

CORRESPONDENCE

Reply to “Comments on ‘MSE minus CAPE is the True Conserved Variable for an Adiabatically Lifted Parcel’”

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(Manuscript received 4 November 2015, in final form 3 March 2016)

ABSTRACT

A standard convention in moist thermodynamics, adopted by D. M. Romps and others, is to set the specific energy and entropy of dry air and liquid water to zero at the triple-point temperature and pressure. P. Marquet claims that this convention leads to physically incorrect results. To support this claim, Marquet presents numerical calculations of a lifted parcel. It is shown here that the claim is false and that the numerical calculations of Marquet are in error. In the context of a simple two-phase thermodynamic system, an analysis is presented here of the freedoms one has to choose additive constants in the definitions of energy and entropy. Many other misconceptions are corrected as well.

1. Introduction

It is difficult to know where to start when replying to a comment like that of Marquet (2016, hereafter M16), which is best summarized as a collection of general confusion, misconceptions, and numerical errors. Certainly, nothing in M16 is at all relevant to the claim by Romps (2015, hereafter, R15) that moist static energy minus convective available potential energy (MSE – CAPE) is the conserved thermodynamic variable for an adiabatically lifted parcel. For the sake of the reader, however, I will begin by summarizing the results from R15 in this section. I will then address the three components of M16 listed above—confusion, misconceptions, and errors—in the subsequent sections.

R15 showed that the conserved thermodynamic variable for a parcel adiabatically lifted through an atmosphere is MSE – CAPE and not, in general, MSE, entropy, or equivalent potential temperature. In MSE – CAPE, CAPE is the integral over height of parcel buoyancy b from the parcel’s current height z to some fixed reference height z_{top} , such as its level of neutral buoyancy or the top of the troposphere,

$$\text{CAPE} = \int_z^{z_{\text{top}}} dz' b(z'). \quad (1)$$

Differentiating MSE – CAPE with respect to height and setting it equal to zero (befitting a conserved variable), we get

$$\frac{d}{dz}(\text{MSE}) = -b. \quad (2)$$

Therefore, conservation of MSE – CAPE tells us that the MSE of an adiabatically lifted parcel decreases with height at a rate equal to its buoyancy.

This is not an entirely new idea, and it should not be a controversial one. Riehl and Malkus (1958) wrote down conservation of MSE – CAPE in their Eq. (10), although they made approximations to the moist thermodynamics and they believed (erroneously) that MSE – CAPE is approximately conserved only for small buoyancies. R15 showed that MSE – CAPE is exactly conserved even when accounting for the full details of moist thermodynamics (e.g., the temperature dependence of latent enthalpy and the dependence of heat capacity on water mixing ratios) and that it is exactly conserved even for large buoyancies.

2. General confusion

It is curious that Marquet spends very little time discussing MSE – CAPE in any of the versions of his

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comment, even though that is the topic of the paper on which M16 is ostensibly commenting. In the most recent version of his comment, which is the version published in this journal, Marquet claims that I have erred on the sign: he thinks the minus in MSE – CAPE should be a plus. As defined in Eq. (1) here or in Eq. (4) of R15, the convective *available* potential energy (CAPE) of a parcel at height z is the integral over height of that parcel’s buoyancy as it is lifted from its current height z to some reference height z_{top} , which may be chosen as the parcel’s level of neutral buoyancy for consistency with most other definitions of CAPE. (A typo in the first sentence of the summary section of R15—the “to” should be a “from”—may have contributed to the confusion here.) M16 defines the CAPE of a parcel at height z as the integral of its buoyancy from its level of free convection z_{LFC} up to its current height z ; this, however, is the parcel’s convective *expended* potential energy (CEPE), not its CAPE. We may describe the thermodynamic evolution of an adiabatically lifted parcel using either conservation of MSE – CAPE or MSE + CEPE; the sum of MSE and CAPE is not conserved.

