On the Classical Theory of Reacting Fluid Mixtures

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1. Introduction

The classical theory of fluid mixtures[1] treats the mixture as a single body: balance laws for momentum, energy, and entropy are postulated for the mixture as a whole, rather than for the individual constituents.[2] The effects of diffusion manifest themselves in the appearance of the diffusive energy flux

$$\sum_\alpha \mu'_\alpha \boldsymbol{h}_\alpha, \tag{1.1}$$

where μ'_α is the chemical potential and $\boldsymbol{h}_\alpha$ the relative mass flux of constituent α. These laws are supplemented by an equation of mass balance for each constituent and a Gibbs' relation for the mixture.

It is the purpose of the present paper to show that the classical theory can be formulated within the framework of modern continuum thermodynamics; that several of the assumptions of that theory can be proved as theorems; and that the constitutive class compatible both with the classical assumptions and with the modern general theory is extremely narrow. We treat the mixture as a single body and postulate: (i) balance laws for mass, momentum, and energy together with a law of entropy growth, all for the mixture as a whole; and (ii) a law of mass balance for each constituent. We do not postulate a Gibbs' relation for the mixture, nor do we specify the form of the diffusive energy flux in the energy equation. In our constitutive relations, which are fully compatible with equipresence,[3] we take as independent variables the specific volume υ, the temperature θ, the concentrations c_α, and the gradients of υ, θ, and c_α. As consequences of the second law we prove that:

(i) there are no shearing stresses, *i.e.* the stress reduces to a pressure;

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[1] JAUMANN [1911], LOHR [1917], ECKART [1940], MEIXNER [1941]. See also MEIXNER & REIK [1959].

[2] A second, more general approach, due to TRUESDELL [1957], treats each constituent as a single body. *Cf.* FICK [1855], MAXWELL [1867], STEFAN [1871], NACHBAR, WILLIAMS, & PENNER [1959], TRUESDELL & TOUPIN [1960], KELLY [1964], TRUESDELL [1969]. Within TRUESDELL'S framework, or minor modifications thereof, complete theories for various types of materials have been formulated by ERINGEN & INGRAM [1965], GREEN & NAGHDI [1965], [1967], [1968], [1969], [1971], CROCHET & NAGHDI [1966], GREEN & STEEL [1966], MILLS [1966], BOWEN [1967], [1968], [1969], INGRAM & ERINGEN [1967], DUNWOODY & MÜLLER [1968], MÜLLER [1968], BOWEN & WIESE [1969], BOWEN & GARCIA [1970], [1971], DORIA [1969], CRAINE, GREEN, & NAGHDI [1970], DUNWOODY [1970], GURTIN & DE LA PENHA [1970], GURTIN [1971].

[3] Sometimes called TRUESDELL'S principle of equipresence. See, *e.g.*, TRUESDELL & NOLL [1965].

(ii) the free energy, pressure, and entropy depend only on υ, θ, and c_α and are related by the classical relations of thermostatics;

(iii) there exists a chemical potential for each constituent such that the diffusive energy flux has the form (1.1), and, in addition, the chemical potential is the derivative of the free energy with respect to the corresponding concentration;

(iv) the classical dissipation inequality holds; this inequality is usually taken as a starting point by writers on irreversible thermodynamics;

(v) the Gibbs' relation holds;

(vi) near a strong equilibrium state the linearized constitutive relations have the following properties: the heat flux and relative mass flux depend only on the temperature gradient and the gradients of the chemical potentials, while the mass supply depends only on the chemical potentials.

We consider only nonviscous fluid mixtures. The extension to viscous mixtures is not difficult. For convenience, we omit all smoothness hypotheses; it will be clear from the context what these ought to be.

Notation. Throughout this paper $\mathscr{B}$ denotes a body;[1] we will refer to $\mathscr{B}$ as the *mixture*. Elements X of $\mathscr{B}$ are called *material points*. Given a *motion* $(X, t) \mapsto \boldsymbol{x}(X, t)$ of $\mathscr{B}$, we write grad and div for the *spatial gradient* and *spatial divergence* (*i.e.* with respect to $\boldsymbol{x} = \boldsymbol{x}(X, t)$ holding t fixed), and we use a superimposed dot to denote the *material time derivative* (*i.e.* with respect to t holding X fixed).

Given a second-order tensor $\boldsymbol{A}$, we write $\boldsymbol{A}^T$ for its *transpose*, sym $\boldsymbol{A} = \frac{1}{2}(\boldsymbol{A} + \boldsymbol{A}^T)$ for its *symmetric part*, and tr $\boldsymbol{A}$ for its *trace*. The *inner product* of two tensors $\boldsymbol{A}$ and $\boldsymbol{B}$ is defined by $\boldsymbol{A} \cdot \boldsymbol{B} = \operatorname{tr}(\boldsymbol{A}\boldsymbol{B}^T)$. Finally, we write $\boldsymbol{a} \otimes \boldsymbol{b}$ for the *tensor product* of two vectors $\boldsymbol{a}$ and $\boldsymbol{b}$.

2. Basic Laws

We consider a fluid mixture $\mathscr{B}$ with $N+1$ constituents. Let $(X, t) \mapsto \boldsymbol{x}(X, t)$ denote a *motion* of $\mathscr{B}$. For the basic laws of our theory we postulate the following:

balance of mass

$$\dot{\rho} + \rho \operatorname{div} \dot{\boldsymbol{x}} = 0\,, \tag{2.1}$$

balance of mass for each constituent

$$\rho \dot{c}_\alpha = -\operatorname{div} \boldsymbol{h}_\alpha + m_\alpha \qquad (\alpha = 1, \dots, N)\,, \tag{2.2}$$

balance of forces[2]

$$\operatorname{div} \boldsymbol{T} + \rho \boldsymbol{b} = \boldsymbol{0}\,, \tag{2.3}$$

balance of energy

$$\rho \dot{e} = -\operatorname{div}(\boldsymbol{q} + \boldsymbol{j} - \boldsymbol{T}\dot{\boldsymbol{x}}) + \rho r + \rho \boldsymbol{b} \cdot \dot{\boldsymbol{x}}\,, \tag{2.4}$$

growth of entropy

$$\rho \dot{s} \geqq -\operatorname{div}\left(\frac{\boldsymbol{q}}{\theta}\right) + \frac{\rho r}{\theta}\,. \tag{2.5}$$

Here

$\rho(X, t)$ is the *density*,

$\boldsymbol{T}(X, t)$ is the *stress tensor* ($\boldsymbol{T} = \boldsymbol{T}^T$),

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[1] In the sense of NOLL (TRUESDELL & NOLL [1965], § 15).

[2] The body force $\boldsymbol{b}$ includes the inertial force $-\ddot{\boldsymbol{x}}$.

$\boldsymbol{b}(X, t)$	is the *body force*,
$e(X, t)$	is the *internal energy*,
$s(X, t)$	is the *entropy*,
$\boldsymbol{q}(X, t)$	is the *heat flux*,
$r(X, t)$	is the *heat supply*,
$\theta(X, t)$	is the *temperature* ($\theta > 0$),
$\boldsymbol{j}(X, t)$	is the *energy flux* due to diffusion,
$c_\alpha(X, t)$	is the *concentration*[1] of constituent α,
$\boldsymbol{h}_\alpha(X, t)$	is the *relative mass flux*[2] of constituent α,
$m_\alpha(X, t)$	is the *mass supply* to constituent α (due to chemical reactions).

We call

$$\boldsymbol{L} = \operatorname{grad} \dot{\boldsymbol{x}} \tag{2.6}$$

the *velocity gradient*; using (2.3) and (2.6), we can rewrite (2.4) in the form

$$\rho \dot{e} = -\operatorname{div}(\boldsymbol{q} + \boldsymbol{j}) + \boldsymbol{T} \cdot \boldsymbol{L} + \rho r. \tag{2.7}$$

The *free energy* ψ is defined by

$$\psi = e - \theta s. \tag{2.8}$$

In view of (2.7) and (2.8), the inequality (2.5) can also be written in the form

$$\rho(\dot{\psi} + s\dot{\theta}) - \boldsymbol{T} \cdot \boldsymbol{L} + \operatorname{div} \boldsymbol{j} + \frac{1}{\theta} \boldsymbol{q} \cdot \operatorname{grad} \theta \leqq 0. \tag{2.9}$$

Remark 2.1. If (2.7) and (2.8) hold, then (2.5) and (2.9) are equivalent.

Remark 2.2. For constituent $N+1$ we simply *define* c_{N+1}, $\boldsymbol{h}_{N+1}$, and m_{N+1} by the relations

$$c_{N+1} = 1 - \sum_{\alpha=1}^{N} c_\alpha, \qquad \boldsymbol{h}_{N+1} = -\sum_{\alpha=1}^{N} \boldsymbol{h}_\alpha, \qquad m_{N+1} = -\sum_{\alpha=1}^{N} m_\alpha; \tag{2.10}$$

this insures that balance of mass (2.2) is satisfied when $\alpha = N+1$.

