Notes on
Entropy Production in Multicomponent Fluids

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Updated January 2, 2001 from July 1993 Version

Introduction

We calculate the entropy production in a multicomponent fluid, allowing for chemical reactions and external forces that are species specific. Equations for balance of the mass of each species, energy, momentum, and entropy production are first formulated as integral equations for an arbitrary volume $\mathcal{V}$ with external area $\mathcal{A}$ and then reduced to differential equations. The treatment is rather standard insofar as the balance equations are concerned and follows closely the developments of Bird, Stewart and Lightfoot (BSL) [1] and Fitts [2]. BSL do not, however, give explicit expressions for the entropy production, although they appeal to the literature (see footnote on page 565 of [1]) in connection with the formulation of constitutive equations for the fluxes. Our treatment of entropy production is much more explicit, and extends the work of Sekerka and Mullins [3] along lines developed by Sekerka in unpublished notes written in August 1991 at a summer workshop in Aspen. Specifically, external forces and chemical reactions are now allowed.

We also offer an identification of the energy flux that seems to be more self consistent with the entropy flux and with the work done by pressure in a multicomponent system. Based on this flux identification, we are able to make direct contact with the "second-law heat flux" of Fitts [2], page 28, without defining a separate heat flux, "not associated with the flow of matter, " for the first law of thermodynamics, as does Fitts[2], page 27. We also make contact with the total energy flux in a multicomponent solution given by BSL [1], page 566. We are led finally to results that are in agreement with expressions for the entropy production of a multicomponent system by Fitts [2], page 31, and de Groot and Mazur [4], pages 26-27, and for a binary fluid system by Landau and Lifshitz [5], page 222.

Furthermore, in the case for which the external forces can be can be expressed as gradients of potential functions that are independent of time, we are able to demonstrate that *total* chemical potentials, which are intrinsic chemical potentials augmented by the external potentials corresponding to the external forces, appear as conjugate variables to the fluxes; however, only the *intrinsic* chemical potentials appear as conjugate variables to the chemical reaction rates. For the case in which the external potentials are independent of species, as would be the case for gravity, the augmentation of the chemical potentials makes no net contribution to the entropy production. Therefore, for gravity as the only external force, the fluxes can be written in terms of the gradients of only the intrinsic chemical potentials. Nevertheless, we show in this case that the dependence of these chemical potentials on pressure leads to an implicit dependence of the fluxes on the gravitational potential, and with the aid of the Gibbs-Duhem equation, this dependence can be shown to lead to the well-known equilibrium condition that the gravitationally augmented chemical potentials are uniform at equilibrium.

Our general approach in the sections below is to write a balance equation for an arbitrary extensive quantity U of the following form:

(time rate of change of U in volume $\mathcal{V}$) + (flux of U out of $\mathcal{V}$ through $\mathcal{A}$)
= (rate of production of U in $\mathcal{V}$)

Subscripts v and m will be used to denote quantities per unit volume and unit mass, respectively, whereas subscripts such as $i, j, k = 1, \ldots, \kappa$ will be used to denote chemical species.

1 Mass Balances

The equation for balance of the mass of the i^{th} species of partial density ρ_i may be written in the form

$$\frac{d}{dt}\int_{\mathcal{V}} \rho_i \, d^3x + \int_{\mathcal{A}} \rho_i \mathbf{v}_i \cdot \hat{\mathbf{n}} \, d^2x = \int_{\mathcal{V}} r_i \, d^3x \tag{1}$$

where $\mathbf{v}_i$ is the local velocity of the i^{th} species, $\hat{\mathbf{n}}$ is the unit outward normal to $\mathcal{V}$, and r_i is the volumetric rate of production of mass of the i^{th} species by means of chemical reaction. For fixed $\mathcal{V}$, we can take the time derivative inside the integral as a partial derivative. If we then convert the surface integral to a volume integral by the divergence theorem and recognize that the volume $\mathcal{V}$ is arbitrary, we can equate the integrands and write

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v}_i) = r_i. \tag{2}$$

We introduce the total density $\rho = \sum_{i=1}^{\kappa} \rho_i$, the barycentric velocity (velocity of the local center of mass) $\mathbf{v} = \sum_{i=1}^{\kappa} \rho_i \mathbf{v}_i / \rho$, and the diffusive fluxes (mass flux of each species with respect to the local center of mass)

$$\mathbf{j}_i := \rho_i (\mathbf{v}_i - \mathbf{v}) \tag{3}$$

so that the total mass fluxes

$$\mathbf{J}_i := \rho_i \mathbf{v}_i = \rho_i \mathbf{v} + \mathbf{j}_i. \tag{4}$$

Then Eq(2) may be written in the forms

$$\frac{\partial \rho_i}{\partial t} + \nabla \cdot \mathbf{J}_i \;\; = \;\; r_i \tag{5}$$

$$\begin{aligned} \frac{\partial \rho_i}{\partial t} + \nabla \cdot (\rho_i \mathbf{v} + \mathbf{j}_i) &= r_i \qquad (6) \\ \frac{\mathcal{D}\rho_i}{\mathcal{D}t} + \rho_i \nabla \cdot \mathbf{v} + \nabla \cdot \mathbf{j}_i &= r_i \qquad (7) \end{aligned}$$

where

$$\frac{\mathcal{D}}{\mathcal{D}t} := \frac{\partial}{\partial t} + \mathbf{v} \cdot \nabla \qquad (8)$$

is the substantial derivative.

From Eq(3) and the definition of $\mathbf{v}$, we see that

$$\sum_{i=1}^{\kappa} \mathbf{j}_i = 0. \qquad (9)$$

Moreover, total mass is conserved by chemical reactions, so that

$$\sum_{i=1}^{\kappa} r_i = 0. \qquad (10)$$

Consequently we can sum Eq(6) and Eq(7) over all chemical species to obtain

$$\begin{aligned} \frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{v}) &= 0 \qquad (11) \\ \frac{\mathcal{D}\rho}{\mathcal{D}t} + \rho \nabla \cdot \mathbf{v} &= 0 \qquad (12) \end{aligned}$$

which are familiar forms of the continuity equation.