In section 3 of M16, Marquet wonders aloud how the pressure $p(\mathbf{x})$ at the location \mathbf{x} of a parcel can equal the environmental pressure $p_e(z)$ while the parcel simultaneously experiences drag forces through pressure perturbations $p'(\mathbf{x}) = p(\mathbf{x}) - p_e(z)$. The answer to this, which is given in R15, is that drag forces are felt through pressure gradients, so it is perfectly consistent for a parcel’s pressure to be equal to that of the environment [$p(\mathbf{x}) = p_e(z)$] while also feeling drag forces [$\partial p(\mathbf{x})/\partial z \neq \partial p_e(z)/\partial z$]. Indeed, this behavior is observed in large-eddy simulations [see Fig. 4 of Romps and Charn (2015)].

These points of confusion are all that M16 has to offer about MSE – CAPE. The rest of his comment harps on the third law of entropy, which is a common theme in his publications about entropy. Indeed, both the adiabatic and pseudoadiabatic parcel calculations presented by M16 are performed with zero parcel buoyancy, which is a poor choice for testing the conservation of MSE – CAPE since CAPE is identically zero. For adiabatic ascent, zero buoyancy implies that MSE should be exactly conserved, although Marquet seems unbothered by the fact that his calculation of adiabatic ascent violates this conservation in a rather spectacular way. This will be discussed further in section 4.

3. Misconceptions

In section 4 of M16, the discussion begins by sounding the alarm on the definition of specific internal energy E_i that is used by R15 for moist air:

$$E_i = c_{vm}(T - T_{\text{trip}}) + q_v E_{0v} - q_s E_{0s}. \quad (3)$$

Here, c_{vm} is the heat capacity at constant volume of moist air, defined as

$$c_{vm} = q_a c_{va} + q_v c_{vv} + q_l c_{vl} + q_s c_{vs},$$

where q with subscripts denote the mass fractions of dry air (subscript a), water vapor (subscript v), liquid water (subscript l), and solid water (subscript s) and c_v with subscripts are the constant-volume heat capacities of those constituents. M16 objects to the “assumption” that E_{0v} is the difference in specific internal energy between water vapor and liquid at the triple-point temperature and that E_{0s} is the difference in specific internal energy between liquid and solid at the triple-point temperature. But, these are not assumptions: the meanings of E_{0v} and E_{0s} are immediately obvious from Eq. (3). For pure water vapor at the triple point ($T = T_{\text{trip}}$, $q_v = 1$, $q_s = 0$), $E_i = E_{0v}$. For pure liquid water at the triple point ($T = T_{\text{trip}}$, $q_v = 0$, $q_s = 0$), $E_i = 0$. For pure solid water at the triple point ($T = T_{\text{trip}}$, $q_v = 0$, $q_s = 1$), $E_i = -E_{0s}$. Clearly, then, E_{0v} is the difference in specific internal energy between vapor and liquid at the triple point, and similarly for E_{0s} .

The main objection raised by M16, however, is that R15 and others (Emanuel 1994; Romps 2008; Romps and Kuang 2010; Pauluis et al. 2010) have made a grave mistake by defining the energy and entropy for moist air in such a way that the energy and entropy of liquid water and dry air are zero at a convenient reference temperature and pressure. M16 claims that the equations of moist thermodynamics can only be solved correctly using the additive offsets for the energy and entropy of dry air and liquid water that he prefers. This is a common refrain in Marquet’s publications (e.g., Marquet 2015) and it is demonstrably false. To claim that these overall energy and entropy offsets have any physical consequence is like claiming that one cannot calculate the trajectory of a falling ball using geopotential relative to the floor ($gz - gz_{\text{floor}}$) instead of the “correct” choice of geopotential relative to sea level ($gz - gz_{\text{sea}}$). What do matter are the relative values of internal energy and entropy for states of matter between which mass physically transitions, either through phase changes, chemical reactions, or nuclear reactions. Unless the atmosphere begins converting water to dry air or vice versa through some nuclear alchemy, the offsets we use for the internal energy and entropy of dry air and liquid water are completely arbitrary.

Furthermore, M16 claims that these overall offsets must be defined in the way he prefers or else the resulting definitions of energy, enthalpy, and entropy will

not give the right answer when considering open systems—for example, when there is a sink of water in a parcel due to precipitation fallout. This is also false. Note that M16 talks exclusively about definitions of energy, enthalpy, and entropy and not at all about the equations that govern them. When we go to write down the governing equations, we see that it is trivial to define the correct thermodynamic equations regardless of the choice of offsets. A pedagogical example is given in the [appendix](#) for a two-phase liquid system.

