A New Approach to Thermodynamics of Simple Mixtures

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A general entropy principle is utilized to derive restrictions on the constitutive relations for simple mixtures. The absolute temperature and chemical potentials are introduced in a novel manner and the equality of the coefficients of thermal diffusion and of the diffusion-thermo coefficients is proved for a subclass of simple mixtures by use of macroscopic arguments.

1. Introduction

This paper presents not so much new results but a new and systematic method of derivation of the thermodynamic properties of simple mixtures of fluids. This new approach is based on a general entropy principle, first proposed in 1, that does give restrictions on constitutive functions without making specific assumptions on the entropy supply and the entropy flux. The method used for the exploitation of the entropy inequality is the method of Lagrange multipliers proposed and proved by Liu in 2.

The concepts of absolute temperature and chemical potentials are arrived at in a novel manner by the evaluation of a continuity condition that is postulated for the entropy flux at walls of a particular type.

The results derived here include the results of classical thermostatics for mixtures and the only new result concerns diffusion and heat conduction in a subclass of simple mixtures: Truesdell has shown in 3 that the matrix of diffusion coefficients is symmetric, if the constituents exhibit binary drags only and here it is shown that for such mixtures the thermo-diffusion coefficients are equal to the diffusion-thermo coefficients if the interaction forces are independent of the temperature gradient and if the flux of internal energy depends explicitly on the relative velocities as prescribed by its definition.

2. Equations of Balance

In a mixture of \( r \) constituents let the following notation be introduced for every constituent \( x \):

- \( \varrho_x \) density of mass,
- \( v_x \) velocity,
- \( c_x \) density of mass production,
- \( t_{uj} \) stress,
- \( m_f \) density of momentum production,
- \( \varepsilon_x \) specific internal energy,
- \( q_{x} \) flux of internal energy,
- \( \tau_x \) density of energy production.

These quantities are assumed to obey the equations of balance of mass, momentum and energy (see 4, or 3):

\[
\begin{align*}
\frac{\partial \varrho_x}{\partial t} + \vec{\nabla} \cdot \varrho \vec{v}_x &= m_f, \\
\frac{\partial \varrho_x v_x^2}{\partial t} + \vec{\nabla} \cdot \varrho \vec{v}_x \vec{v}_x &= \left( \frac{\partial}{\partial x_j} \right) \left( \sigma_{xx} - \tau_{xx} \right) - \frac{\partial}{\partial x_j} \left( \varrho \varepsilon_x \right) - \frac{\partial}{\partial x_j} \left( \varrho q_{x} \right) = t_{uj}, \\
\frac{\partial \varrho_x}{\partial t} + \vec{\nabla} \cdot \varrho \vec{v}_x &= m_f, \\
\end{align*}
\]

(2.1)

where the production densities are subject to the conditions

\[
\sum_{a=1}^{r} \varrho_a = 0, \quad \sum_{a=1}^{r} m_f = 0, \quad \sum_{a=1}^{r} \tau_a = 0. \quad (2.2)
\]

which express the conservation laws of mass, momentum and energy of the mixture as a whole.

With the definitions

\[
\begin{align*}
q &= \sum_{a=1}^{r} \varrho_x, \\
v_t &= \sum_{a=1}^{r} \varrho_x v_x, \\
t_{uj} &= \sum_{a=1}^{r} \left( t_{uj} - \varrho u_x \cdot u_y \right), \\
w_x &= \varrho v_x - v_t \quad \text{diffusion velocity,} \\
\end{align*}
\]

(2.3)

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summation of the Eqs. (2.1) over all \( a \) leads to conservation laws of mass, momentum and energy of the mixture which have the same forms as those for a single body, namely (see again 5)

\[
\frac{\partial \rho}{\partial t} + \frac{\partial \rho v_j}{\partial x_j} = 0,
\]

\[
\frac{\partial \rho v_i}{\partial t} + \frac{\partial \rho (v_i v_j - t_{ij})}{\partial x_j} = 0,
\]

\[
\frac{\partial e}{\partial t} + \frac{\partial}{\partial x_j} \left( \rho (e + \frac{1}{2} v^2) v_j + q_j - t_{ij} v_i \right) = 0.
\]

Note that the diffusion velocities \( u_a \), defined in \( (2.3) \), obey the identity

\[
\sum_{a=1}^{r} \rho_a u_a = 0.
\]

Apart from the restriction \( (2.2) \) on the \( c_a \)'s, there are others which are due to the fact that only whole molecules interact and even those in fixed numbers. Let \( n \) be the number of independent reactions and let \( \Lambda^a \ (a = 1, 2, \ldots, n) \) be their reaction rate densities; furthermore, let \( \gamma^a \) be the stoichiometric coefficients of the constituent \( a \) in the reaction \( a \) and \( M_a \) the molecular weight of constituent \( a \) while \( m \) is the mass of a hydrogen atom. Then the equations

\[
\sum_{a=1}^{r} \gamma^a M_a m = 0 \quad (a = 1, 2, \ldots, n)
\]

describe the conservation of mass in the reactions and it is easy to see that

\[
c_a = \sum_{a=1}^{n} (\gamma^a M_a m) \Lambda^a
\]

holds, so that we have only \( n \) independent reaction rate densities rather than \( r \), or \( r - 1 \), mass production densities \( c_a \).

### 3. Thermodynamic Processes and Special Constitutive Relations

One objective of a thermodynamic theory of mixtures of fluids is the determination of the fields of the densities \( \rho_a \) and the velocities \( v_i \) of the constituents and of an empirical temperature \( \theta \) of the mixture. For that one relies on the equations

- The reaction rate density \( \Lambda^a \) is the difference in the number densities of creations of the reaction products and their destructions per unit time in the molecular interaction that corresponds to reaction \( a \).

of balance of mass and momentum for the constituents and on the equation of balance of energy (or internal energy) for the mixture

\[
\frac{\partial \rho_a v_i^a}{\partial t} + \frac{\partial \rho_a (v_i v_j - t_{ij})}{\partial x_j} = \sum_{a=1}^{n} (\gamma^a M_a m) \Lambda^a,
\]

\[
\frac{\partial \rho_a v_i^a}{\partial t} + \frac{\partial}{\partial x_j} \left( \rho_a (v_i v_j - t_{ij}) - t_{ij} v_i \right) = m_i^a,
\]