Later, we shall make use of the following: Let A denote an arbitrary quantity. Then

$$\begin{aligned} \frac{\partial(\rho A)}{\partial t} + \nabla \cdot (\rho A \mathbf{v}) &= \rho \frac{\partial A}{\partial t} + \rho \mathbf{v} \cdot \nabla A \\ &= \rho \frac{\mathcal{D}A}{\mathcal{D}t} \qquad (13) \end{aligned}$$

where Eq(11) has been used. If we apply Eq(13) with $A = v_m := 1/\rho$, the specific volume, we obtain

$$\rho \frac{\mathcal{D}v_m}{\mathcal{D}t} = \nabla \cdot \mathbf{v}, \qquad (14)$$

which illustrates the familiar interpretation of the divergence of $\mathbf{v}$ as a volumetric source. If we apply Eq(13) to Eq(6), with $A = \omega_i := \rho_i/\rho$, the mass fraction of the i^{th} component, we obtain

$$\rho \frac{\mathcal{D}\omega_i}{\mathcal{D}t} + \nabla \cdot \mathbf{j}_i = r_i. \qquad (15)$$

2 Momentum Balance

We write the equation for momentum balance in the form

$$\frac{d}{dt}\int_{\mathcal{V}} \rho\mathbf{v}\, d^3x + \int_{\mathcal{A}} \rho\mathbf{v}\mathbf{v}\cdot\hat{\mathbf{n}}\, d^2x = -\int_{\mathcal{A}} \check{\mathbf{m}}\cdot\hat{\mathbf{n}}\, d^2x + \int_{\mathcal{V}} \sum_{i=1}^{\kappa} \rho_i \mathbf{g}_i\, d^3x \tag{16}$$

where the tensor $\rho\mathbf{v}\mathbf{v}$ is the momentum flux due to fluid transport across the area $\mathcal{A}$ and

$$\check{\mathbf{m}} = \check{\tau} + p\check{\mathbf{1}} \tag{17}$$

is a symmetric stress tensor, equal to the sum of the symmetric viscous stress tensor $\check{\tau}$ and a diagonal tensor that is the product of the thermodynamic pressure and the unit tensor $\check{\mathbf{1}}$. The term containing $\check{\mathbf{m}}\cdot\hat{\mathbf{n}}$ can either be viewed as a force that acts through the area $\mathcal{A}$ or as a flux (into $\mathcal{V}$) of momentum related to surface forces. (Our $\check{\mathbf{m}}$ is the same as the tensor $\check{\mathbf{\Pi}}$ of BSL [1] or the negative of the tensor $\check{\sigma}$ of Fitts [2].) The quantities $\mathbf{g}_i$ represent species specific forces per unit mass of the i^{th} component. Eq(16) can be converted to a differential equation by the same procedure used above to obtain either of the forms

$$\begin{aligned} \frac{\partial(\rho\mathbf{v})}{\partial t} + \nabla\cdot(\rho\mathbf{v}\mathbf{v} + \check{\mathbf{m}}) &= \sum_{i=1}^{\kappa} \rho_i \mathbf{g}_i \qquad (18) \\ \rho\frac{\mathcal{D}\mathbf{v}}{\mathcal{D}t} + \nabla\cdot\check{\mathbf{m}} &= \sum_{i=1}^{\kappa} \rho_i \mathbf{g}_i. \qquad (19) \end{aligned}$$

3 Energy Balance

We write the equation for energy balance in the form

$$\frac{d}{dt}\int_{\mathcal{V}} (e_v + \frac{1}{2}\rho v^2)\, d^3x + \int_{\mathcal{A}} [(e_v + \frac{1}{2}\rho v^2)\mathbf{v} + \mathbf{j}_e]\cdot\hat{\mathbf{n}}\, d^2x = -\int_{\mathcal{A}} \mathbf{v}\cdot\check{\mathbf{m}}\cdot\hat{\mathbf{n}}\, d^2x + \int_{\mathcal{V}} \sum_{i=1}^{\kappa} \rho_i \mathbf{v}_i\cdot\mathbf{g}_i\, d^3x \tag{20}$$

where e_v is the density of internal energy, $\frac{1}{2}\rho v^2$ is the density of kinetic energy, and $\mathbf{j}_e$ is an energy flux that is consistent with the form of the work terms, due to surface forces and external forces, that appear on the right. The corresponding differential equations are

$$\begin{aligned} \frac{\partial(e_v + \frac{1}{2}\rho v^2)}{\partial t} + \nabla\cdot\left[(e_v + \frac{1}{2}\rho v^2)\mathbf{v} + \mathbf{j}_e + \check{\mathbf{m}}\cdot\mathbf{v}\right] &= \sum_{i=1}^{\kappa} \rho_i \mathbf{v}_i\cdot\mathbf{g}_i \qquad (21) \\ \rho\frac{\mathcal{D}(e_m + \frac{1}{2}v^2)}{\mathcal{D}t} + \nabla\cdot(\mathbf{j}_e + \check{\mathbf{m}}\cdot\mathbf{v}) &= \sum_{i=1}^{\kappa} \rho_i \mathbf{v}_i\cdot\mathbf{g}_i. \qquad (22) \end{aligned}$$

These equations for overall energy balance can be simplified by subtracting an equation for the balance of mechanical energy, obtained by taking the dot product of $\mathbf{v}$ with an equation for momentum balance. Thus Eq(19) leads to

$$\rho\frac{\mathcal{D}(\frac{1}{2}v^2)}{\mathcal{D}t} + \nabla\cdot(\mathbf{v}\cdot\check{\mathbf{m}}) - \check{\mathbf{m}}{:}\nabla\mathbf{v} = \sum_{i=1}^{\kappa} \rho_i \mathbf{v}\cdot\mathbf{g}_i \tag{23}$$

where the scalar

$$\begin{aligned}\check{\mathbf{m}}{:}\nabla\mathbf{v} &= \sum_{\alpha,\beta=1}^{3} m_{\alpha\beta}\frac{\partial v_\alpha}{\partial x_\beta} \\ &= p\nabla\cdot\mathbf{v}+\check{\tau}{:}\nabla\mathbf{v} \qquad (24)\end{aligned}$$

where α and β denote cartesian indices. Subtraction of Eq(23) from Eq(21) and Eq(22) then leads, in view of Eq(13), to the results

$$\frac{\partial e_v}{\partial t}+\nabla\cdot(e_v\mathbf{v}+\mathbf{j}_e) = -p\nabla\cdot\mathbf{v}-\check{\tau}{:}\nabla\mathbf{v}+\sum_{i=1}^{\kappa}\mathbf{j}_i\cdot\mathbf{g}_i \qquad (25)$$

$$\rho\frac{\mathcal{D}e_m}{\mathcal{D}t}+\nabla\cdot\mathbf{j}_e = -p\nabla\cdot\mathbf{v}-\check{\tau}{:}\nabla\mathbf{v}+\sum_{i=1}^{\kappa}\mathbf{j}_i\cdot\mathbf{g}_i \qquad (26)$$

where the terms on the right-hand side represent, respectively, the work done by pressure on a compressible fluid, the work done by viscous forces, and the work done by species specific external forces on diffusing species. Note that the latter term would vanish (because the diffusive fluxes sum to zero, see Eq(9)) for the case in which $\mathbf{g}_i$ is independent of i, e.g., for only a gravitational force for which $\mathbf{g}_i = \mathbf{g}$, the acceleration due to gravity.

