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On Conservation Equation Combinations and Closure Relations

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Abstract: Fundamental conservation equations for mass, momentum and energy of chemical species can be combined with thermodynamic relations to obtain secondary forms, such as conservation equations for phases, an internal energy balance and a mechanical energy balance. In fact, the forms of secondary equations are infinite and depend on the criteria used in determining which species-based equations to employ and how to combine them. If one uses these secondary forms in developing an entropy inequality to be used in formulating closure relations, care must be employed to ensure that the appropriate equations are used, or problematic results can develop for multispecies systems. We show here that the use of the fundamental forms minimizes the chance of an erroneous formulation in terms of secondary forms and also provides guidance as to which secondary forms should be used if one uses them as a starting point.

Keywords: species conservation equations; mechanical energy; internal energy; entropy inequality

1. Introduction

The understanding of a range of natural and industrial processes involving contaminant fate, transport and remediation requires modeling tools that accurately capture the dynamic processes involving the chemical species present in the system. In deriving models for multispecies systems, conservation equations for mass, momentum and energy can be proposed for species within a phase rather than for the phase as a whole [1–8]. Of course, if one sums a species-based conservation relation over all species in the phase, the resulting equation is a conservation equation for the phase. By proceeding

from species-based forms to phase-based forms, one obtains insights into the species-based elements that contribute to a phase-based definition of a quantity.

Of additional interest is the fact that dynamic system equations, such as an internal energy or mechanical energy balance, derived from species-based and phase-based conservation equations of mass, momentum and total energy, can take on different forms, depending on how one chooses to combine the precursor equations. This has implications in the use of such equations in modeling systems and in deriving closure relations. Here, we propose a general approach to the development of conservation equations from a species-based perspective and show that the non-uniqueness of equations developed from these forms can impact closure relations and models of system behavior.

The conservation equations we will deal with are localized forms of their counterparts for a domain of interest, and thus, the first order differentiability of the quantities in the equation are assumed. We define a conservation equation to be an expression for which the time rate of change of the conserved quantity in the domain plus its net outward flux is equal to the the rate of production of the quantity within the domain due to body sources, plus the non-advective rate of addition due to boundary fluxes, plus the rate of generation of the conserved quantity within the system, due to interactions among species. In contrast to conservation equations, balance equations require the presence of an additional term that accounts for the gain or loss of the quantity of interest, due to its transformation into another quantity or, in the case of entropy, due to an increase that cannot be equated to a corresponding loss elsewhere in the system.

2. Primary Conservation Equations for Chemical Species

For our development, we will make use of the primary conservation equations for mass, momentum and total energy of a chemical species in a phase. The internal energy and mechanical energy equations are considered to be secondary derived equations dependent on partitioning of the total energy equation into component parts. Thus, these two equations are not independent of the primary relations. The fourth equation of interest is the entropy balance for a species in a phase.

The mass conservation equation for chemical species i may be denoted as $\mathcal{M}_i$ and is written:

$$\mathcal{M}_i = \frac{D_i(\rho\omega_i)}{Dt} + \rho\omega_i \mathbf{l} : \mathbf{d}_i - r_i = 0, \quad (1)$$

where ρ is the mass density, ω_i is the mass fraction of species i and r_i is the rate of production of species i per unit volume due to all chemical reactions in the system; the species velocity is employed, such that:

$$\frac{D_i}{Dt} = \frac{\partial}{\partial t} + \mathbf{v}_i \cdot \nabla, \quad (2)$$

and:

$$\mathbf{d}_i = \frac{1}{2} \left[\nabla \mathbf{v}_i + (\nabla \mathbf{v}_i)^T \right]. \quad (3)$$

The conservation equation for the momentum of species i is denoted $\mathcal{P}_i$ and is written in material derivative form as:

$$\mathcal{P}_i = \frac{D_i(\rho\omega_i \mathbf{v}_i)}{Dt} + \rho\omega_i \mathbf{v}_i \mathbf{l} : \mathbf{d}_i - \nabla \cdot \mathbf{t}_i - \rho\omega_i \mathbf{g}_i - \mathbf{p}_i - r_i \mathbf{v}_i = \mathbf{0}, \quad (4)$$

where $\mathbf{t}_i$ is the stress tensor for species i and $\mathbf{g}_i$ is the acceleration of species i due to an external body force. When this acceleration is gravity, it is equal for all species; we allow for a more general case where

the acceleration is species dependent. In the momentum balance equation for a chemical species, a term is needed that accounts for the transfer of momentum between species due to collisions and chemical reactions. This term is expressed here as $\mathbf{p}_i + r_i \mathbf{v}_i$. Although there has been some discussion in the literature about the most appropriate velocity to use in this expression [9], this is inconsequential if the term $\mathbf{p}_i$ is adjusted to account for whatever velocity is employed. The species-based stress tensor is not necessarily symmetric [10], although for simplicity, here, it will be treated as symmetric without impacting subsequent discussion.

The final primary conservation equation that is considered is the total energy equation for species i . This equation is denoted $\mathcal{E}_i$ and is written:

$$\begin{aligned} \mathcal{E}_i = \frac{D_i}{Dt} \left(U_i + \rho \omega_i \frac{\mathbf{v}_i \cdot \mathbf{v}_i}{2} \right) + \left(U_i + \rho \omega_i \frac{\mathbf{v}_i \cdot \mathbf{v}_i}{2} \right) \mathbf{l} : \mathbf{d}_i - \nabla \cdot (\mathbf{q}_i + \mathbf{t}_i \cdot \mathbf{v}_i) \\ - \rho \omega_i \mathbf{g}_i \cdot \mathbf{v}_i - h_i - e_i - \mathbf{p}_i \cdot \mathbf{v}_i - r_i \left(\frac{1}{2} \mathbf{v}_i \cdot \mathbf{v}_i \right) = 0 . \end{aligned} \quad (5)$$

In this equation, U_i is the internal energy per volume, $\mathbf{q}_i$ is the non-advective energy transport, h_i is the body source of energy and the grouping $e_i + \mathbf{p}_i \cdot \mathbf{v}_i + r_i \left(\frac{1}{2} \mathbf{v}_i \cdot \mathbf{v}_i \right)$ accounts for the energy transfer to species i from other species due to heat exchange, mechanical interactions and chemical reactions. As with the momentum equation, the actual velocity that is used in this transfer term is immaterial, as long as e_i is properly formulated. The energy equation has the property, demonstrated in [11] for phase-based equations, that if the frame of reference for the velocity translates at a constant velocity, $\mathbf{c}$, the species-based momentum and mass conservation equations can be shown to hold. The quantity U_i is an energy density. Alternatively, one can replace this with $U_I = \rho \omega_i u_i$, where u_i is the energy per mass; but this change does not alter any of the conclusions and results to be obtained here.

Equations (1), (4) and (5) are fundamental equations in that they account for the conservation of a total property. This is particularly important in considering energy, where conservation equations are sometimes formulated for internal energy, as well as for kinetic energy. These latter two equations must account for the transfer of energy between alternative forms. Thus, neither equation is a complete or fundamental equation.

One additional species equation is the entropy balance equation. This is called a balance equation rather than a conservation equation, because entropy can be created by irreversible processes and is thus not a conserved quantity. This equation is written:

$$\mathcal{S}_i = \frac{D_i \eta_i}{Dt} + \eta_i \mathbf{l} : \mathbf{d}_i - \nabla \cdot \boldsymbol{\varphi}_i - b_i = \Lambda_i , \quad (6)$$

where η_i is the entropy per volume, $\boldsymbol{\varphi}_i$ is the non-advective entropy flux, b_i is the volumetric entropy source term and Λ_i is the entropy generation associated with species i . This equation is noteworthy on at least two accounts. First, neither entropy nor its volume or surface sources appear in any of the conservation equations. Second, the entropy generation term is not necessarily positive for a chemical species, because it accounts for generation in species i due to irreversible processes, as well as interactions with other species. Thus, for the species-based entropy equation, both the reversible and irreversible contributions to entropy production could be negative, while for the phase-based form, the generation term must be non-negative, based on the second law of thermodynamics.

In addition to the primary conservation equations, it will be convenient to have a mathematical relation between the body acceleration and its potential. We will consider that these are related according to:

$$\mathbf{g}_i + \nabla \psi_i = \mathbf{0} . \quad (7)$$

If we define the potential per volume, Ψ_i , such that:

$$\Psi_i = \rho \omega_i \psi_i , \quad (8)$$

the material derivative of Equation (7) can be manipulated in conjunction with Equation (7), to obtain a quantity designated as $\mathcal{G}_i$, where:

$$\mathcal{G}_i = \frac{D_i \Psi_i}{Dt} + \Psi_i \mathbf{l} : \mathbf{d}_i - r_i \psi_i - \rho \omega_i \frac{\partial \psi_i}{\partial t} + \rho \omega_i \mathbf{v}_i \cdot \mathbf{g}_i = 0 . \quad (9)$$

3. Phase-Based Primary Conservation Equations

The three conservation equations, entropy balance equation and body force potential equation all satisfy the condition that the sums of their species-based forms over all species must be equal to the phase-based equations of interest. However, this summation process leads to the need to define some variables, such as the stress tensor and non-advective heat flux, on a phase basis. These definitions are not unique, but depend on the context of the equations employed. In particular, one need not formulate all equations on a phase basis. Thus, where there is a mix of bases for the equations, the definitions of variables can be altered. Nevertheless, for the five equations listed, we can derive phase-based equations from the species forms. The derivations are most easily carried out by writing the material derivative as expanded out in Equation (2) and combining this with the second term in the equation, such as:

$$\frac{D_i f_i}{Dt} + f_i \mathbf{l} : \mathbf{d}_i = \frac{\partial f_i}{\partial t} + \nabla \cdot (\mathbf{v}_i f_i) . \quad (10)$$

Summation of the form on the right over all species is then accomplished before the resultant equation is written in terms of the material derivative based on the velocity of the phase.