In order to obtain field equations for \( \rho_a, v_i^a \) and \( \theta \) one must supplement these equations of balance by constitutive relations for \( \Lambda^a, t_{ij}, m_i, \varepsilon \), and \( q_j \) whose form depends on the material. I shall consider simple mixtures** whose constitutive relations have the general form

\[
\Lambda^a = \Lambda^a (\rho_a, v_i^a, \theta, \theta), \quad (a = 1, 2, \ldots, n)
\]

\[
t_{ij}^a = t_{ij}^a (\rho_a, v_i^a), \quad (a = 1, 2, \ldots, r)
\]

\[
m_i^a = m_i^a (\rho_a, v_i^a), \quad (a = 1, 2, \ldots, m)
\]

\[
\varepsilon = \varepsilon (\rho_a, v_i^a), \quad (a = 1, 2, \ldots, r)
\]

\[
q_j = q_j (\rho_a, v_i^a), \quad (a = 1, 2, \ldots, m)
\]

Insertion of (3.2) into (3.1) gives the desired field equations and every solution of these will be called a thermodynamic process.

The Eqs. (3.1) represent equations of balance in regular points of the body. We shall also be interested in walls which we represent by singular surfaces and there the equations of balance of the mass of constituent and of momentum and energy assume the form of jump conditions:

\[
[\rho_a (v_j^a - v_j) e_j] = 0,
\]

\[
[\rho_a (v_i v_j - u_i) e_j] - \rho_a t_{ij} e_j = K_i, \quad (a = 1, 2, \ldots, n)
\]

\[
[\rho (e + \frac{1}{2} v^2) (v_j^a - u_j) e_j]
\]

\[
+ [q_j - t_{ij} v_i] e_j = K_i u_i, \quad (a = 1, 2, \ldots, n)
\]

where \( u_j \) is the normal velocity of the singular surface and \( e_j \) is its unit normal vector. \( K_i \) is the shear force acting in the wall referred to unit area of the wall.

While there is good reason to assume that \( \Lambda^a, \varepsilon, q_j \) and \( t_{ij} \) transform as objective scalars, vectors

** In 6 I have called mixtures simple, if the constitutive quantities are independent of density gradients of the constituents.

+ These forms are valid only for plane walls and when \( u_i \) is constant over the wall. [\( \psi \)] denotes the jump of \( \psi \) across the wall.
and tensors, \( m_\alpha \) does not. However, the interaction force \( m_\alpha \alpha - c_\alpha v_\alpha^2 \) does transform as an objective vector \(*\) and therefore we choose it, rather than \( m_\alpha \), as one of the constitutive quantities:

\[
  m_\alpha - c_\alpha v_\alpha^2 = M_\alpha (q_\alpha, v_\alpha^2, \partial, \partial_\alpha). \tag{3.4}
\]

The principle of material frame indifference with respect to Galilei transformations requires that the constitutive functions for \( \Lambda^\alpha \), \( t_\alpha^\beta \), \( M_\alpha^\beta \), \( \varepsilon \) and \( q_\alpha \) be the same ones in every Galileian frame and this implies that not all \( v \) velocities \( v_\alpha^2 \) can occur as independent variables, but only the \( v - 1 \) combinations

\[
  V_\alpha^\alpha \equiv v_\alpha^\alpha - v_\alpha^\alpha. \tag{3.5}
\]

Therefore, the general form of the constitutive relations is

\[
\begin{align*}
  \Lambda^\alpha &= \Lambda^\alpha (q_\beta, V_\alpha^\beta, \partial, \partial_\alpha), \\
  t_\alpha^\beta &= t_\alpha^\beta (---), \\
  m_\alpha - c_\alpha v_\alpha^2 &= M_\alpha^\beta (---), \\
  \varepsilon &= \varepsilon (---), \\
  q_\alpha &= q_\alpha (---)
\end{align*}
\]

and all constitutive functions are isotropic functions with respect to the Galileian group as a consequence of the principle of material frame indifference.

The form of the definitions (2.3) of \( \varepsilon \) and \( q_\alpha \) suggests the decompositions

\[
\begin{align*}
  \varepsilon &= \varepsilon_1 (q_\beta, V_\alpha^\beta, \partial_\alpha) + \sum_{a=1}^r \frac{1}{2} \frac{\partial}{\partial q_\beta} u_\alpha^2, \\
  q_\alpha &= q_1 (---) + \sum_{a=1}^r \frac{1}{2} q_\alpha u_\alpha^2 u_\alpha^2
\end{align*}
\]

into an intrinsic heat flux and an intrinsic internal energy and a contribution due to the kinetic energy of the diffusive motion. From here on I shall consider the case of a mixture in which \( \Lambda^\alpha \), \( t_\alpha^\beta \), \( m_\alpha - c_\alpha v_\alpha^2 \) and the intrinsic quantities \( \varepsilon_1 \), \( q_1^\alpha \), just defined, do not depend on \( V_\alpha^\beta \) and \( \partial_\alpha \) non-linearly. The isotropy of the constitutive functions then implies the following representations

\[
\begin{align*}
  \Lambda^\alpha &= \Lambda^\alpha (q_\beta, \partial), \quad (a = 1, 2, \ldots, n) \\
  t_\alpha^\beta &= -p_\alpha (q_\beta, \partial), \quad (x = 1, 2, \ldots, v) \\
  \varepsilon_1 &= \varepsilon_1 (q_\beta, \partial), \\
  m_\alpha - c_\alpha v_\alpha^2 &= M_\alpha^\beta (q_\beta, \partial) \partial_\alpha + \sum_{y=1}^{r-1} M_\alpha^y (q_\beta, \partial) V_\alpha^y, \quad (x = 1, 2, \ldots, v - 1) \quad (see \quad ***).
\end{align*}
\]

\[
  q_1^\alpha = -\pi (q_\beta, \partial) \partial_\alpha + \sum_{y=1}^{r-1} q_\alpha V_\alpha^y.
\]

** For motivation of this statement see 6, p. 12.

\( p_\alpha \) is called the pressure of component \( x \) and \( \pi \) is called the heat conductivity.

We shall now proceed to derive restrictions for these special constitutive relations from the entropy principle.

I list a useful identity here which follows from the definitions of \( V_\alpha^\alpha \) and \( u_\alpha^\alpha \) and which permits the calculation of one of these sets of relative velocities from the other. We have

\[
  u_\alpha^\alpha = \sum_{y=1}^{r-1} (\delta_{xy} - \delta_{xy} \gamma) V_\alpha^y \quad (x = 1, 2, \ldots, v). \tag{3.9}
\]

4. An Entropy Principle and its Consequences

I postulate that the following principle holds in a body that is not subject to external forces and to an external heat supply.