Remark 2.3. At first sight it might appear that there should be a term of the form $-\operatorname{div} \boldsymbol{l}$ in the entropy inequality (2.5).[3] To see that this is not necessary, let us replace the divergence terms in the right-hand sides of (2.4) and (2.5) by

$$-\operatorname{div}(\boldsymbol{q}' + \boldsymbol{j}' - \boldsymbol{T}\dot{\boldsymbol{x}}) \quad \text{and} \quad -\operatorname{div}\left(\frac{\boldsymbol{q}'}{\theta} + \boldsymbol{l}\right), \tag{2.11}$$

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[1] $c_\alpha = \rho_\alpha / \rho$, where ρ_α is the mass density of constituent α.

[2] $\boldsymbol{h}_\alpha = \rho_\alpha(\boldsymbol{v}_\alpha - \dot{\boldsymbol{x}})$ (no sum on α), where $\boldsymbol{v}_\alpha$ is the velocity of α.

[3] In MÜLLER's [1968] theory the term $\boldsymbol{j}$ is not present in the energy equation and the term $\frac{\boldsymbol{q}}{\theta}$ in the entropy inequality is replaced by an arbitrary entropy flux $\boldsymbol{\Phi}$. The argument given in this remark shows that there is no essential difference between MÜLLER's point of view and ours. Indeed, within the context of classical mixture theory we would view the quantity (1.1) as a flux of energy (as does ECKART [1940]), while MÜLLER would view $\frac{1}{\theta} \sum_\alpha \mu'_\alpha \boldsymbol{h}_\alpha$ as a flux of entropy (as do MEIXNER & REIK [1959]). We take the point of view that the heat flux is that field which when divided by the temperature gives the entropy flux.

respectively. Then if we define

$$\boldsymbol{q}=\boldsymbol{q}'+\theta\boldsymbol{l}, \quad j=j'-\theta\boldsymbol{l}, \tag{2.12}$$

the terms (2.11) reduce to

$$-\operatorname{div}(\boldsymbol{q}+\boldsymbol{j}-\boldsymbol{T}\dot{\boldsymbol{x}}) \quad \text{and} \quad -\operatorname{div}\left(\frac{\boldsymbol{q}}{\theta}\right). \tag{2.13}$$

In (2.12) $\boldsymbol{q}'$ represents a non-diffusive heat flux and $\theta\boldsymbol{l}$ the heat flux due to diffusion.

Remark 2.4. In the standard treatises on mixtures it is usually assumed that

$$j=\sum_{\alpha=1}^{N+1}\mu_\alpha'\boldsymbol{h}_\alpha, \tag{2.14}$$

where μ_α' is the chemical potential of constituent α. If we define the reduced chemical potential μ_α by

$$\mu_\alpha=\mu_\alpha'-\mu_{N+1}', \tag{2.15}$$

then, in view of $(2.10)_2$, (2.14) reduces to

$$j=\mu_\alpha\boldsymbol{h}_\alpha; \tag{2.16}$$[1]

and we can use (2.2) to reduce (2.9) to the more familiar form

$$\begin{aligned}\rho(\dot{\psi}+s\dot{\theta}-\mu_\alpha\dot{c}_\alpha)-\boldsymbol{T}\cdot\boldsymbol{L}+\boldsymbol{h}_\alpha\cdot\operatorname{grad}\mu_\alpha&\\+\frac{1}{\theta}\boldsymbol{q}\cdot\operatorname{grad}\theta+m_\alpha\mu_\alpha\leqq 0.&\end{aligned} \tag{2.17}$$

In this paper *we do not assume that* (2.14) *holds.*

Remark 2.5. Note that in the energy equation (2.4) we do not include a term of the form

$$\sum_{\alpha=1}^{N+1}\boldsymbol{b}_\alpha\cdot\boldsymbol{h}_\alpha, \tag{2.18}$$

where $\boldsymbol{b}_\alpha$ is the body force on constituent α; thus, in view of $(2.10)_2$, our theory is restricted to situations in which $\boldsymbol{b}_\alpha$ is the same for each constituent. It is not much trouble to add a term w, representing the excess power due to diffusion, to the right-hand side of (2.4). If we do this and demand that w be given by a constitutive relation of the form (3.3), then the results of Sections 4, 5, and 6 remain valid provided we demand that w vanish in every homogeneous state and add w to the right-hand sides of (4.5), (4.8), and (4.13). Of course, w cannot, in general, represent a term of the form (2.18), since the body force $\boldsymbol{b}_\alpha$ is usually not given by a constitutive equation of the form (3.3).

The quantity

$$\upsilon=\frac{1}{\rho} \tag{2.19}$$

is called the *specific volume*. A motion $\boldsymbol{x}(X, t)$ and a specific volume field $\upsilon(X, t)$ will be called *compatible* provided they satisfy balance of mass (2.1). As is well

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[1] Summation from 1 to N over repeated *Greek* indices is assumed.

known, this will be the case if and only if

$$\upsilon(X,t)=|\det \boldsymbol{F}(X,t)|\,\upsilon(X,0), \tag{2.20}$$

where $\boldsymbol{F}$ is the deformation gradient taking the configuration at $t=0$ as reference.

3. Constitutive Assumptions

Let

$$\Lambda=(\upsilon,\theta,\mathrm{c},\operatorname{grad}\upsilon,\operatorname{grad}\theta,\operatorname{grad}\mathrm{c}), \tag{3.1}$$

where

$$\mathrm{c}=(c_1,\dots,c_N), \qquad \operatorname{grad}\mathrm{c}=(\operatorname{grad}c_1,\dots,\operatorname{grad}c_N). \tag{3.2}$$

As our constitutive assumption we suppose that

$$\begin{gathered}\psi=\hat{\psi}(\Lambda), \qquad \boldsymbol{T}=\hat{\boldsymbol{T}}(\Lambda), \qquad s=\hat{s}(\Lambda), \qquad \boldsymbol{q}=\hat{\boldsymbol{q}}(\Lambda),\\ j=\hat{j}(\Lambda), \qquad \boldsymbol{h}_\alpha=\hat{\boldsymbol{h}}_\alpha(\Lambda), \quad m_\alpha=\hat{m}_\alpha(\Lambda).\end{gathered} \tag{3.3}$$[1]

Moreover, since the mixture is a fluid, we assume that the *response functions* $\hat{\psi}$, $\hat{\boldsymbol{T}}$, $\hat{s}$, $\hat{\boldsymbol{q}}$, $\hat{j}$, $\hat{\boldsymbol{h}}_\alpha$, $\hat{m}_\alpha$ are *isotropic.*

Let

$$\boldsymbol{H}_{\alpha\beta}(\Lambda)=\operatorname{sym}\left[\frac{\partial \hat{\boldsymbol{h}}_\alpha(\Lambda)}{\partial(\operatorname{grad}c_\beta)}\right]. \tag{3.4}$$

The following two requirements are assumed to hold throughout the paper.

(A) The $N\times N$ matrix $\|\boldsymbol{H}_{\alpha\beta}\|$ (with tensor entries) is invertible, *i.e.*, there exist symmetric tensors $\boldsymbol{H}'_{\lambda\tau}$ ($\lambda,\tau=1,2,\dots,N$) such that

$$\boldsymbol{H}_{\alpha\beta}\boldsymbol{H}'_{\beta\lambda}=\boldsymbol{H}'_{\alpha\beta}\boldsymbol{H}_{\beta\lambda}=\delta_{\alpha\lambda}\boldsymbol{1}. \tag{3.5}$$

(B)[2] Given a material point X_0, a neighborhood $\mathscr{P}'$ of X_0, an initial concentration vector $\mathrm{c}_0(X)$ on $\mathscr{P}'$, a time interval $[0,t_1)$, a motion $\boldsymbol{x}(X,t)$, a specific volume field $\upsilon(X,t)$ compatible with $\boldsymbol{x}(X,t)$, and a temperature field $\theta(X,t)$, all on $\mathscr{P}'\times[0,t_1)$; there exists a solution $\mathrm{c}(X,t)$ of (2.2), $(3.3)_{6,7}$ on $\mathscr{P}\times[0,t_0)$, where $\mathscr{P}\subset\mathscr{P}'$ is a neighborhood of X_0 and t_0 is in $(0,t_1)$, such that

$$\mathrm{c}(X,0)=\mathrm{c}_0(X) \tag{3.6}$$

on $\mathscr{P}$.

An array ($\boldsymbol{x}$, υ, θ, ψ, $\boldsymbol{T}$, s, $\boldsymbol{q}$, j, c_α, $\boldsymbol{h}_\alpha$, m_α; $\alpha=1,\dots,N$) defined for all X in some part $\mathscr{P}$ of $\mathscr{B}$ and all t in some time interval $[0,t_0)$ will be called a *constitutive process* (with *domain* $\mathscr{P}\times[0,t_0)$) if it is consistent with the constitutive equations

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[1] The constitutive assumption $(3.3)_6$ for $\boldsymbol{h}_\alpha$ generalizes Fick's law. A somewhat different generalization was obtained by MÜLLER [1968] as a *consequence* of balance of momentum for the individual constituents. The relation deduced by MÜLLER includes inertial terms, and this, in turn, leads (in certain circumstances) to finite propagation speeds for disturbances in concentration. On the other hand, our theory leads to infinite speeds for such disturbances. Of course, a deficiency such as this is also present in classical heat conduction, and, as in that theory, should not detract from its usefulness in most situations.