For the conservation of mass, the phase-based equation is denoted $\mathcal{M}$ and is obtained as:

$$\sum_{i \in \mathcal{I}_s} \mathcal{M}_i = \mathcal{M} = \frac{D\rho}{Dt} + \rho \mathbf{l} : \mathbf{d} = 0 . \quad (11)$$

To obtain this equation, we make use of the conditions:

$$\sum_{i \in \mathcal{I}_s} \omega_i = 1 \quad (12)$$

and:

$$\sum_{i \in \mathcal{I}_s} r_i = 0 . \quad (13)$$

We also define the phase velocity, $\mathbf{v}$, to be the barycentric velocity, such that:

$$\mathbf{v} = \sum_{i \in \mathcal{I}_s} \omega_i \mathbf{v}_i ; \quad (14)$$

and the material derivative based on the phase velocity as:

$$\frac{D}{Dt} = \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla. \quad (15)$$

Equation (11) is the well-known conservation of mass equation. By deriving it from a sum of the species-based conservation of mass equations, we are forced to explicitly acknowledge that the velocity of the phase is the barycentric velocity. This fact is easily overlooked if one simply determines the equation for a phase without considering which of the many definitions of velocity is appropriate. Certainly, even the species velocity is a weighted sum of the velocities of the molecules that make up species i at the continuum scale.

For momentum conservation, the phase-based form is:

$$\sum_{i \in \mathcal{I}_s} \mathcal{P}_i = \mathcal{P} = \frac{D(\rho \mathbf{v})}{Dt} + \rho \mathbf{v} \mathbf{l} : \mathbf{d} - \nabla \cdot \mathbf{t} - \rho \mathbf{g} = \mathbf{0}. \quad (16)$$

Obtaining this expression requires that we define:

$$\mathbf{t} = \sum_{i \in \mathcal{I}_s} [\mathbf{t}_i - \rho \omega_i (\mathbf{v}_i - \mathbf{v}) (\mathbf{v}_i - \mathbf{v})] \quad (17)$$

and:

$$\mathbf{g} = \sum_{i \in \mathcal{I}_s} \omega_i \mathbf{g}_i. \quad (18)$$

The exchanges of momentum between species must also cancel within the phase, such that:

$$\sum_{i \in \mathcal{I}_s} (\mathbf{p}_i + r_i \mathbf{v}_i) = \sum_{i \in \mathcal{I}_s} (\mathbf{p}_i + r_i \mathbf{u}_i) = \mathbf{0}. \quad (19)$$

In Equation (17), we see that the stress tensor for the phase is impacted by the diffusion velocities, $\mathbf{u}_i$, where:

$$\mathbf{u}_i = \mathbf{v}_i - \mathbf{v}. \quad (20)$$

This is an impact that is not encountered if there are no diffusive processes in the phase. If one wishes, this extra term need not be included in the definition of the phase tensor, but can be retained as a separate contribution that can be accounted for if the diffusion can be modeled. For this approach, one could replace $\mathbf{t}$ with $\mathbf{t}^*$ and $\mathbf{t}^D$, where:

$$\mathbf{t} = \mathbf{t}^* + \mathbf{t}^D \quad (21)$$

and:

$$\mathbf{t}^* = \sum_{i \in \mathcal{I}_s} \mathbf{t}_i \quad (22)$$

and:

$$\mathbf{t}^D = - \sum_{i \in \mathcal{I}_s} \rho \omega_i \mathbf{u}_i \mathbf{u}_i. \quad (23)$$

The conservation of total energy for a phase is:

$$\sum_{i \in \mathcal{I}_s} \mathcal{E}_i = \mathcal{E} = \frac{D}{Dt} \left(U + \rho \frac{\mathbf{v} \cdot \mathbf{v}}{2} + \rho K_E \right) + \left(U + \rho \frac{\mathbf{v} \cdot \mathbf{v}}{2} + \rho K_E \right) \mathbf{l} : \mathbf{d}$$

$$-\nabla \cdot (\mathbf{q} + \mathbf{t} \cdot \mathbf{v}) - \rho \mathbf{g} \cdot \mathbf{v} - \sum_{i \in \mathcal{I}_s} \rho \omega_i \mathbf{g} \cdot \mathbf{u}_i - h = 0 . \quad (24)$$

In this equation,

$$U = \sum_{i \in \mathcal{I}_s} U_i , \quad (25)$$

$$K_E = \sum_{i \in \mathcal{I}_s} \omega_i \frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i , \quad (26)$$

$$\mathbf{q} = \mathbf{q}^* + \sum_{i \in \mathcal{I}_s} \left[\mathbf{t}_i - \left(U_i + \rho \omega_i \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathbf{l} \right] \cdot \mathbf{u}_i , \quad (27)$$

$$\mathbf{q}^* = \sum_{i \in \mathcal{I}_s} \mathbf{q}_i , \quad (28)$$

$$h = \sum_{i \in \mathcal{I}_s} h_i , \quad (29)$$

and:

$$\sum_{i \in \mathcal{I}_s} \left[e_i + \mathbf{p}_i \cdot \mathbf{v}_i + r_i \left(\frac{1}{2} \mathbf{v}_i \cdot \mathbf{v}_i \right) \right] = \sum_{i \in \mathcal{I}_s} \left[e_i + \mathbf{p}_i \cdot \mathbf{u}_i + r_i \left(\frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) \right] = 0 . \quad (30)$$

If desired, the quantity $U + \rho K_E$ can be combined to define an extended internal energy. The fact that K_E does not appear in most versions of the total energy equation suggests that it has been implicitly considered to be negligible or combined into the definition of internal energy. In a similar vein, the non-advective flux vector $\mathbf{q}$ can be broken into its contributing factors, if desired, or left as the combined form indicated here. In either event, the elements of the non-advective energy flux are explicitly known in terms of the contributions from individual species.

The entropy balance equation on a phase basis is obtained as a sum of the species balance given by Equation (6) summed over all species according to:

$$\sum_i \mathcal{S}_i = \mathcal{S} = \frac{D\eta}{Dt} + \eta \mathbf{l} : \mathbf{d} - \nabla \cdot \boldsymbol{\varphi} - b = \Lambda > 0 . \quad (31)$$

In this equation, we have defined:

$$\eta = \sum_{i \in \mathcal{I}_s} \eta_i , \quad (32)$$

$$\boldsymbol{\varphi} = \sum_{i \in \mathcal{I}_s} (\boldsymbol{\varphi}_i - \eta_i \mathbf{u}_i) , \quad (33)$$

$$b = \sum_{i \in \mathcal{I}_s} b_i , \quad (34)$$

and

$$\Lambda = \sum_{i \in \mathcal{I}_s} \Lambda_i > 0 . \quad (35)$$

The non-advective entropy flux may be expressed alternatively in terms of individual sums of its contributing factors from species-based non-advective flux and dispersion, if desired. Additionally, consistent with the second law of thermodynamics, the sum of Λ_i over the set of species gives a non-negative result, despite the fact that each of the Λ_i themselves is not necessarily zero.

Finally, the mathematical relation between the rate of change of body force potential and gravity given in Equation (9) can be summed over all species to provide:

$$\sum_{i \in \mathcal{I}_s} \mathcal{G}_i = \mathcal{G} = \frac{D\Psi}{Dt} + \Psi \mathbf{l} : \mathbf{d} + \rho \mathbf{v} \cdot \mathbf{g} - \sum_{i \in \mathcal{I}_s} \left(\rho \omega_i \frac{\partial \psi_i}{\partial t} + r_i \psi_i - \rho \omega_i \mathbf{u}_i \cdot \mathbf{g}_i \right) = 0. \quad (36)$$

In cases where the only body force is gravity, such that ψ_i and $\mathbf{g}_i$ are independent of chemical species, the last summation in this equation is zero.

4. Thermodynamic Relations

A final set of equations that is important for system modeling consists of the thermodynamic forms. These are different, in one regard, from the conservation and balance equations in that the species thermodynamic equations are obtained from those for the phase as a whole rather than *vice versa*. Here, we will make use of the classical irreversible thermodynamics (CIT) framework. This is the simplest extension to equilibrium thermodynamics and makes use of a local equilibrium assumption to assert that the dependence of energy on local variables is the same as that in equilibrium thermodynamics [4,12]. CIT has been found to be a suitable approach for describing many systems not at equilibrium, although it does not account for memory effects or non-local behavior. We have chosen to use CIT instead of rational thermodynamics (RT), because of the latter's inability to physically interpret the meaning of temperature and entropy in terms of their equilibrium counterparts [13,14].