In every body there exists an additive quantity, the entropy, that has a non-negative production density, so that the inequality

\[
\frac{\partial \eta}{\partial t} + \frac{\partial}{\partial x_\alpha} (\eta v_\alpha + \Phi_\alpha) \geq 0 \tag{4.1}
\]

holds. The specific entropy \( \eta \) is an objective scalar and the nonconvective entropy flux \( \Phi_\alpha \) an objective vector and both are given by constitutive relations that obey the principle of material frame indifference.

The entropy inequality (4.1) must hold for all thermodynamic processes.

The normal component of the entropy flux is continuous at a wall where the temperature is continuous, and where the tangential components of the velocities vanish *, so that the following jump condition holds

\[
  [\eta (\eta (v_\alpha - u_\alpha) e_\alpha)] + [\Phi_\alpha e_\alpha] = 0,
\]

if \( [\partial] = 0 \) and \( \varepsilon_{ikk} e_\alpha e_\alpha^2 = 0. \tag{4.2}
\]

In some recent papers (e.g. see 1,7) I have proposed the above entropy principle in a form appropriate to a single body, where the convective entropy flux \( \eta (v_\alpha - u_\alpha) e_\alpha \) vanishes at a wall. In the case of mixtures such a flux can be present if the wall is semipermeable. In passing I note that this entropy principle does not make any specific assumptions about the relation between the nonconvective entropy flux \( \Phi_\alpha \), the heat flux \( q_\alpha \) and

*** Note that

\[
  m_\alpha^\alpha - c_\alpha v_\alpha^2 = -\sum_{\alpha=1}^{r-1} [(m_\alpha^\alpha - c_\alpha v_\alpha^2) + c_\alpha V_\alpha^\alpha].
\]

* I assume that the wall has no tangential velocity.
diffusion velocities \( u^x \); nor does it introduce the concepts of absolute temperature and chemical potentials at this stage. These concepts will emerge naturally from the evaluation of (4.2) later.

In a mixture of the type that was characterized in the last section the specific entropy \( \eta \) and the non-convective entropy flux are given by constitutive relations of the form

\[
\eta = \eta(q_\beta, V_i^\beta, \partial, \partial_i),
\]

\[
\Phi_i = \Phi_i \left( \frac{\partial}{\partial x_i} \right), \tag{4.3}
\]

where both functions must be isotropic with respect to Galilei transformations. Here again I wish to exclude non-linear dependence on \( V_i^x \) and \( \partial_i \) and therefore we have

\[
\eta = \eta(q_\beta, \theta),
\]

\[
\Phi_i = q_\beta (q_\beta, \theta) \partial_i + \sum_{\gamma=1}^{r-1} q_{\gamma*}(q_\beta, \theta) V_i^{\gamma}. \tag{4.4}
\]

Liu has shown in ² that the entropy principle implies the requirement that the inequality

\[
\frac{\partial \eta}{\partial t} + \frac{\partial}{\partial x_j} \left( q \eta v_j + \Phi_j \right) - \sum_{x=1}^{r} A^{\alpha x} \left( \frac{\partial q_x}{\partial t} + \frac{\partial}{\partial x_i} q_x v_j - m_i \right) - \sum_{x=1}^{r} A^{\alpha x_0} \left( \frac{\partial q_x v_j}{\partial t} + \frac{\partial}{\partial x_i} q_x v_j - m_i \right) - A^e \left( \frac{\partial \theta}{\partial t} + \frac{\partial}{\partial x_i} (q \theta v_j + q_j) - \theta v_j \right) \geq 0, \tag{4.5}
\]

holds for all analytic fields \( q_x, v_i, \theta \) and \( \partial_i \). The factors \( A^{\alpha x}, A^{\alpha x_0} \) and \( A^e \) are called Lagrange multipliers by Liu and they may be functions of the variables \( q_x, v_i, \theta \), \( \partial_i \).

Insertion of the constitutive relations (3.6) and (4.3) into (4.6) provides an inequality whose left hand side is linear in

\[
\frac{\partial \eta}{\partial t} + \frac{\partial}{\partial x_j} \left( q \eta v_j + \Phi_j \right) - \sum_{x=1}^{r} A^{\alpha x} \left( \frac{\partial q_x}{\partial t} + \frac{\partial}{\partial x_i} q_x v_j - m_i \right) - \sum_{x=1}^{r} A^{\alpha x_0} \left( \frac{\partial q_x v_j}{\partial t} + \frac{\partial}{\partial x_i} q_x v_j - m_i \right) - A^e \left( \frac{\partial \theta}{\partial t} + \frac{\partial}{\partial x_i} (q \theta v_j + q_j) - \theta v_j \right) \geq 0.
\]

The inequality must hold for arbitrary values of these derivatives; therefore, terms containing such derivatives must not contribute to (4.6) or else the inequality could easily be violated. When, for abbreviation, we make the definitions

\[
\Gamma^a \equiv \frac{\partial \eta}{\partial A^a} - A^e \frac{\partial \theta}{\partial A^a} \quad \text{and} \quad A^4 \equiv \frac{\partial \Phi_j}{\partial A^4} - A^e \frac{\partial q_j}{\partial A^4}, \tag{4.6}
\]

we obtain from this argument the following conditions:

\[
\eta \Gamma^{\alpha x} - A^{\alpha x} = 0, \quad (\beta = 1, 2, \ldots, r) \tag{4.7}_1
\]

\[
\eta \Gamma^{\alpha x_0} - A^{\alpha x_0} \theta = 0, \quad (\beta = 1, 2, \ldots, r - 1) \tag{4.7}_2
\]

\[
- \sum_{\beta=1}^{r-1} \Gamma^{\alpha x} \theta = 0, \tag{4.7}_3
\]

\[
\Gamma^e = 0, \tag{4.7}_4
\]

\[
\Gamma^{\alpha x_0} = 0 \tag{4.7}_5
\]

\[
A^{\alpha x} - q_\beta u^\beta \frac{\partial A^{\alpha x}}{\partial q_\beta} + \sum_{\alpha=1}^{r} A^{\alpha x_0} \frac{\partial q_\beta}{\partial A^{\alpha x}} + A^e t^{ij} \frac{1}{q} u_i^\beta = 0, \quad (\beta = 1, 2, \ldots, r) \tag{4.7}_6
\]

