T_r + L_i,
\]
\text{(E27)}

\[
\frac{\partial h'}{\partial q_l}(p, \theta, q_d, q_v, q_i, q_l)
= \theta \left( \frac{P}{P_r} \right)^{\kappa^*} \left[ C_l + \ln \left( \frac{P}{P_r} \right) \left( \frac{R^* C_l}{C_{pd}^*} \right) \right] - C_i T_r.
\]
\text{(E28)}

Note that

\[
\theta \left( \frac{P}{P_r} \right)^{\kappa^*} = T(p, \theta, q_n).
\]

### E.2 Constant-\( \kappa \) system

#### E.2.1 \( \frac{\partial x}{\partial q_a} \) for \( x \in \{u, h, g, f\} \)

Based on the constant-\( \kappa \) thermodynamic potentials from Section 4.1, \( \frac{\partial x}{\partial q_a} \) for \( x \in \{u, h, g, f\} \) are

\[
\frac{\partial u}{\partial q_d}(\alpha, \eta, q_d, q_v, q_i, q_l)
= A \left[ C_{vd} - \frac{R_d}{R^*} \left( \eta - \eta_l - q_d R_d \ln \frac{\alpha}{q_d \alpha_v} \right) + q_v R_v \ln \left( \frac{\alpha}{q_v \alpha_v} \right) + R_d \ln q_d \alpha_v \right] - C_v T_r,
\]
\text{(E29)}

\[
\frac{\partial u}{\partial q_v}(\alpha, \eta, q_d, q_v, q_i, q_l)
= A \left[ C_{vv} R_v - \frac{R_v}{R^*} \left( \eta - \eta_l - q_d R_d \ln \frac{\alpha}{q_d \alpha_v} \right) \right] - C_v T_r.
\]
− q_v R_v \ln \left( \frac{\alpha}{q_v \alpha_v} \right) + R_v \ln \left( \frac{q_v \alpha_v}{\alpha} + R_v - \eta_v \right) 
− \frac{C_v d R_v}{R_d} T_t + L_v r + L_f r - R_v T_r, 
\frac{\partial u}{\partial q_l} (\alpha, \eta, q_d, q_v, q_l, q_l) = -A \eta_l + L_f r, 
(E31)

\frac{\partial u}{\partial q_i} (\alpha, \eta, q_d, q_v, q_l, q_i) = -A \eta_i, 
(E32)

with \( A = T_t \exp \left( \frac{\eta - \eta_d}{\eta_d} \right) \left( \frac{\alpha}{q_v \alpha_v} \right) - \frac{q_v \alpha_v}{\alpha} \left( \alpha - \frac{q_v \alpha_v}{\alpha} \right) \) =

T(\alpha, \eta, q_n).

\frac{\partial h}{\partial q_d} (p, \eta, q_d, q_v, q_l, q_i) 
= A \left( T_v d - \frac{R_d}{R^v} \right) \left( \eta - \eta_t + q_d R_d \ln \frac{q_d R_d p}{R^v p_d} \right) 
+ q_v R_v \ln \left( \frac{q_v R_v p}{R^v p_v} \right) 
+ R_d \ln \left( \frac{q_d R_d p}{R^v p_d} - \eta_d \right) - C_v d T_t + R_d T_t, 
(E33)

\frac{\partial h}{\partial q_l} (p, \eta, q_d, q_v, q_l, q_i) 
= A \left( T_v d - \frac{R_d}{R^v} \right) \left( \eta - \eta_t + q_d R_d \ln \frac{q_d R_d p}{R^v p_d} \right) 
+ q_v R_v \ln \left( \frac{q_v R_v p}{R^v p_v} \right) + R_v \ln \frac{q_v R_v p}{R^v p_{tv}} - \eta_v \right) 
− \frac{C_v d R_v}{R_d} T_t + L_v r + L_f r, 
(E34)

\frac{\partial h}{\partial q_i} (p, \eta, q_d, q_v, q_l, q_i) = -A \eta_i + L_f r, 
(E35)

\frac{\partial h}{\partial q_l} (p, \eta, q_d, q_v, q_l, q_i) = -A \eta_i, 
(E36)

with \( A = T_t \exp \left( \frac{\eta - \eta_d}{\eta_d} \right) \left( \frac{q_v R_v p}{R^v p_d} \right) \frac{\alpha}{q_v \alpha_v} \left( \frac{q_v R_v p}{R^v p_v} \right) \frac{\alpha}{q_v \alpha_v} \) =

T(p, \eta, q_n).