A secondary point made by M16 is that R15 added another adiabatically conserved variable, $q_a R_a T_{\text{trip}}$, to the definition of MSE to put it into a particularly attractive form. This was certainly not necessary and could be omitted to retain the standard relationship between MSE and enthalpy h —namely, $\text{MSE} = h + gz$. Not a single figure or conclusion in R15 would be altered in any way by using this more standard definition of MSE: $\text{MSE} - \text{CAPE}$ is the conserved thermodynamic variable for an adiabatically lifted parcel no matter what adiabatically conserved variables are added (or not added) to the definition of MSE.

4. Numerical errors

M16 objects to the equivalent potential temperature θ_e defined in [Romps and Kuang \(2010\)](#) and used by R15 on the grounds that it is calculated by having omitted the “true” entropy offsets for liquid and dry air. A superior alternative, claims M16 [see, also, the numerous publications by Marquet on this topic dating back to [Marquet \(2011\)](#)], is an equivalent potential temperature denoted by θ_s . In the original version of his comment (see <http://arxiv.org/pdf/1509.09096v2>), Marquet tried to make this point by calculating the thermodynamic properties of a parcel lifted adiabatically with zero buoyancy. Marquet used those numerical results to claim that MSE and θ_s are conserved and that θ_e is not. To the contrary, however, his calculations did not conserve any of these variables. They should be conserved to within numerical round-off error, but Marquet got fractional errors on the order of 10^{-6} – 10^{-3} for MSE, θ_s , and θ_e . This points to serious errors in the way Marquet is calculating the adiabatic ascent.

When calculated properly, all of these are conserved to within round-off error: fractional errors on the order of 10^{-15} for entropy s , Marquet’s θ_s , and Romps’s θ_e , and a fractional error on the order of 10^{-11} for MSE (which accumulates round-off error over 10^4 1-Pa integration steps). The top row of [Fig. 1](#) illustrates the constancy of these profiles to within round-off error for exactly the same process purportedly calculated by Marquet. These profiles are calculated by assuming conservation of entropy and, for a given pressure, using a root solver to

calculate temperature (outside of the triple-point temperature) or $q_l/(q_l + q_s)$ (at the triple-point temperature). This procedure is repeated for each 1-Pa increment between 10^5 and 10^4 Pa. Heights of these pressure levels are integrated upward using hydrostatic balance; these integrated heights are used in the expression for MSE. The profiles displayed in [Fig. 1](#) are subsampled from these solutions every 10 mb (1000 Pa). For context, the bottom row shows the profiles of parcel T , q_v , q_l , and q_s . The takeaway message from [Fig. 1](#) is that, for a parcel lifted adiabatically, reversibly, and with zero buoyancy, all of s , θ_s , θ_e , and MSE are exactly conserved, contrary to the claims by Marquet in the original version of his comment.

Upon receiving a first draft of my reply, Marquet heavily edited his comment to remove his claim that only θ_s is conserved for adiabatic ascent. But, M16 has added a new and equally puzzling result: the supposedly isentropic parcel ascent shown in his new [Fig. 2](#). Where Marquet describes this figure in his section 7, he simultaneously states that he is calculating isentropic ascent of a parcel and that he is freezing the parcel’s liquid water immediately upon reaching the triple-point temperature. These are contradictory statements. A parcel whose pressure is lowered isentropically goes through an isothermal (non-isobaric) transition from liquid condensates to solid condensates at the triple point. Indeed, it is called the “triple point” because all three phases coexist. Incidentally, M16 mischaracterizes [Fig. 8](#) of [Romps and Kuang \(2010\)](#) as also freezing the parcels’ liquid condensates immediately upon reaching the triple-point temperature. This is not true; that paper clearly states that it calculates equilibrium mixed-phase conditions for parcels at the triple-point temperature.