4 Identification of Fluxes

An alternative way of writing Eq(20) would be

$$\begin{aligned}&\frac{d}{dt}\int_{\mathcal{V}}(e_v+\frac{1}{2}\rho v^2)\,d^3x+\int_{\mathcal{A}}[(e_v+\frac{1}{2}\rho v^2)\mathbf{v}+\mathbf{j}'_e]\cdot\hat{\mathbf{n}}\,d^2x = \\ &\quad -\int_{\mathcal{A}}(\mathbf{v}\cdot\check{\tau}+p\sum_{i=1}^{\kappa}\bar{V}_i\rho_i\mathbf{v}_i)\cdot\hat{\mathbf{n}}\,d^2x+\int_{\mathcal{V}}\sum_{i=1}^{\kappa}\rho_i\mathbf{v}_i\cdot\mathbf{g}_i\,d^3x \qquad (27)\end{aligned}$$

where the quantities

$$\bar{V}_i := \left(\frac{\partial V}{\partial M_i}\right)_{p,T,M'_i} \qquad (28)$$

are partial specific volumes (here, M_i is the mass of the i^{th} component and M'_i stands for the set of all masses other than M_i) and $\mathbf{j}'_e$ is a new energy flux that we shall proceed to relate to $\mathbf{j}_e$. Indeed, we show below (see Eq(42)) that the integral over $\mathcal{A}$ on the right-hand side of Eq(27) is a more appropriate form of the external work done by surface forces for a multicomponent system than the integral over $\mathcal{A}$ on the right-hand side of Eq(20).

We first relate $\mathbf{j}'_e$ to $\mathbf{j}_e$ as follows: We note first that the partial specific volumes obey the equation

$$\sum_{i=1}^{\kappa}\bar{V}_i\rho_i = 1 \qquad (29)$$

which allows us to write

$$p\sum_{i=1}^{\kappa}\bar{V}_i\rho_i\mathbf{v}_i = p\mathbf{v} + \sum_{i=1}^{\kappa}p\bar{V}_i\,\mathbf{j}_i. \tag{30}$$

Thus, the energy fluxes may be related by the equation

$$\mathbf{j}'_e = \mathbf{j}_e - \sum_{i=1}^{\kappa}p\bar{V}_i\,\mathbf{j}_i. \tag{31}$$

Below, we shall deduce, in agreement with Fitts [2], that

$$\mathbf{j}_e = \mathbf{q}_c + \sum_{i=1}^{\kappa}\bar{H}_i\,\mathbf{j}_i. \tag{32}$$

where $\mathbf{q_c}$ is a flux of conducted heat (the same as the "second-law heat flux" which Fitts [2] calls $\mathbf{q}$ and which BSL [1] call $\mathbf{q}^{(c)} + \mathbf{q}^{(x)}$) and the $\bar{H}_i$ are partial specific enthalpies. By making use of the relation $\bar{H}_i = \bar{E}_i + p\bar{V}_i$, where $\bar{E}_i$ are the partial specific internal energies, we can combine Eq(31) and Eq(32) to obtain

$$\mathbf{j}'_e = \mathbf{q}_c + \sum_{i=1}^{\kappa}\bar{E}_i\,\mathbf{j}_i \tag{33}$$

which is exactly what one would expect, i.e., the energy flux should result from the sum of the conducted energy and the energy that is transported by diffusion. On the other hand, Fitts [2], page 27, writes

$$\mathbf{j}_e = \mathbf{q}' + \sum_{i=1}^{\kappa}\bar{E}_i\,\mathbf{j}_i \tag{34}$$

which requires the definition of a heat flux $\mathbf{q}'$ that enters the first law of thermodynamics and is "not associated with the flow of matter." This requires

$$\mathbf{q}' = \mathbf{q}_c + \sum_{i=1}^{\kappa}p\bar{V}_i\,\mathbf{j}_i \tag{35}$$

which is awkward because it relates two fluxes that are presumably purely conductive by terms *that do involve the flow of matter.* We contend that $\mathbf{j}'_e$ is a more appropriate internal energy flux than $\mathbf{j}_e$ because of the manner in which it can be decomposed (see Eq(33)) into a conductive heat flux that enters the entropy flux (see Eq(52)) and an internal energy flux associated with diffusion. The fluxes $\mathbf{j}_e$ and $\mathbf{j}'_e$ differ only by the term in Eq(31) that contains the partial specific volumes, and we agree with Fitts [2], page 29, that this term represents "the work associated with the volume increment produced by diffusion of the various components into the volume element at constant temperature and pressure."

We now proceed to justify our identification of fluxes and external work for a multicomponent system. We begin with the fundamental equation of Gibbs

$$dE = TdS - pdV + \sum_{i=1}^{\kappa}\mu_i dM_i \tag{36}$$

where the quantities μ_i are the intrinsic chemical potentials. For simplicity, we assume that there are no viscous forces, external forces or chemical reactions. For a *closed* system, we would have $dM_i = 0$ and for *reversible* changes, we would identify $\delta Q = TdS$ as the heat added to the system and $\delta W = pdV$ as the work done by the system. For an *open* system, we can use the relation $\mu_i = \bar{E}_i + p\bar{V}_i - T\bar{S}_i$ to rewrite Eq(36) in the form

$$dE = T(dS - \sum_{i=1}^{\kappa} \bar{S}_i dM_i) - p(dV - \sum_{i=1}^{\kappa} \bar{V}_i dM_i) + \sum_{i=1}^{\kappa} \bar{E}_i dM_i \tag{37}$$

and for *reversible* changes make the identification

$$\delta Q = T(dS - \sum_{i=1}^{\kappa} \bar{S}_i dM_i) \tag{38}$$

$$\delta W = p(dV - \sum_{i=1}^{\kappa} \bar{V}_i dM_i). \tag{39}$$

This identification [1] is made with the further understanding that all changes are such that there is no net momentum change to the system under consideration, consistent with the fact that E is the *internal* energy in Eq(36).