The extensive Euler equation describing the thermodynamics of a phase is:

$$\mathbb{U} - \theta \mathbb{S} + p \mathbb{V} - \sum_{k \in \mathcal{I}_s} \mu_k \mathbb{M}_k = 0, \quad (37)$$

where θ is temperature, p is pressure and μ_k is the chemical potential of species k with units of energy per mass. The other variables are extensive quantities with $\mathbb{U}$ being energy; $\mathbb{S}$ is entropy; $\mathbb{V}$ is volume; and $\mathbb{M}_k$ is the mass of chemical species k . When the local equilibrium assumption applies, the Euler equation is expressed on a per unit volume basis as:

$$U - \theta \eta + p - \sum_{k \in \mathcal{I}_s} \mu_k \rho \omega_k = 0. \quad (38)$$

Differentiation of this expression using the material derivative, in light of the Gibbs–Duhem equation, gives:

$$\mathcal{T} = \frac{DU}{Dt} - \theta \frac{D\eta}{Dt} - \sum_{k \in \mathcal{I}_s} \mu_k \frac{D(\rho \omega_k)}{Dt} = 0. \quad (39)$$

To obtain the species-based thermodynamic relations, we will make use of partial mass quantities. For an extensive property $\mathbb{F}$, the corresponding partial mass quantity for the i -th species, $\overline{F}_i$, is:

$$\overline{F}_i = \left(\frac{\partial \mathbb{F}}{\partial \mathbb{M}_i} \right)_{p, \theta, \mathcal{M}_i}, \quad (40)$$

where $\mathcal{M}_i$ is the set of masses of chemical species, except species i . Based on Equation (37), we therefore derive:

$$\overline{U}_i - \theta \overline{S}_i + p \overline{V}_i - \mu_i = 0. \quad (41)$$

Multiplication of this equation by $\rho\omega_i$ provides the thermodynamic relation in terms of energy and entropy densities, such that:

$$U_i - \theta\eta_i + pX_i - \rho\omega_i\mu_i = 0, \quad (42)$$

where

$$U_i = \rho\omega_i\bar{U}_i, \quad (43)$$

$$\eta_i = \rho\omega_i\bar{S}_i, \quad (44)$$

and

$$X_i = \rho\omega_i\bar{V}_i. \quad (45)$$

For later use, we also observe that the species enthalpy per volume, H_i , is defined as:

$$H_i = U_i + pX_i. \quad (46)$$

The material derivative of Equation (42) is:

$$\mathcal{T}_i = \frac{DU_i}{Dt} - \theta \frac{D\eta_i}{Dt} + p \frac{DX_i}{Dt} - \mu_i \frac{D(\rho\omega_i)}{Dt} - \rho\omega_i \left(\frac{D\mu_i}{Dt} \right)_{p,\theta} = 0. \quad (47)$$

Summation of Equation (47) over all species i confirms the relation between Equations (39) and (47),

$$\mathcal{T} = \sum_{i \in \mathcal{I}_s} \mathcal{T}_i. \quad (48)$$

5. Combinations of Equations

In the preceding section, we have shown that a set of species-based relations may be summed over all species to obtain a phase-based equation. From a broader perspective, we can combine equations without summing over all species. Additionally, we can sum over equations for different species properties in such a way that mixed equations result. We can denote a general combined equation $\mathcal{C}_\lambda$ that involves a combination of all species-based equations as:

$$\begin{aligned} \mathcal{C}_\lambda = & \sum_{i \in \mathcal{I}_s} \lambda_{S_i} (S_i - \Lambda_i) + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{E}_i} \mathcal{E}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{P}_i} \mathcal{P}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{M}_i} \mathcal{M}_i \\ & + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{G}_i} \mathcal{G}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{T}_i} \mathcal{T}_i = 0. \end{aligned} \quad (49)$$

In this equation, each coefficient, λ , multiplies a quantity that is itself zero. Thus, the coefficients λ are arbitrary in that regardless of the values selected for λ , $\mathcal{C}_\lambda = 0$. Some particular selections of these coefficients provide particularly useful and interesting realizations for $\mathcal{C}_\lambda$. We will consider some of these special cases.

6. Secondary Conservation Equations

In addition to the primary species-based equations and the phase-based equations obtained by summation over the species, some additional secondary conservation equations may be derived from Equation (49) based on the selection of the coefficients. In this section, we will consider some secondary conservation equations for energy that are important in their own right, but that also have important implications for the formation of the constrained entropy inequality used to develop closure relations.

6.1. Energy Equation with Body Force Potential

When the body force is due to gravity only, it is sometimes convenient to express the total energy equation with the gravitational potential, replacing the gravitational acceleration. This can be accomplished for species k by setting λ_{Si} , λ_{Pi} , λ_{Mi} and λ_{Ti} equal to zero for $i \in \mathcal{J}_s$ and letting $\lambda_{\mathcal{E}i} = \lambda_{\mathcal{G}i} = \delta_{ik}$ in Equation (49). With these coefficients, we obtain the total energy equation for species k ,

$$\begin{aligned} \mathcal{C}_\lambda = \mathcal{E}_k + \mathcal{G}_k = & \frac{D_k}{Dt} \left(U_k + \frac{1}{2} \rho \omega_k \mathbf{v}_k \cdot \mathbf{v}_k + \Psi_k \right) + \left(U_k + \frac{1}{2} \rho \omega_k \mathbf{v}_k \cdot \mathbf{v}_k + \Psi_k \right) \mathbf{l} : \mathbf{d}_k \\ & - \nabla \cdot (\mathbf{q}_k + \mathbf{t}_k \cdot \mathbf{v}_k) - h_k - e_k - \mathbf{p}_k \cdot \mathbf{v}_k - r_k \left(\frac{1}{2} \mathbf{v}_k \cdot \mathbf{v}_k + \psi_k \right) - \rho \omega_k \frac{\partial \psi_k}{\partial t} = 0. \end{aligned} \quad (50)$$

The phase-based energy equation with gravitational potential can be obtained with λ_{Si} , λ_{Pi} , λ_{Mi} and λ_{Ti} equal to zero in Equation (49), but with $\lambda_{\mathcal{E}i} = \lambda_{\mathcal{G}i} = 1$ for $i \in \mathcal{J}_s$. We denote this particular combination of coefficients as $\mathcal{C}_\lambda = \mathcal{E} + \mathcal{G}$ and obtain:

$$\mathcal{E} + \mathcal{G} = \sum_{i \in \mathcal{J}_s} \mathcal{E}_i + \sum_{i \in \mathcal{J}_s} \mathcal{G}_i = \sum_{i \in \mathcal{J}_s} (\mathcal{E}_i + \mathcal{G}_i) = 0, \quad (51)$$

or

$$\begin{aligned} \mathcal{E} + \mathcal{G} = & \frac{D}{Dt} \left(U + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \rho K_E + \Psi \right) + \left(U + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \rho K_E + \Psi \right) \mathbf{l} : \mathbf{d} \\ & - \nabla \cdot (\mathbf{q} + \mathbf{t} \cdot \mathbf{v}) - h - \sum_{k \in \mathcal{J}_s} \left(r_k \psi_k + \rho \omega_k \frac{\partial \psi_k}{\partial t} \right) = 0. \end{aligned} \quad (52)$$

This equation is an equivalent alternative to Equation (24). Of importance, as revealed in Equation (51), is that because the λ coefficients are all constants (equal to either zero or one), one obtains a unique equation for $\mathcal{E} + \mathcal{G}$. One can equivalently sum $\mathcal{E}_i$ over all species and add it to the sum of $\mathcal{G}_i$ over all species, or else sum the combination of $\mathcal{E}_i + \mathcal{G}_i$ over all species to obtain the same result. This seemingly innocuous observation will be seen to be important subsequently.

6.2. Mechanical Energy Conservation

A commonly used secondary equation is what is referred to as the mechanical energy conservation equation. We will refer to this as a secondary conservation equation, because it makes use of non-zero, non-constant λ values in more than one of the summations in Equation (49). The mechanical energy

conservation equation is obtained from Equation (49) as a combination of mass and momentum by first setting $\lambda_{\mathcal{S}i}$, $\lambda_{\mathcal{E}i}$, $\lambda_{\mathcal{G}i}$ and $\lambda_{\mathcal{T}i}$ equal to zero for all $i \in \mathcal{I}_s$ to obtain:

$$\mathcal{C}_\lambda = \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{P}i} \cdot \mathcal{P}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i = 0. \quad (53)$$

We can now obtain species-based and phase-based explicit equation forms.

For species k , the mechanical energy conservation equation is obtained by setting:

$$\lambda_{\mathcal{P}i} = \mathbf{v}_k \delta_{ik} \quad \text{for } k \in \mathcal{I}_s \quad (54)$$

and

$$\lambda_{\mathcal{M}i} = -\frac{1}{2} \mathbf{v}_k \cdot \mathbf{v}_k \delta_{ik} \quad \text{for } k \in \mathcal{I}_s. \quad (55)$$

For this selection of parameters, we denote $\mathcal{C}_\lambda$ as $\mathcal{E}_{\text{me}_k}$ and obtain:

$$\mathcal{E}_{\text{me}_k} = \mathbf{v}_k \cdot \mathcal{P}_k - \frac{1}{2} \mathbf{v}_k \cdot \mathbf{v}_k \mathcal{M}_k = 0. \quad (56)$$

This equation can be expanded out to obtain the explicit species mechanical energy conservation equation,

$$\begin{aligned} \mathcal{E}_{\text{me}_k} = \frac{D_k}{Dt} \left(\frac{1}{2} \rho \omega_k \mathbf{v}_k \cdot \mathbf{v}_k \right) + \frac{1}{2} \rho \omega_k \mathbf{v}_k \cdot \mathbf{v}_k \mathbf{l} : \mathbf{d}_k - (\nabla \cdot \mathbf{t}_k) \cdot \mathbf{v}_k \\ - \rho \omega_k \mathbf{g}_k \cdot \mathbf{v}_k - \mathbf{p}_k \cdot \mathbf{v}_k - \frac{1}{2} r_k \mathbf{v}_k \cdot \mathbf{v}_k = 0. \end{aligned} \quad (57)$$