Even more disconcerting is that the MSE of the adiabatically lifted parcel changes by 5000 J kg^{-1} at the freezing temperature in [Fig. 2](#) of M16. Since Marquet is lifting a parcel with zero buoyancy, MSE should be exactly conserved. (Note that, when Marquet and I refer to MSE, we are both including the ice term; the resulting expression is what some people call the “frozen moist static energy,” and it should be conserved in the presence of fusion.) The fact that M16 is finding a nonconservation of MSE by such a large amount—equivalent to a 5-K anomaly in parcel temperature—means that his calculations are still suffering from grave numerical errors.

Marquet tries to justify the jumps in entropy and MSE that he finds at the freezing point for supposedly isentropic ascent by pointing to the jumps in buoyancy seen in [Fig. 8](#) of [Romps and Kuang \(2010\)](#) and [Fig. 2](#) of R15. Of course, this is a meaningless comparison of apples and oranges: a parcel can have a jump in buoyancy with no change in entropy. In [Fig. 8](#) of [Romps and Kuang \(2010\)](#), the dark-blue curve is for an isentropic parcel,

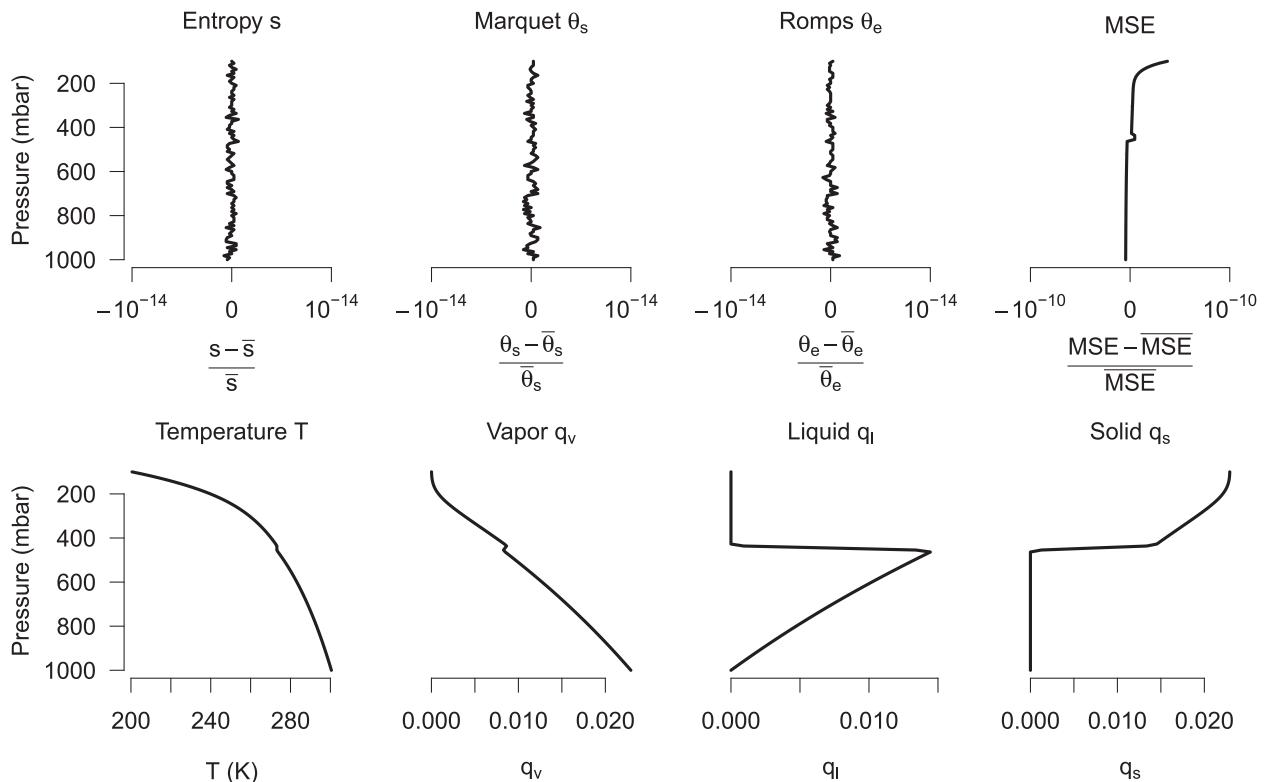


FIG. 1. Thermodynamic profiles for a saturated parcel initially at $T = 300.5$ K and $p = 1$ bar that is then lifted adiabatically, reversibly, and with zero buoyancy. (top) Fractional deviations of entropy s , Marquet θ_s , Romps θ_e , and MSE from their mean values; note that all four of these quantities are conserved to within numerical round-off error. (bottom) Temperature T , vapor mass fraction q_v , liquid mass fraction q_l , and solid mass fraction q_s .