\[
A^{\alpha x_0} - q_\beta u^\beta \frac{\partial A^{\alpha x_0}}{\partial q_\beta} + \sum_{\alpha=1}^{r} A^{\alpha x} \frac{\partial q_\beta}{\partial A^{\alpha x_0}} \tag{4.7}_7
\]

\[
- \sum_{\beta=1}^{r-1} \left( A^{\alpha x_0} - q_\beta u^\beta \frac{\partial A^{\alpha x_0}}{\partial q_\beta} + \sum_{\alpha=1}^{r} A^{\alpha x} \frac{\partial q_\beta}{\partial A^{\alpha x_0}} \right) \theta = 0, \quad (\beta = 1, 2, \ldots, r - 1)
\]

\[
- \sum_{\beta=1}^{r-1} \left( A^{\alpha x_0} - q_\beta u^\beta \frac{\partial A^{\alpha x_0}}{\partial q_\beta} + \sum_{\alpha=1}^{r} A^{\alpha x} \frac{\partial q_\beta}{\partial A^{\alpha x_0}} \right) \theta = 0, \tag{4.7}_8
\]

\[
A^{\alpha x_0} \theta = 0 \quad (\text{see } **). \tag{4.7}_9
\]

There remains the inequality

\[
\sum_{\alpha=1}^{r} A^{\alpha x_0} c_a \geq 0. \tag{4.8}
\]

In the remainder of this section I shall evaluate the restrictions that (4.7) imposes on the constitutive relations (3.8) and (4.4) and on the Lagrange multipliers.

We observe that the only non-vanishing term in \( \Gamma^{\alpha x} \) results from the kinetic energy of the diffusive motion. Therefore, by use of (3.9) the Eqs. (4.7)½,8 can be written as

\[
A^{\alpha x} = - A^e u^\beta. \tag{4.9}
\]

Summation of all Eqs. (4.7)½,8 and use of (4.9) lead to a restriction on \( A^{\alpha x} \) of the form

\[
\sum_{\alpha=1}^{r} A^{\alpha x} q_\beta = - A^e \sum_{\alpha=1}^{r} p_a. \tag{4.10}
\]

The Eq. (4.7)½ is identically satisfied for the simple constitutive class under consideration and (4.7)¹ and (4.7)² can be written in the form

** Round brackets indicate symmetrization.
\[
\frac{\partial \eta}{\partial \vartheta} = \Lambda^e \frac{\partial \varepsilon_1}{\partial \vartheta}, \\
\frac{\partial \eta}{\partial \varphi_{\beta}} = \Lambda^e \frac{\partial \varepsilon_1}{\partial \varphi_{\beta}} + \frac{1}{\varrho} A^{\alpha\nu} \frac{1}{\varrho} \sum_{\alpha=1}^{r} \left( \delta_{\alpha \beta} - \frac{q_\alpha}{\varrho} \right) \frac{1}{2} u_\alpha^2 \quad (\beta = 1, 2, \ldots, v). \tag{4.11}
\]

From (4.11), it is obvious that \( \Lambda^e \) is independent of \( V_f^\nu \) and \( \vartheta_f \) and therefore it follows from (4.11) that \( \Lambda^{\alpha\nu} \) can be decomposed into a part independent of \( V_f^\nu \) and \( \vartheta_f \) and another part whose dependence on the relative velocities is explicit:

\[
\Lambda^{\alpha\nu} = \Lambda^{\alpha\nu}_1 (q_\alpha, \vartheta_f) - \Lambda^{\alpha\nu}_2 \quad (\beta = 1, 2, \ldots, v). \tag{4.12}
\]

Thus the two relations (4.11) may be summarized in the form

\[
\frac{d \eta}{\varrho} = \Lambda^e \frac{\partial \varepsilon_1}{\partial \varrho} \frac{d \varrho}{\varrho} + \frac{1}{\varrho} \sum_{\alpha=1}^{r} \left( \Lambda^e \frac{\partial \varepsilon_1}{\partial \varphi_{\alpha}} + \frac{1}{\varrho} \Lambda^e_1 \right) \frac{d \varphi_{\alpha}}{\varrho}. \tag{4.13}
\]

Division of (4.7) by \( \varrho_{\beta} \) and of (4.7) by \( \varrho_{\nu} \) and subsequent subtraction leads to the relations

\[
\frac{\partial \Phi_{\gamma}}{\partial V_{f}^\nu} - \Lambda^e \frac{\partial q_{\gamma}}{\partial V_{f}^\nu} = \sum_{\beta=1}^{r} \left( \varrho_{\gamma} \delta_{\beta \gamma} - \frac{q_{\gamma}}{\varrho} \right) \Lambda^{\alpha\nu}_1 \vartheta_f, \quad (\gamma = 1, 2, \ldots, v - 1)
\]

where I have used (3.7), (4.12) and, of course the constitutive relations (3.8) and (4.4). While the derivation of the last formula has required extensive calculation, it is trivial to see that (4.7) implies

\[
\frac{\partial \Phi_{\gamma}}{\partial \vartheta_f} - \Lambda^e \frac{\partial q_{\gamma}}{\partial \vartheta_f} = 0.
\]

By integration of the last two equations we obtain

\[
\Phi_{\gamma} = \Lambda^e q_{\gamma} + \sum_{\beta=1}^{r} \Lambda^{\alpha\nu}_1 \varphi_{\beta} u_{\beta}^\gamma,
\]

or, by (3.7) and (4.12)

\[
\Phi_{\gamma} = \Lambda^e q_{\gamma} + \sum_{\beta=1}^{r} \Lambda^{\alpha\nu} \varphi_{\beta} u_{\beta}^\gamma. \tag{4.14}
\]

It remains to evaluate the conditions (4.7). A careful and somewhat long calculation, which makes use of the results obtained so far, shows that (4.7) is equivalent to

\[
\frac{\partial \Lambda^e}{\partial \varphi_{\beta}} q_{\gamma} + \sum_{\gamma=1}^{r} \left( \varrho_{\gamma} \frac{\partial \Lambda^{\alpha\nu}}{\partial \varphi_{\beta}} + \Lambda^e \frac{\partial p_{\gamma}}{\partial \varphi_{\beta}} \right) u_{\beta}^\gamma = 0
\]

or with (3.8) and (3.9)

\[
- \frac{\partial \Lambda^e}{\partial \varphi_{\beta}} u_{\beta}^\gamma + \sum_{\alpha=1}^{r-1} \left( \frac{\partial \Lambda^{\alpha\nu}}{\partial \varphi_{\beta}} q_{\nu} \right) + \sum_{\nu=1}^{\nu} \left( \varrho_{\gamma} \frac{\partial \Lambda^{\alpha\nu}}{\partial \varphi_{\beta}} + \Lambda^e \frac{\partial p_{\gamma}}{\partial \varphi_{\beta}} \right) \left( \delta_{\gamma \beta} - \frac{q_{\gamma}}{\varrho} \right) V_{f}^\nu = 0.
\]