Based on this result, we might expect that the mechanical energy equation for the phase is the sum of the species equations. We denote this form of the phase mechanical energy equation as $\mathcal{E}_{\text{me}}^*$ with:

$$\mathcal{E}_{\text{me}}^* = \sum_{k \in \mathcal{I}_s} \left(\mathbf{v}_k \cdot \mathcal{P}_k - \frac{1}{2} \mathbf{v}_k \cdot \mathbf{v}_k \mathcal{M}_k \right) = 0. \quad (58)$$

Expansion of this equation to its explicit form gives the expression:

$$\begin{aligned} \mathcal{E}_{\text{me}}^* = \frac{D}{Dt} \left(\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \rho K_E \right) + \left(\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} + \rho K_E \right) \mathbf{l} : \mathbf{d} - \nabla \cdot (\mathbf{t} \cdot \mathbf{v}) - \rho \mathbf{g} \cdot \mathbf{v} - \sum_{k \in \mathcal{I}_s} \rho \omega_k \mathbf{g}_k \cdot \mathbf{u}_k \\ + \mathbf{t}^* : \mathbf{d} + \sum_{k \in \mathcal{I}_s} \left\{ \nabla \cdot \left[\left(\frac{1}{2} \rho \omega_k \mathbf{u}_k \cdot \mathbf{u}_k \right) \mathbf{u}_k \right] - (\nabla \cdot \mathbf{t}_k) \cdot \mathbf{u}_k - \mathbf{p}_k \cdot \mathbf{u}_k - \frac{1}{2} \mathbf{u}_k \mathbf{u}_k r_k \right\} = 0. \end{aligned} \quad (59)$$

An alternative approach to obtaining a mechanical energy equation for a phase is to start with phase-based momentum and mass conservation equations. Beginning with Equation (53), we propose that the λ coefficients be independent of chemical species. The result is:

$$\mathcal{C}_\lambda = \lambda_{\mathcal{P}} \cdot \sum_{i \in \mathcal{I}_s} \mathcal{P}_i + \lambda_{\mathcal{M}} \sum_{i \in \mathcal{I}_s} \mathcal{M}_i = 0. \quad (60)$$

The sums in this equation are defined, respectively, as $\mathcal{P}$ in Equation (16) and $\mathcal{M}$ in Equation (11), so that:

$$\mathcal{C}_\lambda = \lambda_{\mathcal{P}} \cdot \mathcal{P} + \lambda_{\mathcal{M}} \mathcal{M} = 0. \quad (61)$$

We now select the coefficients according to

$$\lambda_{\mathcal{P}} = \mathbf{v} \quad (62)$$

and

$$\lambda_{\mathcal{M}} = -\frac{1}{2}\mathbf{v} \cdot \mathbf{v} . \quad (63)$$

For this selection of parameters, we denote $\mathcal{C}_\lambda$ as $\mathcal{E}_{\text{me}}$ and obtain:

$$\mathcal{E}_{\text{me}} = \mathbf{v} \cdot \mathcal{P} - \frac{1}{2}\mathbf{v} \cdot \mathbf{v} \mathcal{M} = 0 \quad (64)$$

which can be expanded out to the explicit form,

$$\mathcal{E}_{\text{me}} = \frac{D}{Dt} \left(\frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} \right) + \frac{1}{2} \rho \mathbf{v} \cdot \mathbf{v} \mathbf{l} : \mathbf{d} - \nabla \cdot (\mathbf{t} \cdot \mathbf{v}) + \mathbf{t} : \mathbf{d} - \rho \mathbf{g} \cdot \mathbf{v} = 0 , \quad (65)$$

where the expression given in Equation (65) is typically referred to as the mechanical energy equation.

What is important to recognize is the fact that although both Equations (58) and (64) have been identified as mechanical energy equations, they contain different terms. Despite including different terms, both $\mathcal{E}_{\text{me}}^*$ and $\mathcal{E}_{\text{me}}$ equal zero. This can be made more concrete if we subtract these two forms to obtain:

$$\mathcal{E}_{\text{me}}^* - \mathcal{E}_{\text{me}} = \sum_{k \in \mathcal{I}_s} \mathbf{u}_k \cdot \left(\mathcal{P}_k - \mathbf{v} \mathcal{M}_k - \frac{1}{2} \mathbf{u}_k \mathcal{M}_k \right) = 0 , \quad (66)$$

or, after expanding out the right side,

$$\begin{aligned} \mathcal{E}_{\text{me}}^* - \mathcal{E}_{\text{me}} = \sum_{k \in \mathcal{I}_s} \left[\frac{D_k}{Dt} \left(\rho \omega_k \frac{1}{2} \mathbf{u}_k \cdot \mathbf{u}_k \right) + \rho \omega_k \frac{1}{2} \mathbf{u}_k \cdot \mathbf{u}_k \mathbf{l} : \mathbf{d}_k - (\nabla \cdot \mathbf{t}_k) \cdot \mathbf{u}_k \right. \\ \left. - \rho \omega_k \mathbf{g}_k \cdot \mathbf{u}_k - \mathbf{p}_k \cdot \mathbf{u}_k - r_k \frac{1}{2} \mathbf{u}_k \cdot \mathbf{u}_k \right] = 0 . \end{aligned} \quad (67)$$

We see that the equation forms provided by $\mathcal{E}_{\text{me}}^*$ and $\mathcal{E}_{\text{me}}$ are identical in the absence of diffusion. Otherwise, these equations are different in the way that they account for diffusion processes as being part of mechanical energy. Both equations are correct, but the designation of one as opposed to the other as “the” mechanical energy equation is somewhat arbitrary. This observation reinforces the notion that a mechanical energy equation is a secondary conservation relation in that it balances a portion of energy, where the portion has been selected arbitrarily. From a more general perspective, we can select coefficients in Equation (49) rather arbitrarily, assuring that the equation dimensions are homogeneous, and refer to the resultant equation by any name desired. However, it is only the fundamental species conservation and balance equations and their sum over all species that are not based on a heuristic division of properties.

6.3. Internal Energy Conservation

Another commonly used secondary equation is the internal energy conservation equation. The internal energy plus mechanical energy is equal to the total energy. Therefore, if we denote the internal energy equation for species k as $\mathcal{U}_k$, by definition, we obtain:

$$\mathcal{U}_k = \mathcal{E}_k - \mathcal{E}_{\text{me}_k} = 0 \quad \text{for } k \in \mathcal{I}_s . \quad (68)$$

Substitution of Equation (56) into this definition gives:

$$\mathcal{U}_k = \mathcal{E}_k - \mathbf{v}_k \cdot \mathcal{P}_k + \frac{1}{2} \mathbf{v}_k \cdot \mathbf{v}_k \mathcal{M}_k = 0 \quad \text{for } k \in \mathcal{J}_s. \quad (69)$$

If we substitute Equations (5) and (57) into Equation (68), we obtain the expanded form of the species internal energy equation,

$$\mathcal{U}_k = \frac{D_k U_k}{Dt} + U_k \mathbf{l} : \mathbf{d}_k - \nabla \cdot \mathbf{q}_k - \mathbf{t}_k : \mathbf{d}_k - h_k - e_k = 0. \quad (70)$$

We can sum $\mathcal{U}_k$ over all species to obtain an alternative form of the internal energy for a phase, $\mathcal{U}^*$, such that:

$$\mathcal{U}^* = \sum_{k \in \mathcal{J}_s} \mathcal{U}_k = \sum_{k \in \mathcal{J}_s} \left(\mathcal{E}_k - \mathbf{v}_k \cdot \mathcal{P}_k + \frac{1}{2} \mathbf{v}_k \cdot \mathbf{v}_k \mathcal{M}_k \right). \quad (71)$$

Based on the first equality in Equation (24) and on Equation (58), this equation confirms that:

$$\mathcal{U}^* = \mathcal{E} - \mathcal{E}_{\text{me}}^*. \quad (72)$$

This expression may be expanded out to obtain:

$$\mathcal{U}^* = \frac{DU}{Dt} + U \mathbf{l} : \mathbf{d} - \nabla \cdot \mathbf{q} - h - \mathbf{t}^* : \mathbf{d} + \sum_{k \in \mathcal{J}_s} \left\{ (\nabla \cdot \mathbf{t}_k) \cdot \mathbf{u}_k - \nabla \cdot \left[\left(\frac{1}{2} \rho \omega_k \mathbf{u}_k \mathbf{u}_k \right) \mathbf{u}_k \right] - e_k \right\} = 0. \quad (73)$$

The most commonly employed form of the phase-based internal energy equation is obtained from Equation (49) with the appropriate choice of the coefficients. An alternative, but equivalent, derivation is based on defining the internal energy equation, $\mathcal{U}$, as:

$$\mathcal{U} = \mathcal{E} - \mathcal{E}_{\text{me}} = 0. \quad (74)$$

With Equation (64) substituted in, we get an expression that can be derived from Equation (49),

$$\mathcal{U} = \mathcal{E} - \mathbf{v} \cdot \mathcal{P} + \frac{1}{2} \mathbf{v} \cdot \mathbf{v} \mathcal{M} = 0. \quad (75)$$

Substitution of Equations (24) and (65) into Equation (70) yields:

$$\mathcal{U} = \frac{D}{Dt} (U + \rho K_E) + (U + \rho K_E) \mathbf{l} : \mathbf{d} - \nabla \cdot \mathbf{q} - \mathbf{t} : \mathbf{d} - \sum_{i \in \mathcal{J}_s} \rho \omega_i \mathbf{g}_i \cdot \mathbf{u}_i - h = 0. \quad (76)$$

Typically, the dispersion kinetic energy, K_E , is not explicitly indicated in this equation. It is either combined into the definition of U or omitted as being negligibly small. Furthermore, when $\mathbf{g}_i$ is independent of the chemical species, the summation term in Equation (76) is zero.