In order to sharpen the connection to the mass fluxes, and to display a volume change that is not equal to zero, we let the boundary of this system move along its normal in time δt by an amount $\mathbf{v}_B \cdot \hat{\mathbf{n}}$ so that

$$dV = \int_{\mathcal{A}} \mathbf{v}_B \cdot \hat{\mathbf{n}}\, d^2x \; \delta t. \tag{40}$$

Similarly, we express the mass that enters the system in time δt in the form

$$dM_i = -\int_{\mathcal{A}} \rho_i(\mathbf{v}_i - \mathbf{v}_B) \cdot \hat{\mathbf{n}}\, d^2x \; \delta t \tag{41}$$

so that

$$\begin{aligned} \delta W &= \int_{\mathcal{A}} p \left[\mathbf{v}_B + \sum_{i=1}^{\kappa} \bar{V}_i \rho_i (\mathbf{v}_i - \mathbf{v}_B) \right] \cdot \hat{\mathbf{n}}\, d^2x \; \delta t \\ &= \int_{\mathcal{A}} p \sum_{i=1}^{\kappa} \bar{V}_i \rho_i \mathbf{v}_i \cdot \hat{\mathbf{n}}\, d^2x \; \delta t \qquad (42) \\ &= \int_{\mathcal{A}} p(\mathbf{v} + \sum_{i=1}^{\kappa} \bar{V}_i \mathbf{j}_i) \cdot \hat{\mathbf{n}}\, d^2x \; \delta t \qquad (43) \end{aligned}$$

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[1] The form of the work given by Eq(39) is easy to interpret for the case of isothermal expansion of an ideal gas by means of a piston that is completely permeable with respect to component i, having constant partial pressure p_i, but impermeable to the other components. By elementary considerations, $\delta W = (p - p_i)dV$. For such a gas, $p_i V = (RT/m_i)M_i$ where m_i is the molecular weight of component i, so $p_i dV = (RT/m_i)dM_i$. But $\bar{V}_i = RT/(p\,m_i)$, so $p_i dV = p\bar{V}_i dM_i$ and therefore $\delta W = p(dV - \bar{V}_i dM_i)$. If the piston were completely permeable to all components, it would not experience any force, resulting in $\delta W = 0$.

where p and the $\bar{V}_i$ are taken inside the integrals consistent with the fact that Eq(36) is applicable only to small changes of a homogeneous system. We note that the rate of doing work by pressure given by Eq(42) is in agreement with the corresponding term on the right-hand side of Eq(27). Similarly, in time δt, we have

$$\begin{aligned}\sum_{i=1}^{\kappa}\bar{E}_i dM_i &= -\int_{\mathcal{A}}\bar{E}_i\rho_i(\mathbf{v}_i-\mathbf{v}_B)\cdot\hat{\mathbf{n}}\,d^2x\ \delta t\\ &= \int_{\mathcal{A}}(e_v\mathbf{v}_B-\sum_{i=1}^{\kappa}\bar{E}_i\rho_i\mathbf{v}_i)\cdot\hat{\mathbf{n}}\,d^2x\ \delta t\\ &= -\int_{\mathcal{A}}\left[e_v(\mathbf{v}-\mathbf{v}_B)+\sum_{i=1}^{\kappa}\bar{E}_i\,\mathbf{j}_i\right]\cdot\hat{\mathbf{n}}\,d^2x\ \delta t \qquad (44)\end{aligned}$$

and

$$\delta Q=-\int_{\mathcal{A}}\mathbf{q}_c\cdot\hat{\mathbf{n}}\,d^2x\ \delta t \qquad (45)$$

where $\mathbf{q}_c$ is the flux of *conducted* heat and where we have used the relation $\sum_{i=1}^{\kappa}\bar{E}_i\rho_i=e_v$, an equation of the form that is generally applicable to partial specific quantities. Substitution of Eqs(43, 44 and 45) into Eq(37) then leads to the result

$$\int_{\mathcal{V}}\rho\frac{\mathcal{D}e_m}{\mathcal{D}t}\,d^3x+\int_{\mathcal{A}}\left[\mathbf{q}_c+\sum_{i=1}^{\kappa}(\bar{E}_i+p\bar{V}_i)\mathbf{j}_i\right]\cdot\hat{\mathbf{n}}\,d^2x=-\int_{\mathcal{A}}p\mathbf{v}\cdot\hat{\mathbf{n}}\,d^2x \qquad (46)$$

where we have used the relation

$$\frac{d}{dt}\int_{\mathcal{V}}e_v\,d^3x+\int_{\mathcal{A}}e_v(\mathbf{v}-\mathbf{v}_B)\cdot\hat{\mathbf{n}}\,d^2x=\int_{\mathcal{V}}\rho\frac{\mathcal{D}e_m}{\mathcal{D}t}\,d^3x \qquad (47)$$

which is applicable for a moving boundary. Converting Eq(46) to a differential equation gives

$$\rho\frac{\mathcal{D}e_m}{\mathcal{D}t}+\nabla\cdot\left[\mathbf{q}_c+\sum_{i=1}^{\kappa}\bar{H}_i\,\mathbf{j}_i\right]=-p\nabla\cdot\mathbf{v} \qquad (48)$$

where, again, p is treated as a constant consistent with Eq(36).[2] Comparison of Eq(48) with Eq(26) for the case of no viscosity and no external forces then leads to Eq(32). Thus the resulting energy flux given by Eq(33) is seen to be compatible with the expression for the work given by Eq(42) and the rate of doing work that appears on the right hand side of Eq(27).