[2] BOWEN [1969] was the first to notice that an assumption of this nature is necessary when chemical reactions are present. See also COLEMAN & GURTIN [1967] who utilize this type of assumption in a slightly different context.

(3.3) and balance of mass (2.1), (2.2). Assumption (B) insures that given X_0, $\boldsymbol{x}$, υ, θ, and c_0, with $\boldsymbol{x}$ and υ compatible, there exists an associated constitutive process in some neighborhood of X_0.

4. Consequences of the Second Law

Given a constitutive process, (2.3) and (2.4) can be used to determine the body force and heat supply necessary to sustain the process. On the other hand, the inequality (2.5) – or equivalently (2.9) – will be satisfied in every process if and only if certain restrictions are placed on the response functions. The next theorem lists these restrictions.

Theorem 4.1. *A necessary and sufficient condition that every constitutive process obey* (2.9) *is that the following five statements be true:*

(i) *The stress $\boldsymbol{T}$ is a pressure:*

$$\boldsymbol{T}=-p\mathbf{1}. \tag{4.1}$$

(ii) *ψ, p and s are independent of* grad υ, grad θ, *and* grad c:

$$\psi=\hat{\psi}(\upsilon,\theta,\mathrm{c}), \qquad p=\hat{p}(\upsilon,\theta,\mathrm{c}), \qquad s=\hat{s}(\upsilon,\theta,\mathrm{c}). \tag{4.2}$$

(iii) *$\hat{\psi}$ determines $\hat{p}$ and $\hat{s}$ through the relations*

$$\hat{p}=-\frac{\partial\hat{\psi}}{\partial\upsilon}, \qquad \hat{s}=-\frac{\partial\hat{\psi}}{\partial\theta}. \tag{4.3}$$

(iv) *The energy flux due to diffusion must have the classical form*

$$\boldsymbol{j}=\mu_\alpha\boldsymbol{h}_\alpha, \qquad \mu_\alpha=\hat{\mu}_\alpha(\upsilon,\theta,\mathrm{c})=\frac{\partial\hat{\psi}}{\partial c_\alpha}. \tag{4.4}$$

(v) *In every constitutive process*

$$\boldsymbol{h}_\alpha\cdot\operatorname{grad}\mu_\alpha+\frac{1}{\theta}\boldsymbol{q}\cdot\operatorname{grad}\theta+m_\alpha\mu_\alpha\leqq 0. \tag{4.5}$$

We postpone until later the proof of this as well as of several subsequent theorems.

We assume for the remainder of the paper that (i)–(v) *hold.* By $(4.4)_2$,

$$\operatorname{grad}\mu_\alpha=\left.\frac{\partial\hat{\mu}_\alpha}{\partial\upsilon}\right|_A\operatorname{grad}\upsilon+\left.\frac{\partial\hat{\mu}_\alpha}{\partial\theta}\right|_A\operatorname{grad}\theta+\left.\frac{\partial\hat{\mu}_\alpha}{\partial c_\beta}\right|_A\operatorname{grad}c_\beta\,; \tag{4.6}$$

hence we conclude from (3.1) that gradμ_α is a function of A in any constitutive process. Therefore, in view of $(3.3)_{4,6,7}$ and $(4.4)_2$, the left-hand side of (4.5) can also be considered a function of A. By Lemma 9.1, given any value of A, we can find an associated constitutive process; thus (4.5), with $\boldsymbol{q}$, $\boldsymbol{h}_\alpha$, m_α, μ_α, and gradμ_α defined by $(3.3)_{4,6,7}$, $(4.4)_2$, and (4.6), must hold for every value of A in the domain of the response functions.

The quantity μ_α defined by $(4.4)_2$ is called the *reduced chemical potential*[1] of constituent α. In view of (4.1)–(4.4) and (2.8), we have the "Gibb's relations"

$$\begin{aligned} \dot{\psi} &= -p\dot{v} - s\dot{\theta} + \mu_\alpha \dot{c}_\alpha, \\ \dot{e} &= -p\dot{v} + \theta\dot{s} + \mu_\alpha \dot{c}_\alpha \end{aligned} \tag{4.7}$$

in every constitutive process. By (2.1), (2.2), (2.18), (4.1), $(4.4)_1$, and $(4.7)_2$, we can rewrite the energy equation as follows:

$$\rho\theta\dot{s} = -\operatorname{div}\boldsymbol{q} + \rho r - \boldsymbol{h}_\alpha \cdot \operatorname{grad}\mu_\alpha - m_\alpha \mu_\alpha. \tag{4.8}$$

Finally, (4.3) and $(4.4)_2$ yield the well-known relations

$$\begin{aligned} &\frac{\partial\hat{s}}{\partial v} = \frac{\partial\hat{p}}{\partial\theta}, \quad \frac{\partial\hat{s}}{\partial c_\alpha} = -\frac{\partial\hat{\mu}_\alpha}{\partial\theta}, \quad \frac{\partial\hat{p}}{\partial c_\alpha} = -\frac{\partial\hat{\mu}_\alpha}{\partial v}, \\ &\frac{\partial\hat{\mu}_\alpha}{\partial c_\beta} = \frac{\partial\hat{\mu}_\beta}{\partial c_\alpha}, \quad \frac{\partial\hat{e}}{\partial\theta} = \theta\frac{\partial\hat{s}}{\partial\theta}, \end{aligned} \tag{4.9}$$

where $\hat{e} = \hat{\psi} + \theta\hat{s}$ is the response function for the internal energy.

Remark 4.1. One can give plausible physical arguments to support the following constitutive relations for the stress and free energy:

$$\begin{aligned} \boldsymbol{T} &= -p(v,\theta,\mathrm{c})\boldsymbol{1} - v\sum_{\alpha=1}^{N+1} \frac{\boldsymbol{h}_\alpha \otimes \boldsymbol{h}_\alpha}{c_\alpha}, \\ \psi &= \psi_I(v,\theta,\mathrm{c}) + \frac{v^2}{2}\sum_{\alpha=1}^{N+1} \frac{\boldsymbol{h}_\alpha^2}{c_\alpha}. \end{aligned} \tag{4.10}$$

In view of $(3.3)_6$ and (2.10), (4.10) are consistent with the constitutive relations $(3.3)_{1,2,6}$. However, the results (4.1) and (4.2) imply that *the constitutive relations* (4.10) *are inconsistent with the present theory. What the second law essentially tells us is that if terms involving squares of the relative mass flux are important, then the classical theory is not applicable.* It is clear from the work of BOWEN [1967], [1969] and MÜLLER [1968], among others, that the more general approach due to TRUESDELL [1957] allows for constitutive relations of the form (4.10).

Remark 4.2. When there are R independent chemical reactions,

$$m_\alpha = \sum_{r=1}^{R} \nu_{\alpha r} J_r, \tag{4.11}$$

where J_r is the reaction rate of reaction r, and $\nu_{\alpha r}$ divided by the molecular mass of constituent α is proportional to the corresponding stoichiometric coefficient. The chemical affinity of reaction r is defined by

$$A_r = \nu_{\alpha r}\mu_\alpha; \tag{4.12}$$

in these circumstances,

$$m_\alpha \mu_\alpha = \sum_{r=1}^{R} J_r A_r, \tag{4.13}$$

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[1] See Remark 2.4.

and (4.5) takes the familiar form

$$\boldsymbol{h}_\alpha \cdot \operatorname{grad}\mu_\alpha + \frac{1}{\theta}\,\boldsymbol{q} \cdot \operatorname{grad}\theta + \sum_{r=1}^{R} J_r A_r \leqq 0. \tag{4.14}$$

Remark 4.3.[1] It is often more convenient to take the constituent densities as independent variables in place of the specific volume and the concentrations. Thus suppose, for the present, that

$$\psi = \bar{\psi}(\rho_1, \dots, \rho_{N+1}, \theta). \tag{4.15}$$

Then

$$\hat{\psi}(\upsilon, \theta, c_1, \dots, c_N) = \bar{\psi}\left(\frac{c_1}{\upsilon}, \dots, \frac{c_{N+1}}{\upsilon}, \theta\right)\Bigg|_{c_{N+1} = 1 - \sum\limits_{\alpha=1}^{N} c_\alpha} \tag{4.16}$$

and (4.2), $(4.4)_2$ imply that

$$\begin{aligned} \mu_\alpha &= \frac{\partial(\rho\bar{\psi})}{\partial\rho_\alpha} - \frac{\partial(\rho\bar{\psi})}{\partial\rho_{N+1}}, \\ p &= \rho \sum_{\alpha=1}^{N+1} \rho_\alpha \frac{\partial\bar{\psi}}{\partial\rho_\alpha}. \end{aligned} \tag{4.17}$$