The difference in the two forms of the internal energy equation resides in whether the dispersion terms are included in the mechanical energy equation or the internal energy equation. Subtraction of Equation (75) from Equation (71) gives:

$$\mathcal{U}^* - \mathcal{U} = - \sum_{k \in \mathcal{J}_s} \mathbf{u}_k \cdot \left(\mathcal{P}_k - \mathbf{v} \mathcal{M}_k - \frac{1}{2} \mathbf{u}_k \mathcal{M}_k \right) = 0. \quad (77)$$

The right side of this equation is the negative of the right side of Equation (67).

Again, although $\mathcal{U}^*$ and $\mathcal{U}$ are both equal to zero, notationally, they contain different terms. Despite their differences, either form is a reasonable choice as the “internal energy” equation.

We observe that:

$$\mathcal{U}^* + \mathcal{E}_{\text{me}}^* = \mathcal{U} + \mathcal{E}_{\text{me}} = \mathcal{E}. \quad (78)$$

Thus, the difference in the the alternative expressions for the internal energy and mechanical energy equations lies in the location of the cleavage point for splitting the total energy equation into two constituent parts. We can make two additional observations. First, one can propose a “total energy equation” that is a sum of internal energy and mechanical energy equations as $\mathcal{E}_1$, where:

$$\mathcal{E}_1 = \mathcal{U}^* + \mathcal{E}_{\text{me}} = 0 \quad (79)$$

or as $\mathcal{E}_2$, where

$$\mathcal{E}_2 = \mathcal{U} + \mathcal{E}_{\text{me}}^* = 0. \quad (80)$$

However, neither $\mathcal{E}_1$ nor $\mathcal{E}_2$ is equal to $\mathcal{E}$, the actual total energy equation. The total energy equation is motivated by conservation principles. On the other hand, both Equations (79) and (80) are secondary conservation balances that account for total energy to some degree, but handle the contributions due to dispersion differently. They are not primary conservation equations. As with all secondary conservation equations, a claim about what property is actually being conserved is somewhat arbitrary and dependent on interpretation. The preceding examples show how the fundamental species conservation equations can be combined to obtain secondary forms. Another motivation for combining the equations, as in Equation (49), is to obtain closure relations. This combination leads to some interesting conclusions concerning the analysis of the entropy balance to obtain closed conservation equations, as will be demonstrated in the next section.

7. Entropy Equation Analysis

Rearrangement of Equation (49) by moving the entropy generation portion to the right side gives:

$$\begin{aligned} \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{S}i} \mathcal{S}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{E}i} \mathcal{E}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{P}i} \cdot \mathcal{P}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i \\ + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{G}i} \mathcal{G}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{T}i} \mathcal{T}_i = \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{S}i} \Lambda_i. \end{aligned} \quad (81)$$

When we are interested in obtaining an expression for the entropy generation, we select $\lambda_{\mathcal{S}i} = 1$ for all i and make use of the definition of the total entropy generation, Λ , as defined in Equation (35), such that:

$$\begin{aligned} \sum_{i \in \mathcal{I}_s} \mathcal{S}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{E}i} \mathcal{E}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{P}i} \cdot \mathcal{P}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i \\ + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{G}i} \mathcal{G}_i + \sum_{i \in \mathcal{I}_s} \lambda_{\mathcal{T}i} \mathcal{T}_i = \Lambda \geq 0. \end{aligned} \quad (82)$$

It is important to realize that Equation (82) provides the local entropy generation rate regardless of the values selected for the remaining λ coefficients. This selection will lead to different groupings in

surviving terms that are summed up to obtain the generation rate, but all groupings will provide the same value of Λ . A combination of the equations in this fashion is similar to that employed in Liu's method [15,16].

If one is to use Equation (82) as a basis for developing closure relations for the conservation equations, it is important to select the λ coefficients, such that time derivatives are eliminated, to the degree possible, so that the entropy generation is expressed as a sum of products of forces and fluxes. It should be fairly clear that depending on whether species-based or phase-based equations are desired in modeling a system, the values of λ employed will be different, and the closure relations required and obtained will also be different. Because the microscale temperature of all species at a point is the same, there is no need to formulate energy-based species equations. However, we will formulate species-based momentum and mass conservation equations. These formulations will be explored in the subsequent subsections.

7.1. Species-Based Mass and Momentum Equations

One approach to modeling flow and transport is to use species-based mass and momentum equations. In this approach, the velocity and mass fraction of each species is solved for. Because a momentum equation is employed for each species, there is no need for a closure relation for a dispersion vector. To close the equation system, expressions are required for the stress tensor $\mathbf{t}_i$ for each species. For the present formulation, the energy is considered on a phase basis. Therefore, in Equation (82),

$$\lambda_{\mathcal{E}i} = \lambda_{\mathcal{E}} \quad \text{for } i \in \mathcal{J}_s, \quad (83)$$

$$\lambda_{\mathcal{G}i} = \lambda_{\mathcal{G}} \quad \text{for } i \in \mathcal{J}_s, \quad (84)$$

and

$$\lambda_{\mathcal{T}i} = \lambda_{\mathcal{T}} \quad \text{for } i \in \mathcal{J}_s. \quad (85)$$

Substitution of these relations into Equation (82) and pulling the coefficients that are species independent out of the summations gives:

$$\begin{aligned} \sum_{i \in \mathcal{J}_s} \mathcal{S}_i + \lambda_{\mathcal{E}} \sum_{i \in \mathcal{J}_s} \mathcal{E}_i + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{P}i} \mathcal{P}_i + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i \\ + \lambda_{\mathcal{G}} \sum_{i \in \mathcal{J}_s} \mathcal{G}_i + \lambda_{\mathcal{T}} \sum_{i \in \mathcal{J}_s} \mathcal{T}_i = \Lambda \geq 0. \end{aligned} \quad (86)$$

Now, make use of the definitions of phase-based equations as sums of primary conservation equations given in Equations (24), (31), (36) and (48) to obtain:

$$\mathcal{S} + \lambda_{\mathcal{E}} \mathcal{E} + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{P}i} \mathcal{P}_i + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i + \lambda_{\mathcal{G}} \mathcal{G} + \lambda_{\mathcal{T}} \mathcal{T} = \Lambda \geq 0. \quad (87)$$

This equation is written in terms of the primary conservation equations of interest. Only the momentum and mass conservation equations are written on a species bases. This equation provides the entropy generation rate written in terms of the variables that actually appear in the equations of interest.

The values of λ that cancel the most time derivatives from Equation (87) are as follows:

$$\lambda_{\mathcal{E}} = -\frac{1}{\theta}, \quad (88)$$

$$\lambda_{\mathcal{P}i} = \frac{\mathbf{v}_i}{\theta}, \quad (89)$$

$$\lambda_{\mathcal{M}i} = \frac{1}{\theta} \left(\mu_i - \frac{\mathbf{v}_i \cdot \mathbf{v}_i}{2} \right), \quad (90)$$

$$\lambda_{\mathcal{G}} = 0, \quad (91)$$

and

$$\lambda_{\mathcal{T}} = \frac{1}{\theta}. \quad (92)$$

After substitution of these values, Equation (87) becomes:

$$\mathcal{S} - \frac{1}{\theta} \mathcal{E} + \sum_{i \in \mathcal{I}_s} \frac{\mathbf{v}_i}{\theta} \cdot \mathcal{P}_i + \sum_{i \in \mathcal{I}_s} \frac{1}{\theta} \left(\mu_i - \frac{\mathbf{v}_i \cdot \mathbf{v}_i}{2} \right) \mathcal{M}_i + \frac{1}{\theta} \mathcal{T} = \Lambda \geq 0. \quad (93)$$

This equation, based on primary conservation equations, may be worked with to obtain closure relations, because the entropy generation rate, Λ , will be in terms of independent force-flux pairs.

We can gain insight into the closure process by expressing $\mathcal{E}$ as a sum over the species energy equation as in Equation (24), and then regrouping the terms in Equation (93) to obtain:

$$\mathcal{S} - \sum_{i \in \mathcal{I}_s} \frac{1}{\theta} \left(\mathcal{E}_i - \mathbf{v}_i \cdot \mathcal{P}_i + \frac{\mathbf{v}_i \cdot \mathbf{v}_i}{2} \mathcal{M}_i \right) + \sum_{i \in \mathcal{I}_s} \frac{1}{\theta} \mu_i \mathcal{M}_i + \frac{1}{\theta} \mathcal{T} = \Lambda \geq 0. \quad (94)$$

From Equation (71), we see that the first summation is equal to $\mathcal{U}^*$, so that Equation (93) may be written equivalently:

$$\mathcal{S} - \frac{1}{\theta} \mathcal{U}^* + \sum_{i \in \mathcal{I}_s} \frac{1}{\theta} \mu_i \mathcal{M}_i + \frac{1}{\theta} \mathcal{T} = \Lambda \geq 0. \quad (95)$$

It is important to emphasize that this equation arises when one is making use of species-based momentum equations. It is easy to lose sight of this fact, since the momentum equation does not appear explicitly in Equation (95). Note the appearance of $\mathcal{U}^*$, rather than $\mathcal{U}$, as the appropriate internal energy equation to be used in developing closure relations. When the species-based momentum equation is used, one does not obtain closure relations for the dispersive velocities, $\mathbf{u}_i$, because the species velocity itself is solved for via the momentum equation. In fact, use of this equation as a basis for obtaining a closure relation for the diffusive velocity would be incorrect. Similarly, although $\mathcal{U}$ can replace $\mathcal{U}^*$ in Equation (95), to still provide a correct equation, this equation would not be appropriate for obtaining closure relations for the set of conservation equations of interest. With the indicated equations substituted into Equation (95), or its equivalent form, Equation (93), closure relations for $\mathbf{t}_i$ and $\mathbf{p}_i$ may be developed.