We can apply the same methodology as above to Eq(38) in order to identify the entropy flux. Thus

$$\begin{aligned}dS &= \frac{\delta Q}{T}+\sum_{i=1}^{\kappa}\bar{S}_i dM_i\\ &= -\int_{\mathcal{A}}\left[s_v(\mathbf{v}-\mathbf{v}_B)+\frac{\mathbf{q}_c}{T}+\sum_{i=1}^{\kappa}\bar{S}_i\,\mathbf{j}_i\right]\cdot\hat{\mathbf{n}}\,d^2x\ \delta t \qquad (49)\end{aligned}$$

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[2] In Eq(36) E is the *internal* energy and no change in the overall kinetic energy is taken into account. Therefore there can be no net body force on the system which requires $\nabla p=0$.

which leads to

$$\int_{\mathcal{V}} \rho \frac{\mathcal{D}s_m}{\mathcal{D}t}\, d^3x + \int_{\mathcal{A}} \left[\frac{\mathbf{q}_c}{T} + \sum_{i=1}^{\kappa} \bar{S}_i\, \mathbf{j}_i \right] \cdot \hat{\mathbf{n}}\, d^2x = 0 \tag{50}$$

and the corresponding differential form

$$\rho \frac{\mathcal{D}s_m}{\mathcal{D}t} + \nabla \cdot \left[\frac{\mathbf{q}_c}{T} + \sum_{i=1}^{\kappa} \bar{S}_i\, \mathbf{j}_i \right] = 0 \tag{51}$$

where the zero on the right-hand side results from the fact that we are considering here a reversible change. We thus identify the entropy flux

$$\mathbf{j}_s = \frac{\mathbf{q}_c}{T} + \sum_{i=1}^{\kappa} \bar{S}_i\, \mathbf{j}_i. \tag{52}$$

4.1 flux identification with chemical reactions

It is instructive to include chemical reactions in our treatment to identify fluxes because in this case

$$dM_i = dM_i^{int} + dM_i^{ext} \tag{53}$$

where

$$dM_i^{int} = \int_{\mathcal{V}} r_i\, d^3x\, \delta t \tag{54}$$

is the change in mass of component i due to chemical reactions and

$$dM_i^{ext} = -\int_{\mathcal{A}} \rho_i(\mathbf{v}_i - \mathbf{v}_B) \cdot \hat{\mathbf{n}}\, d^2x\ \delta t \tag{55}$$

is the change in mass of component i due to a flux through the boundary, which has the same form as Eq(41). Thus Eq(37) can be written in the form

$$dE = T(dS - \sum_{i=1}^{\kappa} \bar{S}_i dM_i^{ext} + \sum_{i=1}^{\kappa} \frac{\mu_i}{T} dM_i^{int}) - p(dV - \sum_{i=1}^{\kappa} \bar{V}_i dM_i^{ext}) + \sum_{i=1}^{\kappa} \bar{E}_i dM_i^{ext} \tag{56}$$

where the grouping of terms is related to the following argument: For a *closed* system, $dM_i^{ext} = 0$ and we assert that the internal energy will be unchanged if no work is done and no heat is added to the system. In other words, the *internal* energy is defined such that it is unchanged by chemical reaction, which can at most change from one *kind* of internal energy (say, the potential energy of certain chemical bonds) to another (say, the potential energy of other chemical bonds or internal kinetic energy). Thus for such a reaction in a closed isolated system, Eq(56) would yield

$$dS^{react} = -\sum_{i=1}^{\kappa} \frac{\mu_i}{T} dM_i^{int} \tag{57}$$

for the *internal* entropy production due to chemical reaction. This interpretation is in agreement with that of Prigogine [6], page 23, Eqs(3.29 - 3.30).

In the general case, we would therefore replace Eq(38) and Eq(39) for *reversible* exchanges with the *environment* by

$$\begin{aligned}\delta Q &= T(dS - \sum_{i=1}^{\kappa} \bar{S}_i dM_i^{ext} + \sum_{i=1}^{\kappa} \frac{\mu_i}{T} dM_i^{int}) &(58)\\ \delta W &= p(dV - \sum_{i=1}^{\kappa} \bar{V}_i dM_i^{ext}). &(59)\end{aligned}$$

Then by using the same methodology as above, we again obtain Eq(48) but Eq(51) is replaced by

$$\rho \frac{\mathcal{D}s_m}{\mathcal{D}t} + \nabla \cdot \left[\frac{\mathbf{q}_c}{T} + \sum_{i=1}^{\kappa} \bar{S}_i \, \mathbf{j}_i \right] = - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T}. \tag{60}$$

5 Entropy Production

We write the equation for entropy balance in the form

$$\frac{d}{dt} \int_{\mathcal{V}} s_v \, d^3x + \int_{\mathcal{A}} (s_v \mathbf{v} + \mathbf{j}_s) \cdot \hat{\mathbf{n}} \, d^2x = \int_{\mathcal{V}} \dot{s}_v^{prod} \, d^3x \tag{61}$$

where s_v is the density of entropy, $\mathbf{j}_s$ is an entropy flux that was identified in section 4, and $\dot{s}_v^{prod}$ is the volumetric rate of entropy production, assumed to be positive *locally* for a natural process. The corresponding differential equations are

$$\begin{aligned}\frac{\partial s_v}{\partial t} + \nabla \cdot (s_v \mathbf{v} + \mathbf{j}_s) &= \dot{s}_v^{prod} &(62)\\ \rho \frac{\mathcal{D}s_m}{\mathcal{D}t} + \nabla \cdot \mathbf{j}_s &= \dot{s}_v^{prod}. &(63)\end{aligned}$$

In order to calculate the volumetric entropy production $\dot{s}_v^{prod}$, we employ Eq(36) and its (Gibbs-Duhem) integrated form $E = TS - pV + \sum_{i=1}^{\kappa} \mu_i M_i$ to deduce the equation

$$de_m = T ds_m - p dv_m + \sum_{i=1}^{\kappa} \mu_i d\omega_i \tag{64}$$

where $v_m = 1/\rho$ is the specific volume. We assume that Eq(64) holds locally, even in an inhomogeneous system. We can therefore apply it to a change of the form $\mathcal{D}$ to obtain

$$\frac{\mathcal{D}s_m}{\mathcal{D}t} = \frac{1}{T} \frac{\mathcal{D}e_m}{\mathcal{D}t} - \frac{p}{T\rho^2} \frac{\mathcal{D}\rho}{\mathcal{D}t} - \sum_{i=1}^{\kappa} \frac{\mu_1}{T} \frac{\mathcal{D}\omega_i}{\mathcal{D}t} \tag{65}$$