Further, if we define

$$\mu'_\alpha = \frac{\partial(\rho\bar{\psi})}{\partial\rho_\alpha}, \tag{4.18}$$

we arrive at the well-known result

$$\sum_{\alpha=1}^{N+1} c_\alpha \mu'_\alpha = \psi + \frac{p}{\rho}. \tag{4.19}$$

5. Homogeneous States

An element $A = \mathring{A}$ in the domain of the response functions will be called a *homogeneous state* provided it has the form

$$\mathring{A} = (\upsilon, \theta, \mathrm{c}, \mathbf{0}, \mathbf{0}, \mathbf{0}), \tag{5.1}$$

i.e. provided $\operatorname{grad}\upsilon = \operatorname{grad}\theta = \operatorname{grad}c_\alpha = \mathbf{0}$. In view of Lemma 10.1, (4.5), and the remarks made in the paragraph containing (4.6), we have

Proposition 5.1. *Let $\mathring{A}$ be a homogeneous state. Then*

$$\hat{\boldsymbol{h}}_\alpha(\mathring{A}) = \hat{\boldsymbol{q}}(\mathring{A}) = \mathbf{0}, \qquad \hat{m}_\alpha(\mathring{A})\,\hat{\mu}_\alpha(\mathring{A}) \leqq 0. \tag{5.2}$$

Further, if τ denotes υ, θ, or c_α, and if g denotes $\operatorname{grad}\upsilon$, $\operatorname{grad}\theta$, *or* $\operatorname{grad}c_\alpha$, *then*

$$\left.\frac{\partial\hat{m}_\alpha}{\partial g}\right|_{\mathring{A}} = \left.\frac{\partial\hat{\boldsymbol{h}}_\alpha}{\partial\tau}\right|_{\mathring{A}} = \left.\frac{\partial\hat{\boldsymbol{q}}}{\partial\tau}\right|_{\mathring{A}} = \mathbf{0}. \tag{5.3}$$

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[1] These observations contained in this remark are due to R. M. BOWEN (private communication).

The results $(5.2)_{1,2}$ assert that there is no flow of heat or mass in a homogeneous state. If we expand $\hat{\boldsymbol{q}}(A)$ and $\hat{\boldsymbol{h}}_\alpha(A)$ in a Taylor series about a homogeneous state $\mathring{A}$, and use Proposition 5.1 and Lemma 10.1, we arrive at

Proposition 5.2. *Let $\mathring{A}$ be a homogeneous state. Then there exist scalars κ, λ_α, ζ, λ'_α, $\lambda_{\alpha\beta}$, and ω_α such that*

$$\begin{aligned}\boldsymbol{q} &= -\kappa \operatorname{grad}\theta - \lambda_\alpha \operatorname{grad} c_\alpha - \zeta \operatorname{grad} v + O(|A-\mathring{A}|^2),\\ \boldsymbol{h}_\alpha &= -\lambda'_\alpha \operatorname{grad}\theta - \lambda_{\alpha\beta} \operatorname{grad} c_\beta - \omega_\alpha \operatorname{grad} v + O(|A-\mathring{A}|^2)\end{aligned} \tag{5.4}$$[1]

as $|A-\mathring{A}|\to 0$. Here $A=(v, \theta, \mathrm{c}, \operatorname{grad} v, \operatorname{grad}\theta, \operatorname{grad}\mathrm{c})$ and $\boldsymbol{q}$, $\boldsymbol{h}_\alpha$ are given by $(3.3)_{4,6}$.

The second and third terms in $(5.4)_1$ represent, respectively, a *flow of heat due to concentration gradients* (Dufour effect) and a *flow of heat due to a density gradient* (piezo-caloric effect); the first and third terms in $(5.4)_2$ represent, respectively, *mass transport due to a temperature gradient* (Soret effect) and *mass transport due to a density gradient* (piezo-diffusive effect).

6. Linearized Theory Near Equilibrium

By an equilibrium state we mean a homogeneous state $\mathring{A}$ with the property that

$$\hat{m}_\alpha(\mathring{A})=0 \quad (\alpha=1, \ldots, N). \tag{6.1}$$

Clearly, the result (5.4) holds near an equilibrium state. The next proposition gives an analogous result for the mass supply.

Proposition 6.1. *Let $\mathring{A}$ be an equilibrium state. Then there exist scalars $\tau_{\alpha\beta}$, δ_α, and δ'_α such that*

$$m_\alpha = -\tau_{\alpha\beta}(c_\beta-\mathring{c}_\beta) - \delta_\alpha(\theta-\mathring{\theta}) - \delta'_\alpha(v-\mathring{v}) + O(|A-\mathring{A}|^2) \tag{6.2}$$

as $|A-\mathring{A}|\to 0$. Here A is given by (3.1) and m_α by $(3.3)_7$. Moreover, if $\mathring{\mu}_\alpha=\hat{\mu}_\alpha(\mathring{v}, \mathring{\theta}, \mathring{\mathrm{c}})$, then

$$\tau_{\alpha\beta}\,\mathring{\mu}_\alpha = \delta_\alpha\,\mathring{\mu}_\alpha = \delta'_\alpha\,\mathring{\mu}_\alpha = 0. \tag{6.3}$$[2]

The proof of this proposition is given in Section 9. The inequality (4.5) and the remarks given in the paragraph containing (4.6) yield certain inequalities for the coefficients in Propositions 5.2 and 6.1; we shall not list these inequalities.

Since $\mu_\alpha=\hat{\mu}_\alpha(A)=\mathring{\mu}_\alpha+O(|A-\mathring{A}|)$, we conclude from (6.2) and (6.3) that

$$m_\alpha\,\mathring{\mu}_\alpha = O(|A-\mathring{A}|^2), \qquad m_\alpha\,\mu_\alpha = O(|A-\mathring{A}|^2); \tag{6.4}$$

thus, to within terms of $O(|A-\mathring{A}|^2)$, the mass supply and the reduced chemical potential are "orthogonal"

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[1] Here $|A-\mathring{A}|^2=|v-\mathring{v}|^2+|\theta-\mathring{\theta}|^2+|\operatorname{grad} v|^2+|\operatorname{grad}\theta|^2+\sum_\alpha[(c_\alpha-\mathring{c}_\alpha)^2+|\operatorname{grad} c_\alpha|^2]$.

[2] A result similar to the first of these was established by BOWEN [1969], Eq. (7.19).

Now let $\mathring{A}$ be a fixed equilibrium state and consider a constitutive process with

$$|A-\mathring{A}|\leqq\varepsilon, \qquad |\operatorname{grad}\dot{\boldsymbol{x}}|,\ |\dot{\theta}|,\ |\dot{c}|\leqq\varepsilon. \tag{6.5}$$

By (2.1), (2.19), $(5.4)_2$, and (4.6),

$$\dot{\upsilon}=O(\varepsilon), \qquad \boldsymbol{h}_\alpha\cdot\operatorname{grad}\mu_\alpha=O(\varepsilon^2); \tag{6.6}$$

therefore, in view of $(6.4)_2$, (4.8) yields

$$a_1\dot{\theta}+a_2\dot{\upsilon}+d_\alpha\dot{c}_\alpha=-\operatorname{div}\boldsymbol{q}+\mathring{\rho}r+O(\varepsilon^2), \tag{6.7}$$

where, by (4.9),

$$\begin{gathered} a_1=\mathring{\rho}\mathring{\theta}\frac{\partial\hat{s}}{\partial\theta}\bigg|_{\mathring{A}}=\mathring{\rho}\frac{\partial\hat{e}}{\partial\theta}\bigg|_{\mathring{A}}, \qquad a_2=\mathring{\rho}\mathring{\theta}\frac{\partial\hat{s}}{\partial\upsilon}\bigg|_{\mathring{A}}=\mathring{\rho}\mathring{\theta}\frac{\partial\hat{p}}{\partial\theta}\bigg|_{\mathring{A}}, \\ d_\alpha=\mathring{\rho}\mathring{\theta}\frac{\partial\hat{s}}{\partial c_\alpha}\bigg|_{\mathring{A}}=-\mathring{\rho}\mathring{\theta}\frac{\partial\hat{\mu}_\alpha}{\partial\theta}\bigg|_{\mathring{A}}, \qquad \mathring{\rho}=\frac{1}{\mathring{\upsilon}}. \end{gathered} \tag{6.8}$$