After algebraic rearrangement that also makes use of the Euler thermodynamic equations for a phase, Equation (94) expands to:

$$\begin{aligned} & - \nabla \cdot \left(\varphi - \frac{1}{\theta} \left\{ \mathbf{q} + \sum_{i \in \mathcal{I}_s} \left[\rho \omega_i \left(\mu_i + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathbf{l} - (\mathbf{t}_i + p X_i \mathbf{l}) \right] \cdot \mathbf{u}_i \right\} \right) \\ & - \left(b - \frac{1}{\theta} h \right) + \frac{1}{\theta} \sum_{i \in \mathcal{I}_s} (\mathbf{t}_i + p X_i \mathbf{l}) : \mathbf{d}_i \\ & - \left\{ \mathbf{q} + \sum_{i \in \mathcal{I}_s} \left[\rho \omega_i \left(\bar{H}_i + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathbf{l} - (\mathbf{t}_i + p X_i \mathbf{l}) \right] \cdot \mathbf{u}_i \right\} \cdot \nabla \left(\frac{1}{\theta} \right) \end{aligned}$$

$$\begin{aligned}
& -\frac{1}{\theta} \sum_{i \in \mathcal{J}_s} [\mathbf{p}_i + \rho \omega_i \nabla (\mu_i|_{\theta} + \psi_i) - \nabla (pX_i) + \rho \omega_i \mathbf{g}_i] \cdot (\mathbf{v}_i - \mathbf{v}_r) \\
& - \frac{1}{\theta} \sum_{i \in \mathcal{J}_s} \left[\mu_i + \frac{1}{2} (\mathbf{v}_i - \mathbf{v}_r) \cdot (\mathbf{v}_i - \mathbf{v}_r) \right] r_i = \Lambda \geq 0.
\end{aligned} \quad (96)$$

In obtaining this equation, we have made use of the thermodynamic identity:

$$\nabla \mu_i = \nabla \mu_i|_{\theta} + \theta (\bar{H}_i - \mu_i) \nabla \left(\frac{1}{\theta} \right). \quad (97)$$

Further investigation of Equation (96) to develop closure relations is possible. However, that is not the main point of the derivation. What we want to show is that this form of the equation is consistent with force-flux forms of the entropy inequality. Equation (96) can be used to obtain closure relations for $\mathbf{t}_i$, $\mathbf{q}$ and $\mathbf{p}_i$.

7.2. Species-Based Mass and Phased-Based Momentum

An alternative approach to obtaining a model of chemical species flow and transport is to formulate the mass conservation equations on a species basis while formulating a single momentum equation for the phase as a whole. This approach is used predominantly and is specified based on Equation (82) with the appropriate selection of the coefficients. For this approach, Equations (83)–(85) are employed, so that the energy and thermodynamic equations are formulated on a phase basis. In addition, the condition is imposed that the multipliers for the species-based momentum equation are independent of the chemical species, so that:

$$\lambda_{\mathcal{P}i} = \lambda_{\mathcal{P}} \quad \text{for } i \in \mathcal{J}_s. \quad (98)$$

These coefficient conditions can be substituted into Equation (82) to obtain:

$$\begin{aligned}
& \sum_{i \in \mathcal{J}_s} \mathcal{S}_i + \lambda_{\mathcal{E}} \sum_{i \in \mathcal{J}_s} \mathcal{E}_i + \lambda_{\mathcal{P}} \cdot \sum_{i \in \mathcal{J}_s} \mathcal{P}_i + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i \\
& + \lambda_{\mathcal{G}} \sum_{i \in \mathcal{J}_s} \mathcal{G}_i + \lambda_{\mathcal{T}} \sum_{i \in \mathcal{J}_s} \mathcal{T}_i = \Lambda \geq 0,
\end{aligned} \quad (99)$$

where the coefficients that are independent of species have been pulled outside of the summation signs. The summations of species-based fundamental equations over all of the species yields the phase-based equations, so it is that Equation (99) can be expressed as:

$$\mathcal{S} + \lambda_{\mathcal{E}} \mathcal{E} + \lambda_{\mathcal{P}} \cdot \mathcal{P} + \sum_{i \in \mathcal{J}_s} \lambda_{\mathcal{M}i} \mathcal{M}_i + \lambda_{\mathcal{G}} \mathcal{G} + \lambda_{\mathcal{T}} \mathcal{T} = \Lambda \geq 0. \quad (100)$$

Equation (100) differs from Equation (87) in that only one momentum coefficient is needed and the contributions of the different species to the overall momentum has been made implicit.

The next task is to select values of the remaining λ coefficients that eliminate the time derivatives to the degree possible. The values determined after substitution of the conservation and thermodynamic equations into Equation (100) are:

$$\lambda_{\mathcal{E}} = -\frac{1}{\theta}, \quad (101)$$

$$\lambda_{\mathcal{P}} = \frac{\mathbf{v}}{\theta}, \quad (102)$$

$$\lambda_{\mathcal{M}i} = \frac{1}{\theta} \left(\mu_i - \frac{\mathbf{v} \cdot \mathbf{v}}{2} + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right), \quad (103)$$

$$\lambda_{\mathcal{G}} = 0, \quad (104)$$

and

$$\lambda_{\mathcal{T}} = \frac{1}{\theta}. \quad (105)$$

Note that the fact that only a single velocity is being solved for has led to $\lambda_{\mathcal{M}i}$ being different from the value obtained with Equation (90) for the species-based momentum case. Substitution of Equations (101)–(105) into Equation (100) gives:

$$\mathcal{S} - \frac{1}{\theta} \mathcal{E} + \frac{\mathbf{v}}{\theta} \cdot \mathcal{P} + \sum_{i \in \mathcal{J}_s} \frac{1}{\theta} \left(\mu_i - \frac{\mathbf{v} \cdot \mathbf{v}}{2} + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathcal{M}_i + \frac{1}{\theta} \mathcal{T} = \Lambda \geq 0, \quad (106)$$

Because only one momentum equation is employed, this equation will be used to obtain closure relations for $\mathbf{t}$ and the diffusion velocity, $\mathbf{u}$. Neither the species velocities, $\mathbf{v}_i$, nor the species-based stress tensors, $\mathbf{t}_i$, appear in the formulation. Furthermore, the intraphase momentum exchange term does not enter the formulation.

Because $\mathbf{v}$ is independent of chemical species, we can sum over the species mass conservation equation that multiplies this term, so that:

$$\sum_{i \in \mathcal{J}_s} \frac{1}{\theta} \left(\mu_i - \frac{\mathbf{v} \cdot \mathbf{v}}{2} + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathcal{M}_i = \sum_{i \in \mathcal{J}_s} \frac{1}{\theta} \left(\mu_i + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathcal{M}_i - \frac{1}{\theta} \left(\frac{\mathbf{v} \cdot \mathbf{v}}{2} \right) \mathcal{M}. \quad (107)$$

Substitution of this expression into Equation (106) and regrouping the terms yields:

$$\mathcal{S} - \frac{1}{\theta} \left(\mathcal{E} - \mathbf{v} \cdot \mathcal{P} + \frac{\mathbf{v} \cdot \mathbf{v}}{2} \mathcal{M} \right) + \sum_{i \in \mathcal{J}_s} \frac{1}{\theta} \left(\mu_i + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathcal{M}_i + \frac{1}{\theta} \mathcal{T} = \Lambda \geq 0. \quad (108)$$

We can then make use of the definition given by Equation (75) for a phase-based internal energy equation to simplify Equation (108) to:

$$\mathcal{S} - \frac{1}{\theta} \mathcal{U} + \sum_{i \in \mathcal{J}_s} \frac{1}{\theta} \left(\mu_i + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathcal{M}_i + \frac{1}{\theta} \mathcal{T} = \Lambda \geq 0. \quad (109)$$

The differences between Equations (95) and (109) are important. They have been derived under different scenarios. The former deals with species-based momentum equations and is useful for obtaining closure relations for $\mathbf{t}_i$ and $\mathbf{p}_i$. The latter makes use of a phase-based momentum equation and is useful for obtaining closure relations for $\mathbf{t}$ and $\mathbf{u}_i$. To achieve these ends, the equations make use of different multipliers of the species-based mass conservation equation. Also of importance is the fact that if one wishes to make use of an “internal energy equation”, different forms are appropriate for the two equations. This points to the fact that assembling an entropy inequality using secondary conservation equations directly can lead one down the wrong path. One can replace $\mathcal{U}$ in Equation (109) with $\mathcal{U}^*$, and the result will still be correct and true, without any other changes. However, the utility of the equation for obtaining closure relations will be compromised.