which we can use to evaluate the left-hand side of Eq(63) with the aid of Eq(12), Eq(15) and Eq(26) and the definitions of the fluxes. The result can be written in the forms

$$\begin{aligned}\dot{s}_v^{prod} &= \mathbf{j}_e \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \left[\nabla \left(\frac{\mu_i}{T} \right) - \frac{\mathbf{g}_i}{T} \right] - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T} &(66)\\ \dot{s}_v^{prod} &= (\mathbf{j}_e - \sum_{i=1}^{\kappa} \mu_i \, \mathbf{j}_i) \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^{\kappa} \frac{\mathbf{j}_i \cdot (\nabla \mu_i - \mathbf{g}_i)}{T} - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T} &(67)\end{aligned}$$

where the four terms on the right represent the rate of entropy production associated, respectively, with energy flux, diffusive fluxes, viscosity, and chemical reactions. Eq(67) has the same form as Eq(57.7) of Landau and Lifshitz [5] for the simple case of a binary fluid that they treat. By using Eq(32) and Eq(52), we can write the energy flux that appears on the the left-hand side of Eq(67) in the form

$$\mathbf{j}_e - \sum_{i=1}^{\kappa} \mu_i \, \mathbf{j}_i = \mathbf{q}_c + \sum_{i=1}^{\kappa} T \bar{S}_i \, \mathbf{j}_i = T \, \mathbf{j}_s \tag{68}$$

which allows us to rewrite Eq(67) in the form

$$\dot{s}_v^{prod} = -\frac{\mathbf{j}_s \cdot \nabla T}{T} - \sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \left[\frac{\nabla \mu_i}{T} - \frac{\mathbf{g}_i}{T} \right] - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T} \tag{69}$$

which is in agreement with one of the forms given by de Groot and Mazur [4], page 27, Eq(28).

We can further isolate the role of temperature gradients by introducing the operator ∇^T which is the gradient operator at constant temperature. Then for the variable set T, p, ω_i we have [3]

$$\begin{aligned} \nabla \mu_i &= \nabla^T \mu_i + \left(\frac{\partial \mu_i}{\partial T} \right) \nabla T \\ &= \nabla^T \mu_i - \bar{S}_i \nabla T \\ &= \nabla^T \mu_i + T^2 \bar{S}_i \nabla \left(\frac{1}{T} \right) . \end{aligned} \tag{70}$$

Thus we can write the entropy production in the forms

$$\dot{s}_v^{prod} = \mathbf{q}_c \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^{\kappa} \frac{\mathbf{j}_i \cdot (\nabla^T \mu_i - \mathbf{g}_i)}{T} - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T} \tag{71}$$

$$\dot{s}_v^{prod} = \frac{1}{T} \left[-\mathbf{q}_c \cdot \nabla (\ln T) - \sum_{i=1}^{\kappa} \mathbf{j}_i \cdot (\nabla^T \mu_i - \mathbf{g}_i) - \check{\tau} : \nabla \mathbf{v} - \sum_{i=1}^{\kappa} \mu_i r_i \right] \tag{72}$$

in which the “driving force” of a temperature gradient is conjugate to the purely conductive heat flux $\mathbf{q}_c$.

6 External Potentials

In event that the external forces can be expressed in the form

$$\mathbf{g}_i = -\nabla \phi_i, \tag{73}$$

we can write

$$\begin{aligned} \rho_i \mathbf{v}_i \cdot \mathbf{g}_i &= -\rho_i \mathbf{v}_i \cdot \nabla \phi_i \\ &= -\nabla \cdot (\phi_i \rho_i \mathbf{v}_i) + \phi_i \cdot \nabla (\rho_i \mathbf{v}_i) \\ &= -\nabla \cdot (\phi_i \rho_i \mathbf{v} + \phi_i \, \mathbf{j}_i) + \phi_i r_i - \frac{\partial (\rho_i \phi_i)}{\partial t} + \rho_i \frac{\partial \phi_i}{\partial t} \end{aligned} \tag{74}$$

where Eq(2) has been used. We introduce the potential energy per unit mass, $\psi := \sum_{i=1}^{\kappa} \omega_i \phi_i$ of de Groot and Mazur [4], page 16, and then sum Eq(74) over i to obtain

$$\frac{\partial(\rho\psi)}{\partial t} - \sum_{i=1}^{\kappa} \rho_i \frac{\partial \phi_i}{\partial t} + \nabla \cdot (\rho\psi\mathbf{v} + \sum_{i=1}^{\kappa} \phi_i \, \mathbf{j}_i) = -\sum_{i=1}^{\kappa} \rho_i \mathbf{g}_i \cdot \mathbf{v} - \sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \mathbf{g}_i + \sum_{i=1}^{\kappa} \phi_i r_i \tag{75}$$

which is in agreement with Groot and Mazur (their Eq(26), page 16) for ϕ_i independent of time. Then if the potentials ϕ_i are independent[3] of time, we can rewrite Eq(21) and Eq(22) in the forms

$$\begin{aligned} \frac{\partial e_v^{tot}}{\partial t} + \nabla \cdot \left[(e_v^{tot} \mathbf{v} + \mathbf{j}_e + \sum_{i=1}^{\kappa} \phi_i \, \mathbf{j}_i + \check{\mathbf{m}} \cdot \mathbf{v}) \right] &= \sum_{i=1}^{\kappa} \phi_i r_i && (76) \\ \rho \frac{\mathcal{D} e_m^{tot}}{\mathcal{D} t} + \nabla \cdot (\mathbf{j}_e + \sum_{i=1}^{\kappa} \phi_i \, \mathbf{j}_i + \check{\mathbf{m}} \cdot \mathbf{v}) &= \sum_{i=1}^{\kappa} \phi_i r_i. && (77) \end{aligned}$$

where

$$\begin{aligned} e_v^{tot} &= e_v + \rho\psi + \frac{1}{2}\rho v^2 && (78) \\ e_m^{tot} &= e_m + \psi + \frac{1}{2} v^2 && (79) \end{aligned}$$

are *total* energies per unit volume and per unit mass, respectively. The term $\sum_{i=1}^{\kappa} \phi_i r_i$ represents the potential energy associated with the creation of species by chemical reaction; it would vanish, due to Eq(10), for ϕ_i independent of i, as would be the case for gravitational forces for which $\phi_i = gz$. Eq(76) and Eq(77) should agree with Eq(31) of de Groot and Mazur [4], page 17, but they do not because de Groot and Mazur have dropped the term due to potential energy created by chemical reactions on the right-hand sides of their Eqs(28-31). On the other hand, this term due to chemical reactions cancels exactly when they obtain their Eq(34), page 18, which is in agreement with our Eq(25) and Eq(26). We will see shortly that the external potentials lead to consideration of total chemical potentials.