\frac{\partial g}{\partial q_d} (p, T, q_d, q_v, q_l, q_i) 
= T \left( C_v d - C_v d \ln \frac{T}{T_t} + R_d \ln \frac{q_d R_d p}{R^v p_d} - \eta_d \right) 
− C_v d T_t + R_d T_t, 
(E37)

\frac{\partial g}{\partial q_l} (p, T, q_d, q_v, q_l, q_i) 
= T \left( C_v d - C_v d \ln \frac{T}{T_t} + R_v \ln \frac{q_v R_v p}{R^v p_{tv}} - \eta_v \right) 
− C_v d R_v T_t + L_v r + L_f r, 
(E38)

\frac{\partial g}{\partial q_i} (p, T, q_d, q_v, q_l, q_i) = -T \eta_i + L_f r, 
(E39)

\frac{\partial f}{\partial q_l} (p, \eta, q_d, q_v, q_l, q_i) 
= T(C_v d - C_v d \ln \frac{T}{T_t} + R_v \ln \frac{q_v \alpha_v}{\alpha} - \eta_v) - C_v d T_t, 
(E40)

\frac{\partial f}{\partial q_d} (p, \eta, q_d, q_v, q_l, q_i) 
= T \left( C_v d R_v - C_v d \ln \frac{T}{T_t} + R_v \ln \frac{q_v \alpha_v}{\alpha} - \eta_v \right) 
− C_v d R_v T_t + L_v r + L_f r - R_v T_r, 
(E41)

\frac{\partial f}{\partial q_l} (p, \eta, q_d, q_v, q_l, q_i) = -T \eta_l + L_f r, 
(E42)

\frac{\partial f}{\partial q_i} (p, \eta, q_d, q_v, q_l, q_i) = -T \eta_i. 
(E43)

E.2.2 \( \frac{\partial x'}{\partial q_n} \) for \( x' \in \{u', h'\} \) for potential temperature \( \theta \)

Based on the thermodynamic potentials from Section 4.1, \( \frac{\partial x'}{\partial q_n} \) for \( x' \in \{u', h'\} \) for potential temperature \( \theta \) are:

\frac{\partial u'}{\partial q_d} (\alpha, \theta, q_d, q_v, q_l, q_i) = A \left( C_v d \ln R_d - C_v d T_t, 
(E45)

\frac{\partial u'}{\partial q_l} (\alpha, \theta, q_d, q_v, q_l, q_i) 
= A \left( C_v d \ln R_d - C_v d \ln R_d T_t + L_v r + L_f r - R_v T_r, 
(E46)

\frac{\partial u'}{\partial q_i} (\alpha, \theta, q_d, q_v, q_l, q_i) = L_f r, 
(E47)
\[ \frac{\partial u}{\partial q_i}(\alpha, \theta, q_d, q_v, q_l, q_i) = 0 \]  

(E48) \[ \frac{\partial h'}{\partial q_i}(p, \theta, q_d, q_v, q_l, q_i) = L_{fr}, \]  

(E59) \[ \frac{\partial h'}{\partial q_i}(p, \theta, q_d, q_v, q_l, q_i) = 0. \]  

(E60)

It is key to note that these are all constants, in contrast to the very complicated expressions found for \( \partial X/\partial q_n \) and those found for the other systems.

### E.3 Dry heat capacities system

#### E.3.1 \( \frac{\partial x}{\partial q_n} \) for \( x \in \{u, h, g, f\} \)

Based on the dry heat capacities thermodynamic potentials from Section 4.2, \( \partial x/\partial q_n \) for \( x \in \{u, h, g, f\} \) are

\[ \frac{\partial u}{\partial q_d}(\alpha, \eta, q_d, q_v, q_l, q_i) = A \left[ R_d - R_d \ln \frac{\alpha}{q_d \sigma_{rd}} - \eta_{rd} \right]. \]  

(E61) \[ \frac{\partial u}{\partial q_i}(\alpha, \eta, q_d, q_v, q_l, q_i) = -\eta_{il} X + L_{fr}, \]  

(E62) \[ \frac{\partial u}{\partial q_i}(\alpha, \eta, q_d, q_v, q_l, q_i) = -\eta_{il} X, \]  

(E63)

\[ A = T_r \exp \left( \frac{\eta_{il}}{C_{v_d}} \right) \left( \frac{\alpha}{q_d \sigma_{rd}} \right)^{-\frac{\eta_{il}}{C_{v_d}}} \left( \frac{\alpha}{q_d \sigma_{rd}} \right)^{-\frac{\eta_{il}}{C_{v_d}}} = T_r \eta_{il} \right). \]

(E64)

\[ \frac{\partial h'}{\partial q_d}(p, \eta, q_d, q_v, q_l, q_i) = A \left[ \frac{R_d}{C_{pd}} \ln \frac{q_d R_d p}{R^2 p_{rd}^2} - \eta_{ld} \right] + R_d T_r, \]  

(E65) \[ \frac{\partial h'}{\partial q_i}(p, \eta, q_d, q_v, q_l, q_i) = -\eta_{il} X + L_{fr}, \]  