If we neglect terms of $O(\varepsilon^2)$ in (2.1), (2.2), (5.4), (6.2), and (6.7), and combine the resulting relations, we arrive at the following equations:[1]

$$\begin{gathered} \mathring{\rho}\dot{\upsilon}=\operatorname{div}\dot{\boldsymbol{x}} \\ \mathring{\rho}\dot{c}_\alpha=\lambda_{\alpha\beta}\Delta c_\beta+\lambda'_\alpha\Delta\theta+\omega_\alpha\Delta\upsilon+m_\alpha, \\ m_\alpha=-\tau_{\alpha\beta}(c_\beta-\mathring{c}_\beta)-\delta_\alpha(\theta-\mathring{\theta})-\delta'_\alpha(\upsilon-\mathring{\upsilon}), \\ a_1\dot{\theta}+a_2\dot{\upsilon}+d_\alpha\dot{c}_\alpha=\kappa\Delta\theta+\lambda_\beta\Delta c_\beta+\zeta\Delta\upsilon+\mathring{\rho}r, \end{gathered} \tag{6.9}$$

provided we assume that $r=O(\varepsilon)$. Further, if we let

$$E_1=-\frac{\partial\hat{p}}{\partial\upsilon}\bigg|_{\mathring{A}}, \qquad E_2=-\frac{\partial\hat{p}}{\partial\theta}\bigg|_{\mathring{A}}=-\frac{a_2}{\mathring{\rho}\mathring{\theta}}\bigg|_{\mathring{A}}, \qquad F_\alpha=-\frac{\partial\hat{p}}{\partial c_\alpha}\bigg|_{\mathring{A}}=\frac{\partial\hat{\mu}_\alpha}{\partial\upsilon}\bigg|_{\mathring{A}}, \tag{6.10}$$

then, if we neglect terms of $O(\varepsilon^2)$, (2.3) and (4.1) imply

$$E_1\operatorname{grad}\upsilon+E_2\operatorname{grad}\theta+F_\alpha\operatorname{grad}c_\alpha+\mathring{\rho}\boldsymbol{b}=\boldsymbol{0}, \tag*{(6.11)^2}$$

provided, of course, that $\boldsymbol{b}=O(\varepsilon)$.

To the same degree of approximation *material* time derivatives are equal to the corresponding *spatial* time derivatives, and in what follows we shall assume this is so. Then the operator "·" commutes with the operators grad and div. Let

$$\boldsymbol{b}=\boldsymbol{b}_0-\ddot{\boldsymbol{x}}, \tag{6.12}$$

where $\boldsymbol{b}_0$ is the non-inertial body force. If we take the time derivative of $(6.9)_1$ and the divergence of (6.11), we conclude, with the aid of (6.12), that

$$\mathring{\rho}^2\ddot{\upsilon}=E_1\Delta\upsilon+E_2\Delta\theta+F_\alpha\Delta c_\alpha+\mathring{\rho}\operatorname{div}\boldsymbol{b}_0 \tag{6.13}$$

provided $\mathring{\rho}$ is a constant. Equations $(6.9)_{2,4}$ and (6.13), supplemented by $(6.9)_3$, constitute the basic field equations of the linearized theory. If the "coupling

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[1] Here $\Delta=\operatorname{div}\operatorname{grad}$ is the spacial Laplacian.

[2] Recall that $\boldsymbol{b}$ includes the inertial body force $-\ddot{\boldsymbol{x}}$.

coefficients" $E_2=F_\alpha=\omega_\alpha=\zeta=\delta'_\alpha=0$ and if the resulting coefficients have appropriate signs, then (6.13) results in a *hyperbolic* equations for the specific volume υ, while $(6.9)_{2,4}$ reduce to coupled *parabolic* equations for the concentrations c_α and the temperature θ.

7. Linearized Constitutive Relations Near a Strong Equilibrium State

In view of $(6.4)_1$,

$$\hat{m}_\alpha(\Lambda)\mathring{\mu}_\alpha=O(|\Lambda-\mathring{\Lambda}|^2) \tag{7.1}$$

provided $\mathring{\Lambda}$ is an equilibrium state and $\mathring{\mu}_\alpha=\hat{\mu}_\alpha(\mathring{\Lambda})$. We say that $\mathring{\Lambda}$ is a *strong equilibrium state* if, in addition to (6.1),

$$\hat{m}_\alpha(\Lambda)\mathring{\mu}_\alpha=O(|\Lambda-\mathring{\Lambda}|^3) \tag{7.2}$$

as $|\Lambda-\mathring{\Lambda}|\to 0$.[1]

Remark 7.1. To see that this is a natural generalization of the usual notion of strong equilibrium, we assume, for the time being, that there are R independent chemical reactions, so that (4.11) and (4.12) hold. In this instance it is customary to call $\mathring{\Lambda}$ a "strong equilibrium state" provided[2]

$$J_r(\mathring{\Lambda})=A_r(\mathring{\Lambda})=0. \tag{7.3}$$

By (4.11), the first of (7.3) implies (6.1). Further, (4.11), (4.12), and $(7.3)_2$ yield

$$\hat{m}_\alpha(\Lambda)\mathring{\mu}_\alpha=\sum_{r=1}^{R} J_r(\Lambda)A_r(\mathring{\Lambda})\equiv 0. \tag{7.4}$$

Thus our notion of a strong equilibrium state is somewhat weaker than the classical definition. For all of our results it suffices to use the definition containing (7.2).

Let $\mathring{\Lambda}$ be an equilibrium state and let

$$a_{\alpha\beta}=\left.\frac{\partial\hat{\mu}_\alpha}{\partial c_\beta}\right|_{\mathring{\Lambda}}. \tag{7.5}$$

We suppose that

(C) the $N\times N$ matrix $\|a_{\alpha\beta}\|$ is invertible.

This assumption insures that $\boldsymbol{\mu}$ and $\operatorname{grad}\boldsymbol{\mu}$ can be used as independent variables in place of $\mathbf{c}$ and $\operatorname{grad}\mathbf{c}$, at least in a neighborhood of $\mathring{\Lambda}$. The next theorem provides a rational basis for some of the linear formulae that appear in texts on nonequilibrium thermodynamics.

Theorem 7.1. *Let $\mathring{\Lambda}$ be a strong equilibrium state and let $\mathring{\mu}_\alpha=\hat{\mu}_\alpha(\mathring{\upsilon},\mathring{\theta},\mathring{\mathbf{c}})$. Then there exist scalars k, l_α, l'_α, $l_{\alpha\beta}$, and $t_{\alpha\beta}$ such that*

$$\begin{aligned}
\boldsymbol{q}&=-k\operatorname{grad}\theta-l_\alpha\operatorname{grad}\mu_\alpha+O(|\Lambda-\mathring{\Lambda}|^2),\\
\boldsymbol{h}_\alpha&=-l'_\alpha\operatorname{grad}\theta-l_{\alpha\beta}\operatorname{grad}\mu_\beta+O(|\Lambda-\mathring{\Lambda}|^2),\\
m_\alpha&=-t_{\alpha\beta}(\mu_\beta-\mathring{\mu}_\beta)+O(|\Lambda-\mathring{\Lambda}|^2),
\end{aligned} \tag{7.6}$$

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[1] Gurtin [1971].

[2] Truesdell [1969], p. 107. See also Bowen [1969], p. 121.

as $|A-\mathring{A}|\to 0$. *Here* A *is given by* (3.1) *and* $\boldsymbol{q}$, $\boldsymbol{h}_\alpha$, m_α, μ_α, *and* $\operatorname{grad}\mu_\alpha$ *correspond to* A *in the sense of* (3.3), $(4.4)_2$, *and* (4.6). *Further,*

$$t_{\alpha\beta}\mathring{\mu}_\alpha=0, \tag{7.7}$$

and the matrices

$$\|t_{\alpha\beta}\|, \qquad \left\| \begin{matrix} \frac{1}{\mathring{\theta}}k & \frac{1}{\mathring{\theta}}l_1 & \cdots & \frac{1}{\mathring{\theta}}l_N \\ l'_1 & l_{11} & \cdots & l_{1N} \\ \vdots & \vdots & & \vdots \\ l'_N & l_{N1} & \cdots & l_{NN} \end{matrix} \right\| \tag{7.8}$$

are positive semi-definite.

Theorem 7.1 asserts that to within terms of $O(|A-\mathring{A}|^2)$, $\boldsymbol{q}$ *and* $\boldsymbol{h}_\alpha$ *depend only on* $\operatorname{grad}\theta$ *and* $\operatorname{grad}\mu$, *while* m_α *depends only on* μ. Also, a simple consequence of (7.8) is that the conductivity k is non-negative and the matrix $\|l_{\alpha\beta}\|$ positive semi-definite. Finally, note that if $t_{\alpha\beta}=t_{\beta\alpha}$, then $(7.6)_3$ takes the form

$$m_\alpha=-t_{\alpha\beta}\mu_\beta+O(|A-\mathring{A}|^2). \tag{7.9}$$

The coefficients in (7.6) are related to those in (5.4) and (6.2). Indeed, by $(4.4)_2$, (4.6), and (7.5),

$$\begin{aligned} &\mu_\alpha-\mathring{\mu}_\alpha=a_{\alpha\beta}(c_\beta-\mathring{c}_\beta)+\gamma_\alpha(\upsilon-\mathring{\upsilon})+\eta_\alpha(\theta-\mathring{\theta})+O(|A-\mathring{A}|^2),\\ &\operatorname{grad}\mu_\alpha=a_{\alpha\beta}\operatorname{grad}c_\beta+\gamma_\alpha\operatorname{grad}\upsilon+\eta_\alpha\operatorname{grad}\theta+O(|A-\mathring{A}|^2), \end{aligned} \tag{7.10}$$

where

$$\gamma_\alpha=\left.\frac{\partial\hat{\mu}_\alpha}{\partial\upsilon}\right|_{\mathring{A}}, \qquad \eta_\alpha=\left.\frac{\partial\hat{\mu}_\alpha}{\partial\theta}\right|_{\mathring{A}}, \tag{7.11}$$

and thus

$$\begin{aligned} &\kappa=k+l_\alpha\eta_\alpha, && \lambda_\alpha=l_\alpha a_{\alpha\beta}, && \zeta=l_\alpha\gamma_\alpha,\\ &\lambda'_\alpha=l'_\alpha+l_{\alpha\beta}\eta_\beta, && \lambda_{\alpha\beta}=l_{\alpha\varphi}a_{\varphi\beta}, && \omega_\alpha=l_{\alpha\beta}\gamma_\beta,\\ &\tau_{\alpha\beta}=t_{\alpha\varphi}a_{\varphi\beta}, && \delta_\alpha=t_{\alpha\beta}\eta_\beta, && \delta'_\alpha=t_{\alpha\beta}\gamma_\beta. \end{aligned} \tag{7.12}$$