The introduction of potentials for the external forces does not simplify Eq(25) and Eq(26) in any significant way because the term $\sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \mathbf{g}_i$ already represents the contribution of external forces to the *internal* energy. On the other hand, the equations for entropy production take on a transparent form if we introduce *total* chemical potentials[4] defined by

$$\mu_i^{tot} = \mu_i + \phi_i. \tag{80}$$

Then Eq(66) and Eq(67) can be written in the forms

$$\dot{s}_v^{prod} = (\mathbf{j}_e + \sum_{i=1}^{\kappa} \phi_i \, \mathbf{j}_i) \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \nabla \left(\frac{\mu_i^{tot}}{T} \right) - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T} \tag{81}$$

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[3] In the unusual case that the ϕ_i depend on time, it is necessary to add a term $\sum_{i=1}^{\kappa} \rho_i \frac{\partial \phi_i}{\partial t}$ to the right-hand sides of Eq(76) and Eq(77).

[4] Note that these total chemical potentials do not include kinetic energy of the local center of mass, which is included in e_v^{tot} and e_m^{tot}.

$$\dot{s}_v^{prod} = (\mathbf{j}_e - \sum_{i=1}^{\kappa} \mu_i \, \mathbf{j}_i) \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^{\kappa} \frac{\mathbf{j}_i \cdot \nabla \mu_i^{tot}}{T} - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T}. \tag{82}$$

In the case that the external potentials ϕ_i are independent of T, we can also express Eq(71) and Eq(72) in the forms

$$\dot{s}_v^{prod} = \mathbf{q}_c \cdot \nabla \left(\frac{1}{T} \right) - \sum_{i=1}^{\kappa} \frac{\mathbf{j}_i \cdot \nabla^T \mu_i^{tot}}{T} - \frac{\check{\tau} : \nabla \mathbf{v}}{T} - \sum_{i=1}^{\kappa} \frac{\mu_i r_i}{T} \tag{83}$$

$$\dot{s}_v^{prod} = \frac{1}{T} \left[-\mathbf{q}_c \cdot \nabla (\ln T) - \sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \nabla^T \mu_i^{tot} - \check{\tau} : \nabla \mathbf{v} - \sum_{i=1}^{\kappa} \mu_i r_i \right] \tag{84}$$

where the latter form is in agreement with Fitts [2], page 31, Eq(3-38).

7 Constitutive Laws for Fluxes and Onsager Symmetry

Following standard procedure in irreversible thermodynamics, one can postulate linear constitutive laws between the generalized forces and fluxes that appear in the various forms for the local rate of entropy production, $\dot{s}^{prod}$, given above. We concentrate here on only the energy flux and the diffusive fluxes of the components, which are tensors of rank one. According to Curie's Principle (see [4], page 31 or [2], page 35), these fluxes can only couple to forces that differ in tensoral rank by an even number. Therefore, the energy and diffusive fluxes do not couple to the generalized forces associated with chemical reactions or viscosity, but do couple to the generalized forces associated with one another. Corresponding to Eq(66), we therefore postulate

$$\mathbf{j}_i = - \sum_{j=0}^{\kappa} B_{ij} \left[\nabla \left(\frac{\mu_j}{T} \right) - \frac{\mathbf{g}_j}{T} \right], \quad (i = 0, \ldots, \kappa) \tag{85}$$

where

$$\mathbf{j}_0 := \mathbf{j}_e, \quad \mu_0 = -1, \quad \mathbf{g}_0 = 0. \tag{86}$$

Under conditions for which there are no external magnetic fields, we can follow the procedure of Sekerka and Mullins [3] to show, for *these* fluxes, forces and reference frames, that

$$B_{ij} = B_{ji}, \quad (i, j = 1, \ldots, \kappa), \tag{87}$$

which is the so-called Onsager symmetry. We note also that the matrix B_{ij} is singular because

$$\sum_{i=1}^{\kappa} B_{ij} = 0, \quad (j = 1, \ldots, \kappa), \tag{88}$$

which arises because the κ *mass* fluxes with respect to the center of mass are not independent (see Eq(9)) but all $\kappa + 1$ of the forces are independent.

As shown explicitly by Sekerka and Mullins [3], one can transform Eq(85) to obtain other forms of the forces and fluxes that are also related by a transport matrix that has the Onsager symmetry. One such choice is related to the entropy production in the form of Eq(72) and yields

$$\mathbf{j}_i' = -\hat{B}_{i0}\nabla(\ln T) - \sum_{j=1}^{\kappa}\hat{B}_{ij}(\nabla^T\mu_j - \mathbf{g}_j), \quad (i = 0, \ldots, \kappa) \tag{89}$$

or for the case of external potentials independent of time and temperature,

$$\mathbf{j}_i' = -\hat{B}_{i0}\nabla(\ln T) - \sum_{j=1}^{\kappa}\hat{B}_{ij}\nabla^T\mu_j^{tot}, \quad (i = 0, \ldots, \kappa) \tag{90}$$

which corresponds to Eq(84) for the entropy production, where

$$\mathbf{j}_0' := \mathbf{q}_c, \quad \mathbf{j}_i' := \mathbf{j}_i, \quad (i = 1, \ldots, \kappa). \tag{91}$$

Here,

$$\hat{B}_{ij} = \hat{B}_{ji}, \quad (i, j = 1, \ldots, \kappa) \tag{92}$$

where

$$\sum_{i=1}^{\kappa}\hat{B}_{ij} = 0, \quad (j = 1, \ldots, \kappa) \tag{93}$$

is a singular, symmetric matrix that is related linearly to B_{ij} by

$$\begin{aligned}
\hat{B}_{ij} &= \frac{1}{T}B_{ij}, \quad (i, j = 1, \ldots, \kappa) \\
\hat{B}_{0j} &= \frac{1}{T}\left(B_{0j} - \sum_{k=1}^{\kappa}\bar{H}_k B_{kj}\right) \quad (j = 1, \ldots, \kappa) \\
\hat{B}_{i0} &= \frac{1}{T}\left(B_{i0} - \sum_{k=1}^{\kappa}\bar{H}_k B_{ik}\right) \quad (j = 1, \ldots, \kappa) \\
\hat{B}_{00} &= \frac{1}{T}\left[B_{i0} - \sum_{k=1}^{\kappa}\bar{H}_k(B_{0k} + B_{k0}) + \sum_{k,m=1}^{\kappa}\bar{H}_k B_{km}\bar{H}_m\right].
\end{aligned} \tag{94}$$

The properties of $\hat{B}_{ij}$ follow from those of B_{ij}, and Eqs(89,90,91,92,93) are in agreement with Fitts [2], page 44.