This relation can obviously only be satisfied for all \( \vartheta_{ij} \) and \( V_{f}^\nu \) if

\[
\Lambda^e = \Lambda^e (\vartheta_f)
\]

and

\[
\frac{\partial (\Lambda^{\alpha\nu}_1 - \Lambda^{\alpha\nu}_1)}{\partial \varphi_{\beta}} = - \frac{\partial \Lambda^e}{\partial \varphi_{\beta}} \left( \frac{1}{\varrho} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \frac{1}{\varrho} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \right) \tag{4.15}
\]

In particular we thus see that the Lagrange multiplier \( \Lambda^e \) depends on \( \vartheta_f \) only.

While the Eqs. (4.9) through (4.15) exhaust the conditions (4.7), they all still contain the multipliers \( \Lambda^e, \Lambda^{\alpha\nu}_1 \) and \( \Lambda^e \), and until we learn more about these in the next section, we are left with but a few specific results that follow from (4.13) as integrability conditions for \( \eta \):

\[
\frac{\partial}{\partial \varphi_{\beta}} \left( \frac{1}{\varrho} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \right) = \frac{1}{\varrho} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \frac{1}{\varrho} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \tag{4.16}
\]

By use of the identity

\[
A^{\alpha\nu} = \sum_{\gamma=1}^{r-1} \left( \delta_{\alpha \gamma} - \frac{\varrho_{\gamma}}{\varrho} \right) (A^{\alpha\nu} + \sum_{\gamma=1}^{r} \frac{\varrho_{\gamma}}{\varrho} A^{\alpha\nu})
\]

and (4.10), (4.15) one can easily show that (4.16) is equivalent to

\[
\frac{1}{\varrho_{\gamma}} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} = \frac{1}{\varrho_{\gamma}} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \tag{4.17}
\]

On the other hand the Eqs. (4.15) imply integrability conditions for \( \Lambda^{\alpha\nu}_1 - \Lambda^{\alpha\nu}_1 \) and these come out as

\[
\frac{1}{\varrho_{\gamma}} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} = \frac{1}{\varrho_{\gamma}} \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \tag{4.18}
\]

Here we choose \( \gamma = \alpha + \beta \) and obtain \( \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} = 0 \) for \( \alpha + \beta \) and \( \beta + \nu \), whereas, if \( \alpha + \nu \) and \( \beta = \nu, \) we

\[
\frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} = \frac{\partial \gamma_\nu}{\partial \varphi_{\beta}} \tag{4.19}
\]

*** Note that according to (4.15) the expression on the right hand side of (4.16) is independent of the densities \( \varrho_{\gamma} \) and depends on \( \vartheta_f \) only.
obtain
\[ \frac{1}{q_x^2} \frac{\partial p_x}{\partial q_x} = - \frac{1}{\mu_x} \frac{\partial p_r}{\partial q_r} \]
and that is incompatible with the above results
\[ \frac{1}{q_x} \frac{\partial p_x}{\partial q_x} = \frac{1}{\mu_g} \frac{\partial p_g}{\partial q_g} \]
unless both \( \frac{\partial p_x}{\partial q_x} \) and \( \frac{\partial p_g}{\partial q_g} \) vanish. Hence we have
\[ p_x = p_x(q_x, \theta), \quad (4.17) \]
or, in words, the pressure of constituent \( x \) depends only on the density of that constituent, and on \( \theta \) of course. This result makes it clear that we are dealing with a very special kind of mixtures which I have called simple mixtures in a previous paper where I employed a more specific entropy principle*. The special character of the simple mixtures considered here is confirmed by the following argument. With all the results known so far, little effort is required to see that (4.7)6 can be written as
\[ \frac{\partial}{\partial q_x} \left( \Phi_x - \Lambda^x \left( \eta_x \sum_{a=1}^r \nu_x \right) \right) = 0 \]
whence we obtain as an integrability condition for the square bracket
\[ \frac{\partial}{\partial q_x} \left( \eta - \Lambda^x \eta_1 \right) + \frac{\partial^2}{\partial q_x^2} \left( \eta - \Lambda^x \eta_1 \right) = 0 \]
or
\[ \frac{\partial^2}{\partial q_x^2} \left[ \eta - \Lambda^x \eta_1 \right] = 0 \]
for \( x \neq \beta \). The general solution of these differential equations restricts \( \eta - \Lambda^x \eta_1 \) to be a sum of functions which depend on one density only. Now, by (4.11)1 we have
\[ \frac{\partial}{\partial \theta} \left( \eta - \Lambda^x \eta_1 \right) = - \frac{\partial}{\partial \theta} \left( \eta \right) \]
so that \( \eta \eta_1 \) and hence \( \eta \eta \) are also of this additive form and we may write
\[ \eta \eta_1 = \sum_{a=1}^r q_x \eta_a(q_x, \theta) \quad \text{and} \quad \eta \eta = \sum_{a=1}^r q_x \eta_a(q_x, \theta), \quad (4.18) \]
where, of course, we now interpret \( \eta_x \) and \( \eta_x \) as the specific internal energy and the specific entropy of constituent \( x \) and we note that these depend only the density of that constituent.