Remark 6.1. Let us now suppose that (4.11) and (4.12) hold, that

$$\sum_{r=1}^{R}\nu_{\alpha r}f_r=0 \quad (\alpha=1,\dots,N) \quad \text{only when} \quad f_1=\dots=f_R=0, \tag{7.13}$$

and that

$$J_r=-\sum_{s=1}^{R}L_{rs}(A_s-\mathring{A}_s)+O(|A-\mathring{A}|^2), \tag{7.14}$$

where

$$\mathring{A}_s=\nu_{\alpha s}\mathring{\mu}_\alpha. \tag{7.15}$$

Then, by (4.11), (4.12), $(7.6)_3$, (7.14), and (7.15),

$$t_{\alpha\beta}=\sum_{r,s=1}^{R}\nu_{\alpha r}\nu_{\beta s}L_{rs}, \tag{7.16}$$

and, using (7.13) and the fact that $\|t_{\alpha\beta}\|$ is positive semi-definite, it is not difficult to prove that $\|L_{rs}\|$ is positive semi-definite. Further, by (7.7), (7.15), and (7.16),

$$\sum_{r,s=1}^{R} \nu_{\beta s} L_{rs} \overset{\circ}{A}_r = \sum_{r,s=1}^{R} \nu_{\beta s} \nu_{\alpha r} L_{rs} \overset{\circ}{\mu}_\alpha = t_{\alpha\beta} \overset{\circ}{\mu}_\alpha = 0, \tag{7.17}$$

and thus we conclude from (7.13) that

$$\sum_{r=1}^{R} L_{rs} \overset{\circ}{A}_r = 0. \tag{7.18^1}$$

Therefore, in view of (7.14),

$$\sum_{r=1}^{R} J_r \overset{\circ}{A}_r = O(|\Lambda - \overset{\circ}{\Lambda}|^2), \tag{7.19}$$

and, if $L_{rs} = L_{sr}$, (7.14) reduces to

$$J_r = -\sum_{s=1}^{R} L_{rs} A_s + O(|\Lambda - \overset{\circ}{\Lambda}|^2). \tag{7.20}$$

Of course, if (7.3) holds, then (7.14) automatically reduces to (7.20). Finally, if (7.3) holds, then (7.15) and (7.16) imply that

$$t_{\alpha\beta} \overset{\circ}{\mu}_\beta = 0;$$

thus, in this instance, $(7.6)_3$ reduces to (7.9) without the assumption $t_{\alpha\beta} = t_{\beta\alpha}$.[2]

8. Incompressible Materials

Assume now that the body is incompressible in the sense of the constraint

$$\dot{v} \equiv 0. \tag{8.1}$$

In this instance the stress is determined only to within an arbitrary pressure; thus we replace $(3.3)_2$ by the constitutive relation

$$T - \tfrac{1}{3}(\operatorname{tr} T)\mathbf{1} = \hat{S}(\Lambda), \tag{8.2}$$

where now

$$\Lambda = (\theta, \mathrm{c}, \operatorname{grad}\theta, \operatorname{grad}\mathrm{c}). \tag{8.3}$$

The remaining relations in (3.3) are still assumed to hold, but with (3.1) replaced by (8.3). Theorem (4.1) remains valid in the present circumstances with (4.1), (4.2), (4.3), and $(4.4)_2$ replaced by

$$\begin{gathered} \hat{S} = 0 \\ \psi = \hat{\psi}(\theta, \mathrm{c}), \quad s = \hat{s}(\theta, \mathrm{c}), \quad \hat{s} = -\frac{\partial \hat{\psi}}{\partial \theta}, \\ \mu_\alpha = \hat{\mu}_\alpha(\theta, \mathrm{c}) = \frac{\partial \hat{\psi}}{\partial c_\alpha}; \end{gathered} \tag{8.4}$$

the results $(4.4)_1$ and (4.5) remain unchanged.

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[1] A similar result is derived by BOWEN [1969], Eq. (7.22).

[2] This observation is due to R. M. BOWEN (private communication).

Homogeneous states and equilibrium states are defined analogously, and Theorem 7.1 remains valid. Further, the equations (6.9) have the following counterparts:

$$\begin{aligned} \mathring{\rho}\,\dot{c}_\alpha &= \lambda_{\alpha\beta}\,\Delta c_\beta + \lambda'_\alpha \Delta\theta + m_\alpha,\\ m_\alpha &= -\tau_{\alpha\beta}(c_\beta - \mathring{c}_\beta) - \delta_\alpha(\theta - \mathring{\theta}),\\ a_1\dot{\theta} + d_\alpha\,\dot{c}_\alpha &= \kappa\Delta\theta + \lambda_\beta\,\Delta c_\beta + \mathring{\rho}\,r. \end{aligned} \tag{8.5}$$

9. Proofs of Main Results

Lemma 9.1. *Let $a>0$, $g>0$, d_α, $\overset{*}{a}$, and $\overset{*}{g}$ be given scalars, let $\boldsymbol{a}$, $\boldsymbol{g}$, $\boldsymbol{d}_\alpha$, $\overset{*}{\boldsymbol{a}}$, $\overset{*}{\boldsymbol{g}}$, and $\overset{*}{\boldsymbol{d}}_\alpha$ be given vectors, let $\boldsymbol{M}$ be a given tensor with $\operatorname{tr}\boldsymbol{M}=0$, and let $\boldsymbol{A}$, $\boldsymbol{G}$, and $\boldsymbol{D}_\alpha$ be given symmetric tensors. Let X_0 be a given material point. Then there exists a constitutive process whose domain contains $(X_0, 0)$ such that when $X=X_0$ and $t=0$:*

$$\begin{gathered} \upsilon = a,\quad \theta = g,\quad c_\alpha = d_\alpha,\quad \operatorname{grad}\upsilon = \boldsymbol{a},\quad \operatorname{grad}\theta = \boldsymbol{g},\quad \operatorname{grad} c_\alpha = \boldsymbol{d}_\alpha,\\ \dot{\upsilon} = \overset{*}{a},\quad \dot{\theta} = \overset{*}{g},\quad \dot{\overline{\operatorname{grad}\upsilon}} = \overset{*}{\boldsymbol{a}},\quad \dot{\overline{\operatorname{grad}\theta}} = \overset{*}{\boldsymbol{g}},\quad \dot{\overline{\operatorname{grad} c_\alpha}} = \overset{*}{\boldsymbol{d}}_\alpha,\\ \operatorname{grad}^2\upsilon = \boldsymbol{A},\quad \operatorname{grad}^2\theta = \boldsymbol{B},\quad \operatorname{grad}^2 c_\alpha = \boldsymbol{D}_\alpha,\quad \operatorname{grad}\dot{\boldsymbol{x}} - \tfrac{1}{3}(\operatorname{div}\dot{\boldsymbol{x}})\boldsymbol{1} = \boldsymbol{M}. \end{gathered} \tag{9.1}$$

Proof. It is a simple matter to construct a motion $\boldsymbol{x}$, a compatible specific volume field υ, and a temperature field θ on $\mathscr{P}' \times [0, t_1)$, where $\mathscr{P}'$ is a neighborhood of X_0 and $t_1>0$, such that for $X=X_0$ and $t=0$ the results in (9.1) concerning $\boldsymbol{x}$, υ, and θ hold. Now let c_0 be an initial concentration vector on $\mathscr{B}$ with the property that

$$\operatorname{grad} c_{0\alpha}(X_0) = \boldsymbol{d}_\alpha,\qquad \operatorname{grad}^2 c_{0\alpha} = \boldsymbol{D}_\alpha,\qquad \operatorname{grad}^3 c_{0\alpha}(X_0) = \boldsymbol{\Gamma}_\alpha, \tag{9.2}$$

where Γ_α is a completely symmetric third order tensor, as yet unspecified. In view of assumption (B), there exists a constitutive process whose domain $\mathscr{P}\times[0, t_0)$ contains $(X_0, 0)$ such that

$$\mathrm{c}(X, 0) = \mathrm{c}_0(X) \tag{9.3}$$

for every $X\in\mathscr{P}$. Thus to complete the proof we have only to show that Γ_α can be chosen so that

$$\dot{\overline{\operatorname{grad} c_\alpha}}(X_0, 0) = \overset{*}{\boldsymbol{d}}_\alpha. \tag{9.4}$$