and its jump in buoyancy is not discontinuous but spread out over an isothermal triple-point layer. In the right panel of Fig. 2 of R15, the “hooks” in parcel buoyancy are not caused by discontinuous jumps in entropy as Marquet claims, but instead by the fact that the lifted parcels reach the temperatures bracketing the mixed-phase region at slightly different altitudes than the environment; this is as expected, since the parcels are warmer at every height than the environment.

In his section 8, Marquet turns his attention to the calculation of parcels lifted pseudoadiabatically. He begins by arguing that adiabatic ascent is not common in the real world. I agree. And neither is the pseudoadiabatic ascent that Marquet studies. In reality, cloud parcels lose condensed water by fallout and they dilute their MSE by entrainment. But, any ascent can be calculated numerically by subjecting the parcel to a repeated sequence of adiabatic ascent, fallout, and entrainment over sufficiently small height increments. The argument made by R15 is that the adiabatic-ascent part of this calculation must be performed conserving MSE – CAPE. The inclusion of fallout and entrainment does not alter the central message of R15: for any parcel lifted through the

atmosphere (that suffers from any combination of drag, fallout, entrainment, etc.), there is a sink of MSE proportional to buoyancy times vertical velocity.

M16 attempts to show that θ_s is “valid” for pseudoadiabatic ascent while θ_e is not. What M16 never defines, however, is what is meant by valid. Neither θ_e nor θ_s are conserved for pseudoadiabatic ascent: they are the exponentials of entropy, and entropy is only conserved for adiabatic transformations. In fact, in Fig. 4 of M16, the changes in θ_s are an order of magnitude larger than the changes in θ_e . On the other hand, the thermodynamic equation for a moist atmosphere can be written in terms of either θ_e and θ_s ; in this sense, they are both valid.

5. Conclusions

The concluding section of M16 is devoted to some lengthy and irrelevant discussion about the entropy of perfect crystals at absolute zero, Debye’s law, and a Nobel Prize presentation speech. I will, therefore, not spare any space to comment on it. Instead, I will summarize here the two most important lessons that have emerged from this discussion.

One lesson is that there are many ways to define the energy and entropy of a thermodynamic system. When choosing a set of definitions, it is important to give physical values to the differences between the energies and entropies of states between which matter transitions (e.g., between vapor and liquid and between liquid and solid). But, there is unlimited freedom to choose an overall additive energy constant for any set of states within which matter is conserved (e.g., an overall additive constant for the energies of vapor, liquid, and solid or an overall additive constant for the energy of dry air) and similarly for an overall additive entropy constant. This allows us to adopt some convenient conventions, such as setting the energy and entropy of both dry air and liquid water to zero at the triple-point temperature and pressure.

Another lesson is that there are many ways to define equivalent potential temperature. Loosely speaking, equivalent potential temperature is the exponential of entropy. Since there are several choices of factors when taking this exponential, and because the expression can be adorned with various instances of the dry-air mass fraction q_a (also a conserved variable for adiabatic transformations), different definitions of equivalent potential temperature may look very different even though they are conserved for the same process. Two such examples are θ_e of R15 and θ_s of M16.

Acknowledgments. This work was supported by the Scientific Discovery through Advanced Computing (SciDAC) program funded by the U.S. Department of Energy Office of Advanced Scientific Computing Research and Office of Biological and Environmental Research under Contract DE-AC02-05CH11231.