Substitution of the indicated equations into Equation (109), cancellation of the material derivatives as possible and rearrangement of the resultant equation yields:

$$\begin{aligned}
 & -\nabla \cdot \left\{ \varphi - \frac{1}{\theta} \left[\mathbf{q} + \sum_{i \in \mathcal{I}_s} \rho \omega_i \left(\mu_i + \frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) \mathbf{u}_i \right] \right\} \\
 & - \left\{ b - \frac{1}{\theta} \left[h - \sum_{i \in \mathcal{I}_s} \rho \omega_i \frac{D}{Dt} \left(\frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) \right] \right\} \\
 & + \frac{1}{\theta} (p \mathbf{I} + \mathbf{t}) : \mathbf{d} \\
 & - \left[\mathbf{q} + \sum_{i \in \mathcal{I}_s} \rho \omega_i \left(\bar{H}_i + \frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) \mathbf{u}_i \right] \cdot \nabla \left(\frac{1}{\theta} \right) \\
 & - \frac{1}{\theta} \sum_{i \in \mathcal{I}_s} \rho \omega_i \mathbf{u}_i \cdot \nabla \left[\mu_i|_{\theta} + \frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i + \psi_i - \left(\mu_r|_{\theta} + \frac{1}{2} \mathbf{u}_r \cdot \mathbf{u}_r + \psi_r \right) \right] \\
 & - \frac{1}{\theta} \sum_{i \in \mathcal{I}_s} \left(\mu_i + \frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) r_i = \Lambda \geq 0 .
 \end{aligned} \tag{110}$$

In contrast to Equation (96), this equation can be used to obtain closure relations for $\mathbf{t}$, $\mathbf{q}$ and $\mathbf{u}_i$. Thus, the stress tensor is obtained on an entity basis for use in the entity-based momentum equation. The fact that the equation system is written in terms of the phase velocity also requires that a closure relation be obtained for the dispersion vector, $\mathbf{u}_i$ for each species i . The species dispersion kinetic energy that appears in Equation (110) is typically taken to be unimportant in obtaining linearized closure relations.

8. Example: Two-Species Fluid

The entropy inequalities given by Equation (96) for species-based momentum and mass conservation equations and Equation (110) for a phase-based momentum and species-based mass conservation equations can be used to develop closure relations for multi-species systems. Here, for the purposes of demonstration, we will restrict the system to being composed of two species, A and B , such that:

$$\mathcal{I}_s = \{A, B\} . \tag{111}$$

Additionally, we will consider the situation where the only body force is due to gravity, such that:

$$\mathbf{g}_A = \mathbf{g}_B = \mathbf{g} \tag{112}$$

and

$$\psi_A = \psi_B = \psi \tag{113}$$

The chemical reaction rate expressions can be rearranged making use of the chemical affinity [4]. However, this will not be addressed here, because our interest is in fluxes, rather than the reaction rates. For the purposes of this example, we will not consider cross-coupling that gives rise to phenomena, such as the Dufour and Soret effects. These are neglected in the interest of simplicity, only as they do not present significant theoretical challenges. We will obtain sets of mass, momentum and energy equations based on the two alternative approaches previously described.

8.1. Closed Species-Based Mass and Momentum Conservation Equations

This situation makes use of Equation (96). The entropy and energy fluxes are assumed to be related according to:

$$\varphi - \frac{1}{\theta} \left\{ \mathbf{q} + \sum_{i \in \mathcal{I}_s} \left[\rho \omega_i \left(\mu_i + \frac{\mathbf{u}_i \cdot \mathbf{u}_i}{2} \right) \mathbf{l} - (\mathbf{t}_i + p X_i \mathbf{l}) \right] \cdot \mathbf{u}_i \right\} = 0. \quad (114)$$

The body sources of entropy and energy are assumed to be related with:

$$b - \frac{1}{\theta} h = 0. \quad (115)$$

It is perhaps interesting to note that these two equations are respectively equivalent to:

$$\sum_{i \in \mathcal{I}_s} \left(\varphi_i - \frac{1}{\theta} \mathbf{q}_i \right) = 0 \quad (116)$$

and

$$\sum_{i \in \mathcal{I}_s} \left(b_i - \frac{1}{\theta} h_i \right) = 0 \quad (117)$$

because of the definitions of the variables, φ , $\mathbf{q}$, b and h , as provided in Equations (33), (27), (34) and (29), respectively. Linearization of the remaining fluxes in Equation (96), except for the reaction term, as functions of conjugate forces yields:

$$\mathbf{t}_i + p X_i \mathbf{l} = \hat{\mathbf{a}}_{4i} : \mathbf{d}_i \quad \text{for } i \in \{A, B\}, \quad (118)$$

$$\mathbf{q} + \rho (\bar{H}_A - \bar{H}_B) \omega_A (1 - \omega_A) (\mathbf{v}_A - \mathbf{v}_B) = -\hat{\mathbf{k}}_\theta \cdot \nabla \left(\frac{1}{\theta} \right), \quad (119)$$

and

$$\mathbf{p}_A + \rho \omega_A \nabla (\mu_A|_\theta + \psi) - \nabla (p X_A) + \rho \omega_A \mathbf{g} = -\hat{\mathbf{R}}_A \cdot (\mathbf{v}_A - \mathbf{v}_B). \quad (120)$$

For the stress tensor to satisfy Equation (17) to first order,

$$\hat{\mathbf{a}}_{4i} = \omega_i \hat{\mathbf{b}}_4 \quad \text{for } i \in \{A, B\}. \quad (121)$$

Furthermore, we obtain:

$$\mathbf{p}_B + \rho \omega_B \nabla (\mu_B|_\theta + \psi) - \nabla (p X_B) + \rho \omega_B \mathbf{g} = -\hat{\mathbf{R}}_B \cdot (\mathbf{v}_B - \mathbf{v}_A), \quad (122)$$

subject to:

$$\hat{\mathbf{R}}_A - \hat{\mathbf{R}}_B = r_A \mathbf{l}, \quad (123)$$

so that Equation (19) is satisfied.

Substitution of these closure relations into conservation equations results in a set of closed conservation equations. For mass, we have:

$$\frac{D_i(\rho \omega_i)}{Dt} + \rho \omega_i \mathbf{l} : \mathbf{d}_i - r_i = 0 \quad \text{for } i \in \{A, B\}. \quad (124)$$

The closed momentum equations are:

$$\begin{aligned} \frac{D_A(\rho\omega_A\mathbf{v}_A)}{Dt} + \rho\omega_A\mathbf{v}_A\mathbf{l}:\mathbf{d}_A - \nabla \cdot (\omega_A\hat{\mathbf{b}}_4:\mathbf{d}_A) + \rho\omega_A\nabla(\mu_A|_\theta + \psi) \\ + \hat{\mathbf{R}}_A \cdot (\mathbf{v}_A - \mathbf{v}_B) - r_A\mathbf{v}_A = \mathbf{0} \end{aligned} \quad (125)$$

and

$$\begin{aligned} \frac{D_B(\rho\omega_B\mathbf{v}_B)}{Dt} + \rho\omega_B\mathbf{v}_B\mathbf{l}:\mathbf{d}_B - \nabla \cdot (\omega_B\hat{\mathbf{b}}_4:\mathbf{d}_B) + \rho\omega_B\nabla(\mu_B|_\theta + \psi) \\ + \hat{\mathbf{R}}_A \cdot (\mathbf{v}_B - \mathbf{v}_A) + r_A\mathbf{v}_A = \mathbf{0} . \end{aligned} \quad (126)$$

The internal energy balance we will employ is $\mathcal{U}^*$, as defined in Equation (71). The summation of the species-based internal energy balance given in Equation (70) can be arranged in terms of the unknowns considered in this problem to obtain:

$$\begin{aligned} \frac{D_A(\omega_A U)}{Dt} + \frac{D_B(\omega_B U)}{Dt} + \omega_A U \mathbf{l}:\mathbf{d}_A + \omega_B U \mathbf{l}:\mathbf{d}_B - \nabla \cdot \mathbf{q} + \nabla \cdot [\omega_A \mathbf{t}_A \cdot (\mathbf{v}_A - \mathbf{v}_B)] \\ + \nabla \cdot [\omega_B \mathbf{t}_B \cdot (\mathbf{v}_B - \mathbf{v}_A)] - \mathbf{t}_A:\mathbf{d}_A - \mathbf{t}_B:\mathbf{d}_B - h + \mathbf{p}_A \cdot (\mathbf{v}_A - \mathbf{v}_B) \\ + \frac{1}{2}(\mathbf{v}_A - \mathbf{v}_B) \cdot (\mathbf{v}_A - \mathbf{v}_B) r_A = 0 . \end{aligned} \quad (127)$$

Other rearrangements are possible. In the form provided, Equations (118)–(120) can be substituted in to provide the final closed form. Instead of using $\mathcal{U}^*$ as the energy relation, one could use the total energy equation. The preceding equation set, supplemented by thermodynamic equations of state, provides a model of a two-species system. We emphasize that in this formulation, the dispersion vector does not appear and is not approximated by a closure relation.