Let

$$\boldsymbol{k}_\alpha = \operatorname{grad}\dot{\boldsymbol{x}}(X_0, 0)^T \boldsymbol{d}_\alpha,\qquad \boldsymbol{d}'_y = \overset{*}{\boldsymbol{d}}_\alpha + \boldsymbol{k}_\alpha. \tag{9.5}$$

Since

$$\dot{\overline{\operatorname{grad} c_\alpha}} = \operatorname{grad}\dot{c}_\alpha - (\operatorname{grad}\dot{\boldsymbol{x}})^T \operatorname{grad} c_\alpha, \tag{9.6}$$

to establish (9.4) it suffices to show that $\boldsymbol{\Gamma}_\alpha$ can be chosen so that

$$\operatorname{grad}\dot{c}_\alpha(X_0, 0) = \boldsymbol{d}'_\alpha. \tag{9.7}$$

By (2.2) and (2.19),

$$\operatorname{grad}\dot{c}_\alpha = -\upsilon\operatorname{grad}\operatorname{div}\boldsymbol{h}_\alpha + \upsilon\operatorname{grad} m_\alpha + (-\operatorname{div}\boldsymbol{h}_\alpha + m_\alpha)\operatorname{grad}\upsilon. \tag{9.8}$$

Assume now that a Cartesian coordinate system (x_1, x_2, x_3) is specified, and let $H_{\alpha\beta}(i,j)$ denote the components of the tensor $\boldsymbol{H}_{\alpha\beta}$ defined in (3.4). Then, by (9.8), $(3.3)_{6,7}$, and (3.1),

$$\frac{\partial}{\partial x_k}\dot{c}_\alpha = -\sum_{i,j=1}^{3} \upsilon H_{\alpha\beta}(i,j)\frac{\partial^3 c_\beta}{\partial x_i \partial x_j \partial x_k} + f(k), \tag{9.9}$$

where $f(k)$ is the k-th component of a vector field $\boldsymbol{f}$ of the form

$$\begin{gathered}\boldsymbol{f} = \hat{\boldsymbol{f}}(\upsilon, \theta, \mathrm{c}, \operatorname{grad}\upsilon, \operatorname{grad}\theta, \operatorname{grad}\mathrm{c}, \operatorname{grad}^2\upsilon, \operatorname{grad}^2\theta,\\ \operatorname{grad}^2\mathrm{c}, \operatorname{grad}^3\upsilon, \operatorname{grad}^3\theta).\end{gathered} \tag{9.10}$$

We now assume that the components $\Gamma_\alpha(i,j,k)$ of $\boldsymbol{\Gamma}_\alpha$ have the form

$$\Gamma_\alpha(i,j,k) = H'_{\alpha\beta}(i,j)\,v_\beta(k) + H'_{\alpha\beta}(k,j)\,v_\beta(i) + H'_{\alpha\beta}(i,k)\,v_\beta(j), \tag{9.11}$$

where $H'_{\alpha\beta}(i,j)$ are the components of the tensor $\boldsymbol{H}'_{\alpha\beta}$ of assumption (A) and $v_\beta(k)$ are the components of the vector

$$\boldsymbol{v}_\beta = -\frac{1}{5a}\left(\boldsymbol{d}'_\alpha - \boldsymbol{f}(X_0, 0)\right). \tag{9.12}$$

Then, if we evaluate (9.9) at $(X_0, 0)$ and use (3.5), $(9{,}2)_3$, (9.3), (9.11), and (9.12), we arrive at the desired result (9.7). ▌

Proof of Theorem 4.1. The proof of *sufficiency* follows upon direct substitution. To establish the *necessity* of (i)–(v) we assume that every constitutive process obeys (2.9), or equivalently, by $(3.3)_1$, (2.1), and (2.19), that every constitutive process obeys

$$\begin{aligned}\rho\Bigg[&\left(\frac{\partial\hat{\psi}}{\partial\upsilon}+p\right)\dot{\upsilon} + \left(\frac{\partial\hat{\psi}}{\partial\theta}+s\right)\dot{\theta} + \frac{\partial\hat{\psi}}{\partial(\operatorname{grad}\upsilon)}\cdot\dot{\overline{\operatorname{grad}\upsilon}} + \frac{\partial\hat{\psi}}{\partial(\operatorname{grad}\theta)}\cdot\dot{\overline{\operatorname{grad}\theta}}\\ &+\frac{\partial\hat{\psi}}{\partial(\operatorname{grad}c_\alpha)}\cdot\dot{\overline{\operatorname{grad}c_\alpha}}\Bigg]\\ &-[\boldsymbol{T}+p\boldsymbol{1}]\cdot\left[\operatorname{grad}\dot{\boldsymbol{x}} - \frac{1}{3}(\operatorname{div}\dot{\boldsymbol{x}})\boldsymbol{1}\right]\\ &+\operatorname{div}\boldsymbol{k} + \boldsymbol{h}_\alpha\cdot\operatorname{grad}\mu_\alpha + \frac{1}{\theta}\,q\cdot\operatorname{grad}\theta + m_\alpha\mu_\alpha \leqq 0,\end{aligned} \tag{9.13}$$

where

$$\begin{aligned}p &= -\tfrac{1}{3}(\operatorname{tr}\boldsymbol{T})\boldsymbol{1}\\ \boldsymbol{k} &= \hat{\boldsymbol{k}}(\Lambda) = \boldsymbol{j} - \mu_\alpha \boldsymbol{h}_\alpha,\\ \mu_\alpha &= \hat{\mu}_\alpha(\Lambda) = \frac{\partial\hat{\psi}}{\partial c_\alpha}.\end{aligned} \tag{9.14}$$

It is clear from Lemma 9.1 and the constitutive equations (3.3) that (i), (ii), and (iii) hold and that

$$\operatorname{div}\boldsymbol{k} + \boldsymbol{h}_\alpha\cdot\operatorname{grad}\mu_\alpha + \frac{1}{\theta}\,\boldsymbol{q}\cdot\operatorname{grad}\theta + m_\alpha\mu_\alpha \leqq 0 \tag{9.15}$$

is satisfied in every constitutive process. Thus to complete the proof it suffices to show that

$$\boldsymbol{k}\equiv\mathbf{0}. \tag{9.16}$$

By $(9.14)_3$, $(4.4)_2$ holds; hence $\operatorname{grad}\mu_\alpha$ is a function of υ, θ, c, $\operatorname{grad}\upsilon$, $\operatorname{grad}\theta$, and grad c (and is independent of $\operatorname{grad}^2\upsilon$, $\operatorname{grad}^2\theta$, and grad^2c) and, by (3.1) and (3.3), (9.15) has the form

$$\operatorname{div}\boldsymbol{k}+f(\Lambda)\leqq 0. \tag{9.17}$$

On the other hand,

$$\begin{aligned}\operatorname{div}\boldsymbol{k}=&\left[\frac{\partial\hat{\boldsymbol{k}}}{\partial(\operatorname{grad}\upsilon)}\right]\cdot\operatorname{grad}^2\upsilon+\left[\frac{\partial\hat{\boldsymbol{k}}}{\partial(\operatorname{grad}\theta)}\right]\cdot\operatorname{grad}^2\theta\\&+\left[\frac{\partial\hat{\boldsymbol{k}}}{\partial(\operatorname{grad}c_\alpha)}\right]\cdot\operatorname{grad}^2 c_\alpha+g(\Lambda),\end{aligned}\tag{9.18}$$

and since (9.17) must hold in every constitutive process, we conclude from Lemma 9.1 that

$$\left[\frac{\partial\hat{\boldsymbol{k}}}{\partial(\operatorname{grad}\upsilon)}\right]\cdot\boldsymbol{A}=\left[\frac{\partial\hat{\boldsymbol{k}}}{\partial(\operatorname{grad}\theta)}\right]\cdot\boldsymbol{B}=\left[\frac{\partial\hat{\boldsymbol{k}}}{\partial(\operatorname{grad}c_\alpha)}\right]\cdot\boldsymbol{D}_\alpha=0\ \text{(no sum on }\alpha) \tag{9.19}$$

whenever $\boldsymbol{A}$, $\boldsymbol{B}$ and $\boldsymbol{D}_\alpha$ are symmetric tensors. Thus the symmetric parts of the partial gradients of $\hat{\boldsymbol{k}}$ with respect to $\operatorname{grad}\upsilon$, $\operatorname{grad}\theta$, and $\operatorname{grad}c_\alpha(\alpha=1,\dots,N)$ vanish,[1] and we conclude from Lemma 10.2 that (9.16) holds. ∎