APPENDIX

Example: Two-Phase Liquid

Mathematically, the primary claim of M16 is that very precise values must be chosen for the specific energy of dry air at the triple point e_{ia0} , the specific energy of liquid water at the triple point e_{il0} , the specific entropy of dry air at the triple point s_{ar} , and the specific entropy of liquid water at the triple point s_{lr} . It is straightforward to show that this is false and that, in fact, they can be set to any value, including the convenient choice of zero. Rather than go through that exercise for four states of matter (dry air, water vapor, liquid water, and solid water), let us consider a much simpler system: two incompressible liquids with the

same density ρ . The equations for this system are simpler and, yet, contain all of the physics that is relevant for understanding energy and entropy offsets.

Let us denote these two types of liquid by subscripts 1 and 2, and let their specific internal energies be

$$e_1 = c_1(T - T_r) + e_{r1} \quad \text{and} \quad (\text{A1})$$

$$e_2 = c_2(T - T_r) + e_{r2}, \quad (\text{A2})$$

where T is the temperature, c_i is the heat capacity at constant volume for phase i , T_r is an arbitrary reference temperature, and e_{ri} is the internal energy of phase i at $T = T_r$. The specific entropy of each phase can be found by integrating $Tds_i = de_i$, which gives

$$s_1 = c_1 \log(T/T_r) + s_{r1} \quad \text{and} \quad (\text{A3})$$

$$s_2 = c_2 \log(T/T_r) + s_{r2}, \quad (\text{A4})$$

where s_{r1} and s_{r2} are integration constants. The total specific internal energy e , total specific entropy s , and the heat capacity of the mixture c are

$$e = q_1 e_1 + q_2 e_2, \quad (\text{A5})$$

$$s = q_1 s_1 + q_2 s_2, \quad \text{and} \quad (\text{A6})$$

$$c = q_1 c_1 + q_2 c_2, \quad (\text{A7})$$

where q_1 and q_2 are the mass fractions of the two liquids (with $q_1 + q_2 = 1$).

The equations for this system are explored in the subsections below. We begin in the first subsection by imagining that mass is never converted between these two types of liquid. In this case, all of the energy and entropy offsets can be chosen arbitrarily and independently of each other; this is analogous to dry air and liquid water, whose offsets can likewise be chosen arbitrarily and independently. In the second subsection, we imagine that mass is able to transition between these two phases of liquid. In this case, there is a phase boundary at a fixed temperature and the difference between the two energy offsets (and the difference between the two entropy offsets) must be chosen appropriately to give the right physics at that phase boundary; this is analogous to water vapor and liquid water, for which the relative energy offset must be chosen appropriately while leaving the overall offset for both phases (i.e., the liquid-water triple-point energy) free to be chosen arbitrarily, and similarly for the entropy offset. Finally, the third subsection adds sources of these two liquid phases to the equations to produce an open system. In this case, it is trivial to define the appropriate equations no matter what overall offsets have been chosen for energy and entropy.

a. No conversion

The governing equations for mass and energy can be written as

$$\frac{\partial}{\partial t}(\rho e) + \nabla \cdot (\rho \mathbf{u} e) = Q, \quad (\text{A8})$$

$$\frac{\partial}{\partial t}(q_1 \rho) + \nabla \cdot (q_1 \rho \mathbf{u}) = 0, \quad \text{and} \quad (\text{A9})$$

$$\frac{\partial}{\partial t}(q_2 \rho) + \nabla \cdot (q_2 \rho \mathbf{u}) = 0, \quad (\text{A10})$$

where Q is the heating rate ($\text{J m}^{-3} \text{s}^{-1}$). From these, we can derive

$$\rho c \frac{dT}{dt} = Q, \quad (\text{A11})$$

$$\rho \frac{dq_1}{dt} = 0, \quad \text{and} \quad (\text{A12})$$

$$\rho \frac{dq_2}{dt} = 0. \quad (\text{A13})$$

The entropy equation follows immediately from Eqs. (A11)–(A13) applied to the definition of entropy given by Eqs. (A3), (A4), and (A6). This is an important point that was emphasized by Romps (2008): the entropy equation contains no information that is not already present in the governing equations for mass and energy. In practice, we find the equation for entropy by taking d/dt of s and rewriting it in terms of energy sources and mass sources using Eqs. (A11)–(A13). This produces