The integrability conditions for \( \Lambda^x \eta - \Lambda^x \eta \) that are implied by (4.15)2 and (4.16)2 read
\[ \frac{\partial}{\partial \theta} \left( \Lambda^x \left( \frac{1}{q_x} \frac{\partial p_x}{\partial q_x} - \frac{1}{q_r} \frac{\partial p_r}{\partial q_r} \right) \right) \]
\[ = \frac{\partial}{\partial \theta} \left( \frac{1}{q_x} \frac{\partial p_x}{\partial q_x} \eta \eta_1 \right) \]
and, by use of (4.17) and (4.18), this can be written as
\[ \frac{\partial}{\partial q_x} \left( \eta^2 \frac{\partial \eta}{\partial q_x} - p_x - \frac{\partial}{\partial q_x} \ln \Lambda^x \right) = 0. \quad (4.19) \]
For a single fluid results corresponding to (4.9) through (4.16) may be obtained by setting \( r = 1 \) and one gets
\[ \Lambda^x \eta = 0, \quad \Lambda^x \theta = - \Lambda^x \eta \quad (4.20) \]
there should be an index 1 on \( \Lambda^x \), \( \Lambda^x \), \( \theta \) and \( \eta \), but that may be dropped when only one constituent is present. For \( r = 1 \) the equation (4.13), by virtue of (4.20)2 reduces to
\[ d\eta = \Lambda^x \frac{\partial \eta}{\partial \theta} d\theta + \left( \frac{\partial \eta}{\partial \theta} \right) d\eta \quad (4.21) \]
and, of course, there is no distinction between \( \varepsilon \) and \( \eta_1 \) in a single body. The entropy flux (4.14) becomes
\[ \Phi_\ell = \Lambda^x \eta_i \quad (4.22) \]
and \( \Lambda^x \) is a function of \( \theta \) only by (4.15)1. The Eqs. (4.15)2 and (4.16)1,2 are identically satisfied while (4.16)3 gives
\[ \frac{\partial}{\partial \theta} \left( \frac{\partial \eta}{\partial \theta} \right) = q_x^2 \frac{\partial \varepsilon}{\partial q_x} \frac{\partial \eta}{\partial \theta} \quad (4.23) \]
It is now imperative to learn more about the Lagrange multipliers which are contained in all our results except (4.17), (4.18).

5. Absolute Temperature and Chemical Potentials

Let us consider an impermeable wall which separates two different simple mixtures I and II of the type considered here, and which cannot support a jump in temperature; also let the tangential velocities of all constituents vanish at the wall.
Such a wall is represented by a material singular surface in the theory and we have
\[ u_i = v_i^a = v_i \] (5.1)
on either side. I eliminate the force \( K_i \) from (3.3)\textsubscript{2,3} and obtain
\[ [q_l e_l] = 0 \] (5.2)
whereas (4.2) in the present case becomes
\[ [\phi_i e_l] = 0 \quad \text{if} \quad [\theta] = 0. \] (5.3)
By (5.1) and (4.14) we have \( \Phi_i = \Lambda^\varepsilon q_i \) at the wall so that (5.3) and (5.2) lead to
\[ \Lambda^\varepsilon (\theta) = \Lambda_{\Pi}^\varepsilon (\theta), \] (5.4)
that is to say: \( \Lambda^\varepsilon (\theta) \) is a universal function of \( \theta \). In particular (5.4) holds if either one or both of the "mixtures" I and II are in fact single fluids, and then (4.21) shows that the reciprocal of \( \Lambda^\varepsilon (\theta) \) is the absolute temperature \( T(\theta) \),
\[ \Lambda^\varepsilon (\theta) = 1/T(\theta), \] (5.5)
because in thermodynamics of single bodies the absolute temperature is defined as the integrating denominator of the expression \( d\varepsilon - \left( p/\rho^2 \right) dq \) that is a universal function of the temperature alone. \( \Lambda^\varepsilon (\theta) \) can be calculated from (4.23) by integration, if only \( p \) and \( \partial \varepsilon /\partial q \) are known as functions of \( q \) and \( \theta \) for any single body—as they are for an ideal gas for instance. Thus \( \Lambda^\varepsilon (\theta) \) can now be considered as a known function of \( \theta \). In fact, it is found that \( T(\theta) \) is a monotonically increasing function of \( \theta \) and is therefore often used as a measure for the empirical temperature. I adopt this choice too from here on and thus consider all constitutive quantities as functions of \( \theta \), tacitly replacing \( \theta \) by \( T \) in what follows.

For the following argument we shall have to suppose that the functions \( \varepsilon(q,T) \) and \( \eta(q,T) \) are also known in single fluids. Indeed, \( \partial \varepsilon/\partial q \) is known from (4.23), after \( p(q,T) \) has been determined experimentally, and all that is needed in addition for the determination of \( \varepsilon(q,T) \) can be obtained from measurements of the specific heat \( \partial \varepsilon/\partial T \) for a fixed \( q \) as a function of \( T \). Thus \( \varepsilon(q,T) \) follows by integration to within a constant and \( \eta(q,T) \) follows from (4.21) to within another constant.

Let us consider a semipermeable wall between two simple mixtures I and II that is permeable for constituent \( \gamma \) (say). Here too, we represent that wall by a singular surface, however, now that surface is not material. Instead we have
\[ u_i = v_i^a (\alpha + \gamma) \quad \text{and} \quad v_i = u_i + (\eta/\rho) (v_i^\gamma - u_i) \] (5.6)
at the surface. Elimination of \( K_i \) from (3.3)\textsubscript{2,3} leads to
\[ [q_l e_l] - \left[ \sum_{\beta=1}^\nu \frac{p_\beta}{\rho} - \varepsilon_1 + \frac{1}{2} (v_k^\gamma - u_k)(v_k^\gamma - u_k) \right] \times \rho (v_i - u_i) e_l = 0, \] (5.7)
whereas for the entropy flux we have from (4.2):
\[ [\Phi_i e_l] + [\eta] \rho (v_i - u_i) e_l = 0, \quad \text{if} \quad [\theta] = 0. \] (5.8)
Now \( \Phi_i \) is equal to
\[ (1/T) q_l + \sum_{\beta=1}^\nu A^\varepsilon_\beta q_\beta u_\beta \] by (4.14), so that (5.8) may be written as
\[ [q_l e_l] + T \left[ \eta + \sum_{\beta=1}^\nu \left( \delta \gamma_\beta - \partial \varepsilon_\beta /\partial q \right) A^\varepsilon_\beta \right] \times \rho (v_i - u_i) e_l = 0, \] (5.9)
since \( T \) is continuous because \( \theta \) is and because \( T(\theta) \) is a universal function.