Proof of Proposition 6.1. The result (6.2) follows from (5.3) and (6.1). Next, since $(7.10)_1$ holds in the present circumstances,

$$\mu_\alpha=\overset{\circ}{\mu}_\alpha+O(|\Lambda-\overset{\circ}{\Lambda}|), \tag{9.20}$$

and, letting

$$c'_\alpha=c_\alpha-\overset{\circ}{c}_\alpha,\qquad \upsilon'=\upsilon-\overset{\circ}{\upsilon},\qquad \theta'=\theta-\overset{\circ}{\theta}, \tag{9.21}$$

we conclude from $(5.2)_3$ and (6.2) that

$$\overset{\circ}{\mu}_\alpha[\tau_{\alpha\beta}c'_\beta+\delta_\alpha\theta'+\delta'_\alpha\upsilon']+O(|\Lambda-\overset{\circ}{\Lambda}|^2)\geqq 0 \tag{9.22}$$

as $|\Lambda-\overset{\circ}{\Lambda}|\to 0$ with Λ homogeneous. This clearly implies (6.3). ∎

Proof of Theorem 7.1. Let

$$\xi_\alpha=\operatorname{grad}c_\alpha,\qquad \boldsymbol{v}=\operatorname{grad}\upsilon,\qquad \boldsymbol{g}=\operatorname{grad}\theta, \tag{9.23}$$

and (with the aid of (9.21)) define

$$\begin{aligned}\mu'_\alpha&=a_{\alpha\beta}c'_\beta+\gamma_\alpha\upsilon'+\eta_\alpha\theta',\\ \boldsymbol{u}_\alpha&=a_{\alpha\beta}\xi_\beta+\gamma_\alpha\boldsymbol{v}+\eta_\alpha\boldsymbol{g}.\end{aligned}\tag{9.24}$$

Then, by (7.10),

$$\begin{aligned}\mu'_\alpha&=\mu_\alpha-\overset{\circ}{\mu}_\alpha+O(\varepsilon^2),\\ \boldsymbol{u}_\alpha&=\operatorname{grad}\mu_\alpha+O(\varepsilon^2),\end{aligned}\tag{9.25}$$

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[1] *Cf.* MÜLLER [1968], Eq. (6.2).

where

$$\varepsilon = |\Lambda - \overset{\circ}{\Lambda}|. \tag{9.26}$$

Since $\|\alpha_{\alpha\beta}\|$ is invertible (by assumption (C)), we can solve $(9.24)_1$ for c'_β in terms of μ'_α, υ', and θ' and $(9.24)_2$ for $\boldsymbol{\xi}_\beta$ in terms of $\boldsymbol{u}_\alpha$, $\boldsymbol{v}$, and $\boldsymbol{g}$. If we do this and then substitute the resulting relations into (5.4) and (6.2), we find that

$$\begin{aligned} \boldsymbol{q} &= -k\boldsymbol{g} - l_\alpha \boldsymbol{u}_\alpha - L\boldsymbol{v} + O(\varepsilon^2), \\ \boldsymbol{h}_\alpha &= -l'_\alpha \boldsymbol{g} - l_{\alpha\beta}\boldsymbol{u}_\beta - M_\alpha \boldsymbol{v} + O(\varepsilon^2), \\ m_\alpha &= -t_{\alpha\beta}\mu'_\beta - P_\alpha \theta' - Q_\alpha \upsilon' + O(\varepsilon^2). \end{aligned} \tag{9.27}$$

Next, by (7.2), $(9.25)_1$, and $(9.27)_3$

$$m_\alpha \mu_\alpha = m_\alpha \mu'_\alpha + O(\varepsilon^3); \tag{9.28}$$

thus (9.21), $(9.25)_2$, (9.27), and the remark made in the paragraph containing (4.6) imply that

$$\begin{aligned} &[l'_\alpha \boldsymbol{g} + l_{\alpha\beta}\boldsymbol{u}_\beta + M_\alpha \boldsymbol{v}] \cdot \boldsymbol{u}_\alpha + (\theta)^{-1}[k\boldsymbol{g} + l_\alpha \boldsymbol{u}_\alpha + L\boldsymbol{v}] \cdot \boldsymbol{g} \\ &\quad + t_{\alpha\beta}\mu'_\alpha \mu'_\beta + [P_\alpha \theta' + Q_\alpha \upsilon'] \mu'_\alpha + O(\varepsilon^3) \geqq 0 \end{aligned} \tag{9.29}$$

for all sufficiently small values of θ', υ', μ'_α, $\boldsymbol{g}$, $\boldsymbol{v}$, and $\boldsymbol{u}_\alpha$. Therefore

$$M_\alpha = L = P_\alpha = Q_\alpha = 0; \tag{9.30}$$

thus, by (9.25), (9.26), and (9.27), (7.6) holds. Finally, (9.29) and (9.30) yield (7.8), while $(9.27)_3$, (9.30), and (7.2) yield (7.7).

10. Appendix. Isotropic Functions

In this section we discuss functions of the form

$$\begin{aligned} \varphi &= \hat{\varphi}(\xi_1, \ldots, \xi_K, \boldsymbol{u}_1, \ldots, \boldsymbol{u}_M), \\ \boldsymbol{v} &= \hat{\boldsymbol{v}}(\xi_1, \ldots, \xi_K, \boldsymbol{u}_1, \ldots, \boldsymbol{u}_M), \end{aligned} \tag{10.1}$$

where $\xi_1, \ldots, \xi_K$ are scalars, $\boldsymbol{u}_1, \ldots, \boldsymbol{u}_M$ are vectors, $\hat{\varphi}$ is scalar-valued, and $\hat{\boldsymbol{v}}$ is vector-valued. We assume that $\hat{\varphi}$ and $\hat{\boldsymbol{v}}$ have for their common domain $\mathsf{D} = U \times \mathsf{V}^M$, where U is an open set in R^K. Here R denotes the reals and V the underlying vector space. For convenience, we write

$$\Lambda = (\xi_1, \ldots, \xi_K, \boldsymbol{u}_1, \ldots, \boldsymbol{u}_M) \tag{10.2}$$

for an arbitrary element of D. Given an orthogonal tensor $\boldsymbol{Q}$, we define $\boldsymbol{Q}\Lambda$ by

$$\boldsymbol{Q}\Lambda = (\xi_1, \ldots, \xi_K, \boldsymbol{Q}\boldsymbol{u}_1, \ldots, \boldsymbol{Q}\boldsymbol{u}_M). \tag{10.3}$$

We assume that $\hat{\varphi}$ and $\hat{\upsilon}$ are *isotropic*, *i.e.* we assume that

$$\hat{\varphi}(\Lambda) = \hat{\varphi}(\boldsymbol{Q}\Lambda), \qquad \boldsymbol{Q}\hat{\boldsymbol{v}}(\Lambda) = \hat{\boldsymbol{v}}(\boldsymbol{Q}\Lambda) \tag{10.4}$$

for every orthogonal tensor $\boldsymbol{Q}$ and every Λ in D.

Lemma 10.1. *Let* $\overset{\circ}{A}$ *in* D *have the form* $\overset{\circ}{A}=(\xi_1,\dots,\xi_K,\mathbf{0},\dots,\mathbf{0})$. *Then*[1]

$$\hat{\boldsymbol{v}}(\overset{\circ}{A})=\frac{\partial\hat{\varphi}}{\partial\boldsymbol{u}_m}\bigg|_{\overset{\circ}{A}}=\frac{\partial\hat{\boldsymbol{v}}}{\partial\xi_K}\bigg|_{\overset{\circ}{A}}=\mathbf{0}, \tag{10.5}$$

and there exist scalars $\kappa_1,\dots,\kappa_M$ *such that*

$$\frac{\partial\hat{\boldsymbol{v}}}{\partial\boldsymbol{u}_m}\bigg|_{\overset{\circ}{A}}=\kappa_m\mathbf{1}. \tag{10.6}$$

Proof. The result (10.5) follows from (10.4) with $\boldsymbol{Q}=-\mathbf{1}$. Let $\boldsymbol{K}_m$ denote the left-hand side of (10.6). Since $\boldsymbol{Q}\overset{\circ}{A}=\overset{\circ}{A}$, $(10.4)_2$ and the chain-rule imply that

$$\boldsymbol{Q}\boldsymbol{K}_m=\boldsymbol{K}_m\boldsymbol{Q}.$$

Thus $\boldsymbol{K}_m$ commutes with every orthogonal tensor; as is well known, this can happen only if $\boldsymbol{K}_m=\kappa_m\mathbf{1}$, with κ_m a scalar. ▌

Lemma 10.2.[2] *Assume that the symmetric part of* $\dfrac{\partial\hat{\boldsymbol{v}}}{\partial\boldsymbol{u}_m}\bigg|_A$ *vanishes at every* A *in* D *for* $m=1,\dots,M$. *Then*

$$\hat{\boldsymbol{v}}\equiv\mathbf{0}.$$

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[1] *Cf.* COLEMAN & NOLL [1963], Eq. (3.16).

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