$$\rho \frac{ds}{dt} = \frac{Q}{T}. \quad (\text{A14})$$

For adiabatic processes ($Q = 0$), it is evident from Eq. (A14) that s is conserved for all adiabatic transformations ($Q = 0$), making it a suitable definition of entropy for any values of s_{r1} and s_{r2} . Note, also, that the enthalpy constants e_{r1} and e_{r2} are also completely arbitrary since they do not appear in the governing Eqs. (A11)–(A13). The values of e_{r1} , e_{r2} , s_{r1} , and s_{r2} have no physical consequence when there is no conversion of mass between the two types of liquid. This is analogous to dry air and liquid water, between which there is no conversion of mass: their energy and entropy offsets can be chosen arbitrarily and independently and so can be set to zero at the triple point.

b. Conversion

Let us now allow mass to convert between the two states of matter. Defining $C_{2 \rightarrow 1}$ as the rate of conversion from phase 2 to phase 1 ($\text{kg m}^{-3} \text{s}^{-1}$), the governing equations become

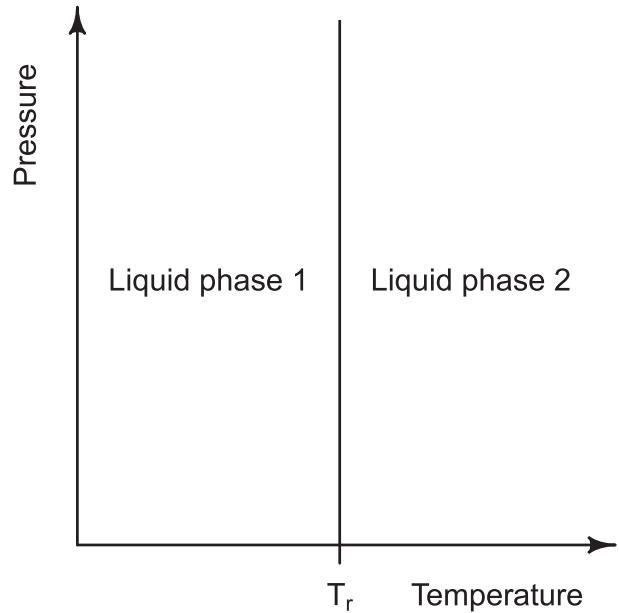


FIG. A1. Phase diagram for two incompressible liquids of the same density that are at thermodynamic equilibrium at temperature T_r .

$$\frac{\partial}{\partial t}(\rho e) + \nabla \cdot (\rho \mathbf{u} e) = Q, \quad (\text{A15})$$

$$\frac{\partial}{\partial t}(q_1 \rho) + \nabla \cdot (q_1 \rho \mathbf{u}) = C_{2 \rightarrow 1}, \quad \text{and} \quad (\text{A16})$$

$$\frac{\partial}{\partial t}(q_2 \rho) + \nabla \cdot (q_2 \rho \mathbf{u}) = -C_{2 \rightarrow 1}. \quad (\text{A17})$$

From these, we can derive

$$\rho c \frac{dT}{dt} = Q + (e_2 - e_1) C_{2 \rightarrow 1}, \quad (\text{A18})$$

$$\rho \frac{dq_1}{dt} = C_{2 \rightarrow 1}, \quad \text{and} \quad (\text{A19})$$

$$\rho \frac{dq_2}{dt} = -C_{2 \rightarrow 1}. \quad (\text{A20})$$

As before, the entropy equation is obtained directly from Eqs. (A18)–(A20), yielding

$$\rho \frac{ds}{dt} = \frac{Q}{T} + \frac{C_{2 \rightarrow 1}}{T} [(e_2 - e_1) - (s_2 - s_1)T]. \quad (\text{A21})$$

The term in square brackets is the difference in Gibb's free energy between the two phases. In order for entropy to be conserved for adiabatic and reversible transformations, this difference in Gibb's free energy must be zero at the phase boundary, which lies at a fixed temperature for these incompressible, same-density liquid phases. For simplicity, we can set the reference temperature T_r to the temperature of this

phase boundary. The phase diagram for these two-liquid-phase system is shown in Fig. A1.