(E66) \[ \frac{\partial h'}{\partial q_i}(p, \eta, q_d, q_v, q_l, q_i) = -\eta_{il} X, \]  

(E67)

\[ \frac{\partial h'}{\partial q_i}(p, \eta, q_d, q_v, q_l, q_i) = -\eta_{il} X + L_{fr}, \]  

(E68)
with $A = T_i \exp \left( \frac{\eta - \eta_i}{C_{pd}} \right) \frac{q_{d}R_p}{R^p_{pd}} \frac{\eta - \eta_i}{C_{pd}} \frac{q_{d}R_p}{R^p_{pd}} = T(p, \eta, q_n)$.

$$
\frac{\partial g}{\partial q_d}(p, T, q_d, q_v, q_l, q_i) = T \left( R_d \ln \frac{q_dR_p}{R^p_{pd}} - \eta_{vd} \right) + R_d T_r.
$$

(E69)

$$
\frac{\partial g}{\partial q_v}(p, T, q_d, q_v, q_l, q_i) = T \left( R_v \ln \frac{q_vR_p}{R^p_{pv}} - \eta_{vv} \right) + L_v + L_{fr},
$$

(E70)

$$
\frac{\partial g}{\partial q_l}(p, T, q_d, q_v, q_l, q_i) = -T \eta_{vl} + L_{fr},
$$

(E71)

$$
\frac{\partial g}{\partial q_i}(p, T, q_d, q_v, q_l, q_i) = -T \eta_{vi},
$$

(E72)

$$
\frac{\partial f}{\partial q_d}(\alpha, T, q_d, q_v, q_l, q_i) = T \left( R_d + R_d \ln \frac{q_d\alpha_{vd}}{\alpha} - \eta_{vd} \right),
$$

(E73)

$$
\frac{\partial f}{\partial q_v}(\alpha, T, q_d, q_v, q_l, q_i) = T \left( R_v + R_v \ln \frac{q_v\alpha_{vv}}{\alpha} - \eta_{vv} \right) + L_v + L_f T_r,
$$

(E74)

$$
\frac{\partial f}{\partial q_l}(\alpha, T, q_d, q_v, q_l, q_i) = -T \eta_{vl} + L_{fr},
$$

(E75)

$$
\frac{\partial f}{\partial q_i}(\alpha, T, q_d, q_v, q_l, q_i) = -T \eta_{vi}.
$$

(E76)

E.3.2 $\frac{\partial x'}{\partial q_n}$ for $x' \in \{u', h'\}$ for potential temperature $\theta$

Based on the thermodynamic potentials from Section 4.2, $\frac{\partial x'}{\partial q_n}$ for $x' \in \{u', h'\}$ for potential temperature $\theta$ are

$$
\frac{\partial u'}{\partial q_v}(\alpha, \theta, q_d, q_v, q_l, q_i)
$$

$$
= A \left[ \ln \left( \frac{R_v}{\alpha p_{fr}} \right) + 1 + \ln T_r \right] R_v + L_v + L_{fr} - R_v T_r.
$$

(E78)

$$
\frac{\partial u'}{\partial q_i}(\alpha, \theta, q_d, q_v, q_l, q_i) = L_{fr},
$$

(E79)

$$
\frac{\partial u'}{\partial q_l}(\alpha, \theta, q_d, q_v, q_l, q_i) = 0,
$$

(E80)

with $A = \theta \left( R_v \frac{\alpha p_{fr}}{p_{fr}} \right) \frac{R^v_{rv}}{C_{rv}} (T_r) \frac{R^v_{rv}}{C_{rv}} = T(\alpha, \theta, q_n)$.

$$
\frac{\partial h'}{\partial q_d}(p, \theta, q_d, q_v, q_l, q_i) = A \ln \left( \frac{p}{p_{fr}} \right) R_v + R_d T_r,
$$

(E81)

$$
\frac{\partial h'}{\partial q_v}(p, \theta, q_d, q_v, q_l, q_i)
$$

$$
= A \ln \left( \frac{p}{p_{fr}} \right) R_v - C_{rv} T_r + L_v + L_{fr},
$$

(E82)

$$
\frac{\partial h'}{\partial q_l}(p, \theta, q_d, q_v, q_l, q_i) = L_{fr},
$$

(E83)

$$
\frac{\partial h'}{\partial q_i}(p, \theta, q_d, q_v, q_i) = 0,
$$

(E84)

with $A = \theta \left( \frac{p}{p_{fr}} \right) \frac{R^v_{rv}}{C_{rv}} = T(p, \theta, q_n)$. 

Based on the thermodynamic potentials from Section 4.2, $\frac{\partial x'}{\partial q_n}$ for $x' \in \{u', h'\}$ for potential temperature $\theta$ are