8.2. Closed Species-Based Mass and Phase-Based Momentum Conservation Equations

This formulation makes use of Equation (110). The entropy and energy fluxes are considered to be related according to:

$$\varphi - \frac{1}{\theta} \left[\mathbf{q} + \sum_{i \in \mathcal{I}_s} \rho\omega_i \left(\mu_i + \frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) \mathbf{u}_i \right] = \mathbf{0} . \quad (128)$$

The body sources of entropy and energy are assumed to be related with:

$$b - \frac{1}{\theta} \left[h - \sum_{i \in \mathcal{I}_s} \rho\omega_i \frac{D}{Dt} \left(\frac{1}{2} \mathbf{u}_i \cdot \mathbf{u}_i \right) \right] = 0 . \quad (129)$$

Linearization of the remaining fluxes in Equation (110), except for the reaction term, as functions of conjugate forces yields:

$$\mathbf{t} + p\mathbf{l} = \hat{\mathbf{a}}_4:\mathbf{d} , \quad (130)$$

$$\mathbf{q} + \rho\omega_A (\bar{H}_A - \bar{H}_B) \mathbf{u}_A = -\hat{\mathbf{k}}_\theta \cdot \nabla \left(\frac{1}{\theta} \right) , \quad (131)$$

and

$$\rho\omega_A \mathbf{u}_A = -\mathbf{D}_{AB} \cdot \nabla (\mu_A|_\theta - \mu_B|_\theta) . \quad (132)$$

Substitution of these closure relations into the appropriate set of conservation equations closes the set. For mass conservation of the two species, A and B , we have:

$$\frac{D(\rho\omega_A)}{Dt} + \rho\omega_A \mathbf{l} : \mathbf{d} - \nabla \cdot [\mathbf{D}_{AB} \cdot \nabla (\mu_A|_\theta - \mu_B|_\theta)] - r_A = 0 \quad (133)$$

and

$$\frac{D(\rho\omega_B)}{Dt} + \rho\omega_B \mathbf{l} : \mathbf{d} - \nabla \cdot [\mathbf{D}_{AB} \cdot \nabla (\mu_B|_\theta - \mu_A|_\theta)] - r_B = 0 . \quad (134)$$

We could replace one of these equations with the total mass conservation, the sum of the two equations over the two species, if desired. The closed phase-based momentum equation is Equation (16) subject to the closure condition for the stress tensor given by Equation (130), such that:

$$\frac{D(\rho\mathbf{v})}{Dt} + \rho\mathbf{v} \mathbf{l} : \mathbf{d} + \nabla p - \nabla \cdot (\hat{\mathbf{a}}_4 : \mathbf{d}) - \rho\mathbf{g} = \mathbf{0} . \quad (135)$$

The internal energy balance we will employ is $\mathcal{U}$, as defined in Equation (76). We will drop the terms denoted K_E , assuming they are of higher order smallness. Thus, with the closure relations for $\mathbf{t}$ and $\mathbf{q}$ incorporated, we obtain:

$$\begin{aligned} \frac{DU}{Dt} + U \mathbf{l} : \mathbf{d} + \nabla \cdot \left[\rho\omega_A (\overline{H}_A - \overline{H}_B) \mathbf{u}_A + \hat{\mathbf{k}}_\theta \cdot \nabla \left(\frac{1}{\theta} \right) \right] \\ + p \mathbf{l} : \mathbf{d} - \mathbf{d} : \hat{\mathbf{a}}_4 : \mathbf{d} - h = 0 . \end{aligned} \quad (136)$$

The four-equation set given by Equations (133)–(136) is certainly simpler than the five equations in Equations (124)–(127) that made use of a species-based momentum equation. This simpler set is also the one typically used in modeling two-species systems.

9. Discussion

We have identified three important themes relating to the use of species-based and phase-based conservation equations. First, fundamental conservation equations can be written for mass, momentum and total energy of a chemical species; and an entropy balance equation can be written for each chemical species in a system, as well. Summation of each of these equation types over all species in the system produces phase-based fundamental equations. The forms of these equations are unique, since they are based on a simple summation. Phase-based forms of these equations derived from species-based forms are useful in that they reveal some elements, such as diffusion kinetic energy, that are easily overlooked if the phase-based forms are postulated directly.

Second, from a general perspective, the fundamental equations can be combined in any dimensionally-consistent way to form secondary conservation equations. In some instances, a secondary equation may be more convenient or appropriate to use than its antecedent forms. As a general rule, the combinations of equations that are most often used involve combinations that alter the quantity appearing in a material derivative. It is tempting to say that this new quantity is the conserved quantity, but that is a bit of an oversimplification. For example, a mechanical energy equation obtained as a combination of the mass and momentum equations retains a term that accounts for the transformation of mechanical

energy into internal energy. Likewise, an internal energy equation retains a term that accounts for this same transformation. In a complete conservation equation, obtained as a sum of mechanical and internal energy equations, this exchange term will not appear. From this perspective, any conservation equation can be split into two parts that, when summed together, reproduce the original equation. Mechanical and internal energy equations are secondary equations formed from a particularly convenient cleavage of the total energy equation. Because the cleavage point is arbitrary, it may not be surprising to find that the forms of the mechanical and internal energy equations are not unique. One cleavage point seems most appropriate if the material derivative of internal and kinetic energy is split in the species-based equation, while a different cleavage point suggests itself if one works from the phase-based equations. The alternative forms of internal energy and mechanical energy equations have been presented.

Third, a question arises as to which equation forms should be combined if one wishes to eliminate the time derivative of entropy from the entropy equation, so that the entropy production term will be a force-flux pairing. Here, we have demonstrated the development of closure relations when the momentum equation is posed on a species basis and on a phase basis. If one begins with the linear combination of fundamental equations being used to describe the system and combines them to form the entropy inequality, different expressions emerge for the two approaches. In one case, a species-based stress tensor and interspecies momentum exchange terms are sought. In the other case, a phase-based stress tensor is approximated along with diffusion vectors for each species. It was shown that when starting from the fundamental equations, one sees that the entropy inequality can be interpreted as making use of an internal energy equation in combination with the entropy balance, as opposed to using the total energy equation and a momentum equation. An important element of this result is that the form of the internal energy equation that actually arises in each case is different. Thus, if one proposes to assemble the conservation and balance equations from the entropy balance, mass conservation, thermodynamic and internal energy equations, it is not immediately obvious which internal energy equation should be selected. The way to avoid this problem is to employ the fundamental conservation equations as a starting point. The use of the wrong internal energy equation in trying to develop a closure scheme for an equation system can lead to erroneous closure results [17]. One must also recognize which variables require closure conditions in light of the set of conservation equations employed in the model formulation.

10. Conclusions

Species-based conservation equations for mass, momentum and total energy, an entropy balance equation and a body force potential equation were employed as a basis for describing conservation equations for phases. It was shown that for multispecies systems, two different, but equally reasonable, forms of phase-based internal energy and mechanical energy conservation equations arise naturally. In one case, mechanical and internal energy equations were obtained from species-based fundamental equations and then summed to obtain the phase-based equations. In the second case, the fundamental species-based equations were summed; and the mechanical and internal energy equations were obtained directly from those equations.

It was shown that if one makes use of an entropy inequality, it is best to construct the appropriate form from the fundamental conservation equations in light of the degree of refinement that one wishes

to incorporate into the model. Construction of the entropy inequality directly making use of a secondary equation, such as an internal energy equation, presents the possibility of producing anomalous results. Because all conservation equations can be put in forms, such that a collection of terms is equal to zero, possibilities for combining the equations are unlimited. However, the selection of the combination of equations is dependent on the modeling detail for the system of interest.

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Author Contributions

William G. Gray provided the impetus for this work and drafted the manuscript. Amanda L. Dye provided insights that led to highlighting some of the distinctions between equations and worked on rewrites and clarifications. Both authors have read and approved the final manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. Bearman, R.J.; Kirkwood, J.G. Statistical mechanics of transport processes. XI. Equations of transport in multicomponent systems. *J. Chem. Phys.* **1958**, *28*, 136–145.
2. Curtiss, C.F.; Bird, R.B. Multicomponent diffusion. *Ind. Eng. Chem. Res.* **1999**, *38*, 2515–2522.
3. Datta, R.; Vilekar, S.A. The continuum mechanical theory of multicomponent diffusion in fluid mixtures. *Chem. Eng. Sci.* **2010**, *65*, 5976–5989.
4. De Groot, S.R.; Mazur, P. *Non-equilibrium Thermodynamics*; Courier Dover Publications: New York, NY, USA, 1984.
5. Miller, C.T.; Gray, W.G. Thermodynamically constrained averaging theory approach for modeling flow and transport phenomena in porous medium systems: 4. Species transport fundamentals. *Adv. Water Resour.* **2008**, *31*, 577–597.
6. Snell, F.M.; Spangler, R.A. A Phenomenological Theory of Transport in Multicomponent Systems. *J. Phys. Chem.* **1967**, *71*, 2503–2510.
7. Truesdell, C.A. *Rational Thermodynamics*; McGraw-Hill: New York, NY, USA, 1969.
8. Woods, L.C. *The Thermodynamics of Fluid Systems*; Clarendon Press: Oxford, UK, 1975.
9. Whitaker, S. Derivation and Application of the Stefan–Maxwell Equations. *Revista Mexicana de Ingeniería Química* **2009**, *8*, 213–243.
10. Alts, T.; Hutter, K. Continuum description of the dynamics and thermodynamics of phase boundaries between ice and water. Part I: Surface balance laws and their interpretation in terms of three-dimensional balance laws averaged over the phase change boundary layer. *J. Non-Equilib. Thermodyn.* **1988**, *13*, 221–257.

11. Jou, D.; Casas-Vázquez, J.; Lebon, G. *Extended Irreversible Thermodynamics*, 3rd ed.; Springer-Verlag: Berlin, Germany, 2001.
12. Prigogine, I. *Introduction to Thermodynamics of Irreversible Processes*; Wiley: New York, NY, USA, 1961.
13. Maugin, G.A. *The Thermomechanics of Nonlinear Irreversible Behaviors: An Introduction*; World Scientific Press: Singapore, Singapore, 1999.
14. Jou, D.; Casas-Vázquez, J.; Lebon, G. *Extended Irreversible Thermodynamics*, 4th ed.; Springer: Berlin, Germany, 2010.
15. Liu, I.S. Method of Lagrange multipliers for exploitation of the energy principle. *Arch. Ration. Mech. Anal.* **1972**, *46*, 131–148.
16. Liu, I.S. *Continuum Mechanics*; Springer-Verlag: Berlin, Germany, 2002.
17. Whitaker, S. Mechanics and thermodynamics of diffusion. *Chem. Eng. Sci.* **2012**, *68*, 362–375.

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