The difference in Gibb's free energies equals zero at the phase boundary if

$$e_{r1} - T_r s_{r1} = e_{r2} - T_r s_{r2}. \quad (\text{A22})$$

To get the correct heat release of conversion, we must also require that $e_{r2} - e_{r1}$ equal the latent enthalpy of conversion at the phase boundary L_r ,

$$e_{r2} - e_{r1} = L_r. \quad (\text{A23})$$

Using Eqs. (A22) and (A23) to eliminate e_{r2} and s_{r2} from Eqs. (A1)–(A4), we can write the specific energies and entropies as

$$e_1 = c_1(T - T_r) + e_{r1}, \quad (\text{A24})$$

$$e_2 = c_2(T - T_r) + L_r + e_{r1}, \quad (\text{A25})$$

$$s_1 = c_1 \log(T/T_r) + s_{r1}, \quad \text{and} \quad (\text{A26})$$

$$s_2 = c_2 \log(T/T_r) + \frac{L_r}{T_r} + s_{r1}. \quad (\text{A27})$$

With these definitions, it is evident from Eq. (A21) that s is conserved for all transformations that are adiabatic ($Q = 0$) and reversible ($C_{2 \rightarrow 1} = 0$ when $T \neq T_r$). Note that the overall energy and entropy offsets e_{r1} and s_{r1} remain completely arbitrary since they do not enter at all into governing Eqs. (A18)–(A20). The values of these constants have no physical consequence whatsoever. This system is analogous to a mixture of vapor and liquid with phase changes; their relative energy and entropy constants are constrained, but the overall offsets of energy and entropy are arbitrary and can be set to zero at the triple point.

c. Sources

If there are mass sources S_1 and S_2 for liquid phases 1 and 2, respectively, then we must add sources of enthalpy and mass to the right-hand side of Eqs. (A15)–(A17), which gives

$$\frac{\partial}{\partial t}(\rho e) + \nabla \cdot (\rho \mathbf{u} e) = Q + S_1 e_1 + S_2 e_2, \quad (\text{A28})$$

$$\frac{\partial}{\partial t}(q_1 \rho) + \nabla \cdot (q_1 \rho \mathbf{u}) = C_{2 \rightarrow 1} + S_1, \quad \text{and} \quad (\text{A29})$$

$$\frac{\partial}{\partial t}(q_2 \rho) + \nabla \cdot (q_2 \rho \mathbf{u}) = -C_{2 \rightarrow 1} + S_2. \quad (\text{A30})$$

The Lagrangian versions of these equations are

$$\rho c \frac{dT}{dt} = Q + (e_2 - e_1) C_{2 \rightarrow 1}, \quad (\text{A31})$$

$$\rho \frac{dq_1}{dt} = C_{2 \rightarrow 1} + S_1 - q_1(S_1 + S_2), \quad \text{and} \quad (\text{A32})$$

$$\rho \frac{dq_2}{dt} = -C_{2 \rightarrow 1} + S_2 - q_2(S_1 + S_2). \quad (\text{A33})$$

From these governing equations, we can derive the entropy equation, which is

$$\rho \frac{ds}{dt} = \frac{Q}{T} + \frac{C_{2 \rightarrow 1}}{T} [(e_2 - e_1) - (s_2 - s_1)T] + s_1 S_1 + s_2 S_2 - s(S_1 + S_2). \quad (\text{A34})$$

With the definitions given by Eqs. (A24)–(A27), it is evident from Eq. (A34) that s is conserved for all transformations that are adiabatic ($Q = S_1 = S_2 = 0$) and reversible ($C_{2 \rightarrow 1} = 0$ when $T \neq T_r$) regardless of the values chosen for e_{r1} and s_{r1} . The values chosen for the overall energy offset e_{r1} and entropy offset s_{r1} have no physical consequence whatsoever since they do not show up in governing Eqs. (A31)–(A33). This system is analogous to a mixture of vapor and liquid with phase changes and a mass source/sink of liquid due to precipitation fallout; their relative energy and entropy constants are constrained, but, despite being an open system, the overall offsets of energy and entropy are arbitrary and can be set to zero at the triple point.

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