Elimination of \( [q_l e_l] \) from (5.7) and (5.8) leads to
\[ \varepsilon_1 - T \eta + \frac{1}{2} (v_k^\gamma - u_k)(v_k^\gamma - u_k) \]
\[ + \sum_{\beta=1}^\nu P_\beta /\rho - T \sum_{\beta=1}^\nu (\delta \gamma_\beta - \partial \varepsilon_\beta /\partial q) A^\varepsilon_\beta = 0, \] (5.10)
or with (4.10) and (5.5)
\[ [\varepsilon_1 - T \eta + \frac{1}{2} (v_k^\gamma - u_k)(v_k^\gamma - u_k) - T A^\varepsilon_\gamma] = 0. \] (5.11)
We conclude that the quantity in brackets is continuous; it is called the chemical potential of constituent \( \gamma \) and we denote it by \( \mu_\gamma \):
\[ \mu_\gamma = \varepsilon_1 - T \eta + \frac{1}{2} (v_k^\gamma - u_k)(v_k^\gamma - u_k) - T A^\varepsilon_\gamma. \] (5.12)
We see that \( \mu_\gamma \) depends on the velocity \( v_k^\gamma - u_k \) in an explicit manner and I find it useful to intro-
duce the intrinsic chemical potential
\[ \mu_\gamma^I \equiv \mu_\gamma - \frac{1}{2} (v_k - u_k)(v_k' - u_k) \]  
(5.13)
which may depend on \( \theta_\beta \) and \( \eta \) only.

Multiplication of (5.12) by \( \varphi_\gamma / Q \) and summation over all \( \gamma \) leads to
\[ \sum_{\beta=1}^{r} (\varphi_\gamma / Q) \mu_\beta^I = \varepsilon_1 - T \eta + \sum_{\beta=1}^{r} p_\beta / Q, \]
(5.14)
because of (4.10). Elimination of \( \varepsilon_1 - T \eta \) from (5.12) and (5.14) gives the equation
\[ \Lambda_\gamma^I = - \frac{1}{T} \left( \sum_{\beta=1}^{r} (\delta_\gamma \beta - \frac{\varphi_\gamma}{Q}) \mu_\beta^I + \sum_{\beta=1}^{r} p_\beta / Q \right). \]
(5.15)

We draw the obvious conclusion that the Lagrange multipliers \( \Lambda_\gamma^I \) can be calculated, if the pressure \( \sum_{\beta=1}^{r} p_\beta \) of the mixture and the chemical potentials \( \mu_\gamma^I \) of all constituents have been measured as functions of \( Q_1, Q_2, \ldots, Q_r, T \). Clearly the measurement of the pressure presents no difficulty, but the experimental determination of the chemical potentials is cumbersome; in principle, it can proceed as follows:

Let us consider a wall of the type described above that is permeable for constituent \( \gamma \) and which separates the pure constituent \( \gamma \) from a mixture of \( r \) constituents which, of course, include \( \gamma \). At that surface we have by (5.11) and (5.12)
\[ \{ \mu_\gamma^I (q_1, \ldots, q_r, T) + \frac{1}{2} (v_k' - u_k)(v_k' - u_k) \text{mixture} = \{ \varepsilon(q, T) - T \eta(q, T) + \frac{1}{2} (v_k' - u_k)(v_k' - u_k) \}	ext{pure constituent } \gamma. \]

Every function on the right hand side of this equation is known according to my discussion below Eq. (5.5) and if, for given values of \( q_1, \ldots, q_r, T, v_k' - u_k \)
in the mixture, the density \( q \) and the velocity \( v_k' - u_k \) of the pure constituent are measured, one value of \( \mu_\gamma^I \) results. We repeat this for different values of \( q_1, \ldots, q_r, T, v_k' - u_k \), eventually we obtain the function \( \mu_\gamma^I (q_1, \ldots, q_r, T) \) to within a linear function of \( T \), since \( \varepsilon(q, T) \) and \( \eta(q, T) \) in the pure constituent are only known to within a constant. From (5.15) we may therefore conclude that the Lagrange multipliers \( \Lambda_\gamma^I \) can be calculated to within functions of the form
\[ \sum_{\beta=1}^{r} (\delta_\gamma \beta - \frac{\varphi_\gamma}{Q}) (z_\beta - T \eta_\beta), \]
(5.16)
where \( z_\beta \) and \( \beta_\gamma \) are the unknown additive constants in the specific internal energy and the specific entropy of the pure constituent \( \beta \).

6. Results in Terms of Absolute Temperature and Chemical Potentials

As I have demonstrated, it is possible to relate the Lagrange multipliers \( \Lambda^\varepsilon \) and \( \Lambda^{\Phi_\gamma} \) to the absolute temperature \( T \) and the chemical potentials \( \mu_\gamma \) which may be measured—to within functions \( x_\gamma - T \beta_\gamma \)—by measurements of the pressure and the specific heat of the pure constituents and of the pressure \( \sum_{\beta=1}^{r} p_\beta \) of the mixture. We have by (5.5) and (5.15):
\[ \Lambda^\varepsilon = 1 / T, \]
\[ \Lambda^{\Phi_\gamma} = -(1 / T) \left( \sum_{\gamma=1}^{r} (\delta_\gamma \beta - \frac{\varphi_\gamma}{Q}) \mu_\beta^I + \sum_{\beta=1}^{r} p_\beta / Q \right) \]
and I remark that by (4.9) the Lagrange multipliers \( \Lambda^{\Phi_\gamma} \) too are now determined:
\[ \Lambda^{\Phi_\gamma} = -(1 / T) \mu_\gamma. \]
(6.2)

I shall now rewrite the results of Section 4, which were derived from the entropy inequality, in terms of \( T \) and \( \mu_\gamma \) rather than \( \Lambda^\varepsilon \) and \( \Lambda^{\Phi_\gamma} \). First of all. I recall from (4.17) that
\[ p_x = p_x(q_x, T) \]
holds, while by (4.18) we have
\[ q \varepsilon_1 = \sum_{x=1}^{r} q_x \varepsilon_x(q_x, T) \quad \text{and} \quad q \eta = \sum_{x=1}^{r} q_x \eta_x(q_x, T). \]
(6.4)