We can take advantage of Eq(92) and Eq(93) to rewrite Eq(89) and Eq(90) in the forms

$$\mathbf{j}_i' = -\hat{B}_{i0}\nabla(\ln T) - \sum_{j=1}^{\kappa-1}\hat{B}_{ij}\left[\nabla^T(\mu_j - \mu_\kappa) - (\mathbf{g}_j - \mathbf{g}_\kappa)\right], \quad (i = 0, \ldots, \kappa - 1) \tag{95}$$

$$\mathbf{j}_i' = -\hat{B}_{i0}\nabla(\ln T) - \sum_{j=1}^{\kappa-1}\hat{B}_{ij}\nabla^T(\mu_j^{tot} - \mu_\kappa^{tot}), \quad (i = 0, \ldots, \kappa - 1) \tag{96}$$

where the submatrix $\hat{B}_{ij}$, $(i, j = 1, \ldots, \kappa - 1)$ is symmetric and not necessarily singular.

Since the symmetric submatrix $\hat{B}_{ij}$ has real elements, it can be diagonalized by an orthogonal similarity transformation and will have real eigenvalues. Since the determinant is preserved by such a transformation and is also the product of the eigenvalues, it follows that none of the eigenvalues are zero if $\hat{B}_{ij}$ is nonsingular. Therefore, in order to obtain a positive definite local rate of entropy production, $\dot{s}^{prod} > 0$, for any nonzero driving force, it is necessary for the eigenvalues of $\hat{B}_{ij}$ to be positive definite.

8 Gravity as the Only External Force

For the case that gravity is the only[5] external force, we have

$$\mathbf{g}_i = \mathbf{g}, \quad \mu_i^{ext} = \mu_i + gz, \quad (i, j = 1, \ldots, \kappa) \tag{97}$$

where $\mathbf{g}$ is the acceleration due to gravity, g is its magnitude, and z is distance measured antiparallel to gravity from some suitable reference plane. It follows immediately that all *explicit* reference to an external force drops out[6] of Eq(95) and Eq(96), either of which can now be written

$$\mathbf{j}_i' = -\hat{B}_{i0}\nabla(\ln T) - \sum_{j=1}^{\kappa-1} \hat{B}_{ij}\nabla^T(\mu_j - \mu_\kappa), \quad (i = 0, \ldots, \kappa - 1) \tag{98}$$

which contains only differences of the *intrinsic* chemical potentials. Yet we know from the work of Gibbs [7], page 282, that the conditions for equilibrium for a multicomponent system in a gravitational field require

$$\mu_i^{ext} = \mu_i + gz = \text{uniform for each } i, \quad (i = 1, \ldots, \kappa). \tag{99}$$

How can this be possible if only the intrinsic chemical potentials appear in Eq(98)?

The answer is that the intrinsic chemical potentials depend on pressure as well as composition, and their dependence on pressure carries the "information" that gravity is present. This can be demonstrated explicitly by making use of the differential form

$$\rho \sum_{i=1}^{\kappa} \omega_i \nabla \mu_i = \nabla p - s_v \nabla T \tag{100}$$

of the Gibbs-Duhem equation. For equilibrium, T must be uniform and all fluxes must vanish, which from Eq(98) requires that[7]

$$\nabla\mu_1 = \nabla\mu_2 = \cdots = \nabla\mu_\kappa. \tag{101}$$

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[5] Similar considerations would apply to other forces per unit mass that are independent of species.

[6] The sum $\sum_{i=1}^{\kappa} \mathbf{j}_i \cdot \nabla^T \mu_i^{tot}$ that appears in Eq(83) and Eq(84) can, in view of Eq(9), be written in the form $\sum_{i=1}^{\kappa-1} \mathbf{j}_i \cdot \nabla^T(\mu_i^{tot} - \mu_\kappa^{tot})$, so the entropy production is also independent of an external force per unit mass that is independent of species.

[7] For constant T, there is no distinction between ∇ and ∇^T.

Substitution of Eq(101) into Eq(100) then gives

$$\rho \nabla \mu_i = \nabla p, \quad (i = 1, \dots, \kappa) \tag{102}$$

which in view of the equation $\nabla p = \rho \mathbf{g}$ for mechanical equilibrium (required since there is no fluid flow at equilibrium) shows that

$$\nabla \mu_i = \mathbf{g} = -g \nabla z, \quad (i = 1, \dots, \kappa) \tag{103}$$

which integrates to give Eq(99).

Acknowledgment

This work was supported by NASA under contract NAG3-1284 through the Lewis Research Center.

References

[1] R. B. Bird, W. E. Stewart and E. N. Lightfoot, *Transport Phenomena*, John Wiley and Sons, NY (1960)

[2] Donald D. Fitts, *Nonequilibrium Thermodynamics*, McGraw-Hill, NY (1962)

[3] R. F. Sekerka and W. W. Mullins, J. Chem. Phys. **73**, 1413-1421 (1980)

[4] S. R. de Groot and P. Mazur, *Non-Equilibrium Thermodynamics*, North Holland, Amsterdam (1962)

[5] L. D. Landau and E. M. Lifshitz, *Fluid Mechanics*, Pergamon Press, London (1959)

[6] I. Prigogine, *Thermodynamics of Irreversible Processes*, Interscience, NY (1955)

[7] J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs, Volume 1:Thermodynamics*, Peter Smith Edition, Dover, NY (1961)

[8] K. S. Førland, T. Førland and S. K. Ratkje, *Irreversible Thermodynamics, Theory and Applications*, John Wiley and Sons, NY (1988)

[9] Ralph J. Tykodi, *Thermodynamics of Steady States*, Macmillan, NY (1967)