Equation (4.10) and the definition (5.12) and (5.13) of \( \mu_\gamma^I \) imply
\[ \varepsilon_1 - T \eta = \sum_{\gamma=1}^{r} \frac{q_\gamma}{Q} \mu_\gamma^I - \sum_{\gamma=1}^{r} \frac{p_\gamma}{Q} \]
(6.5)
which indicates that \( \varepsilon_1 - T \eta \) of the mixture is known to within a function of the form
\[ \sum_{\gamma=1}^{r} (q_\gamma / Q) (x_\gamma - T \beta_\gamma), \]
since the chemical potentials are known to within functions \( x_\gamma - T \beta_\gamma \).
The equation (4.13) now reads
\[
\frac{\partial \varepsilon_i}{\partial T} dT + \frac{1}{T} \sum_{\gamma=1}^{r} \mu_{\gamma} dQ_{\gamma}
\]
and this is called the Gibbs equation for mixtures of fluids. In the present form this equation looks complicated, however, it is easily confirmed by use of (6.5) that (6.6) may be written as
\[
d\left[ \frac{\partial (\varepsilon_i - T \eta_i)}{\partial T} \right] = -Q \eta dT + \sum_{\gamma=1}^{r} \mu_{\gamma} dQ_{\gamma}
\]
and since we already know [see (6.4)] that \( \eta \varepsilon_i \) and \( \eta \) are sums of functions of only one density we conclude that
\[
\frac{\partial \mu_{\gamma}}{\partial \eta_{\gamma}} \frac{\partial \eta_{\gamma}}{\partial Q_{\gamma}} = 0, \quad \text{unless} \quad \gamma = \alpha;
\]
this means that the chemical potential of constituent \( \gamma \) depends on the density of that constituent only, and on \( T \), which again confirms the previous observation that simple mixtures are rather special.

The Eq. (4.14) now shows how the fluxes of entropy and of internal energy are related:
\[
\Phi_j = (1/T) q_j - (1/T) \sum_{\gamma=1}^{r} \mu_{\gamma} u_{\gamma j}
\]
and we conclude that this relation is specific only to within a function of the form
\[
\sum_{\gamma=1}^{r} (\alpha_i/T - \beta_{\gamma}) q_{\gamma} u_{\gamma j}.
\]
By use of (6.1), (6.3) and (6.8) we can reduce (4.15) to
\[
\frac{\partial p_{\gamma}}{\partial Q_{\gamma}} = q_{\gamma} \left( \frac{\partial \mu_{\gamma}}{\partial Q_{\gamma}} \right) (\gamma = 1, 2, \ldots, r)
\]
so that we are able to determine the partial pressures \( p_{\gamma}(T) \) to within a function of \( T \). It is interesting to see that (6.10) can be rewritten in the form
\[
\frac{\partial p_{\gamma}}{\partial Q_{\gamma}} = \left( \frac{\partial}{\partial Q_{\gamma}} \right) \left( \sum_{\beta=1}^{r} \left( \frac{\partial \varepsilon_{\gamma}}{\partial Q_{\gamma}} - \frac{\partial \eta_{\gamma}}{\partial Q_{\gamma}} \right) \frac{\partial \mu_{\gamma}}{\partial Q_{\gamma}} T + \frac{\partial}{\partial Q_{\gamma}} \left( \sum_{\beta=1}^{r} \frac{\partial p_{\beta}}{\partial Q_{\gamma}} \right) \right)
\]
with the help of (6.7) and (6.4). Integration gives
\[
p_{\gamma} = q_{\gamma} \frac{\partial \varepsilon_{\gamma}}{\partial Q_{\gamma}} - T \eta_{\gamma} + f_{\gamma}(T),
\]
where the functions \( f_{\gamma}(T) \) are arbitrary except that they must satisfy the requirement
\[
\sum_{\gamma=1}^{r} f_{\gamma}(T) = 0
\]
which follows from (6.5) by (6.7) and (6.4) again. Of course, \( p_{\gamma} \) ought to vanish when \( q_{\gamma} \) tends to zero and then obviously \( f_{\gamma}(T) = 0 \) holds, if only \( \left( \frac{\partial \varepsilon_{\gamma}}{\partial Q_{\gamma}} - T \eta_{\gamma} \right) \frac{\partial \mu_{\gamma}}{\partial Q_{\gamma}} \) is finite in that limit.

The integrability conditions (4.19) on integration lead to
\[
\frac{\partial q_{\gamma}}{\partial T} = \frac{\partial p_{\gamma}}{\partial Q_{\gamma}} - p_{\gamma} + T \frac{\partial p_{\gamma}}{\partial T} = g_{\gamma}(T)
\]
where \( g_{\gamma}(T) \) comes in as integration constant. Under the reasonable assumptions that \( p_{\gamma} \equiv 0 \) and \( \frac{\partial \varepsilon_{\gamma}}{\partial Q_{\gamma}} \frac{\partial \mu_{\gamma}}{\partial Q_{\gamma}} \) finite for \( q_{\gamma} = 0 \), we thus get
\[
\frac{1}{T} \frac{\partial p_{\gamma}}{\partial T} = \frac{\partial p_{\gamma}}{\partial Q_{\gamma}} - p_{\gamma} \quad \text{or} \quad \frac{1}{T} \frac{\partial p_{\gamma}}{\partial T} = g_{\gamma}(T)
\]
which is the same relation as (4.23) but now for the constituent of a simple mixture rather than for a single fluid.

The integrability conditions (4.16) are identically satisfied here * whereas the integrability conditions (4.16) can be combined to read
\[
\sum_{\beta=1}^{r} \left( \frac{\partial \varepsilon_{\gamma}}{\partial Q_{\gamma}} - T \eta_{\gamma} \right) \frac{\partial \mu_{\gamma}}{\partial Q_{\gamma}} T + \frac{\partial}{\partial Q_{\gamma}} \left( \sum_{\beta=1}^{r} \frac{\partial p_{\beta}}{\partial Q_{\gamma}} \right)
\]
and, if the specific heat \( \frac{\partial \varepsilon_{\gamma}}{\partial T} \) of the mixture has been measured for one set of variables \( q_{1}, \ldots, q_{r} \) as a function of \( T \), integration of (6.12) will determine \( \varepsilon_{\gamma} \) to within a function of the form
\[
\sum_{\beta=1}^{r} \left( \frac{\partial p_{\beta}}{\partial q_{\gamma}} \right) \alpha_{\beta}.
\]
Equation (6.5) may then be used to determine \( \eta \) to within a function of the form
\[
\sum_{\gamma=1}^{r} \left( \frac{\partial \varepsilon_{\gamma}}{\partial q_{\gamma}} \right) \beta_{\gamma}.
\]
We thus conclude that the entropy principle in simple mixtures imposes restrictions on the constitutive relations which are summarized in the

* Note that (4.16) was used to derive (6.3) and (6.4).
Eqs. (6.3) through (6.13). Some of these restrictions are in terms of $\mu^J_\gamma$ and these are not quite specific as a consequence of the fact that the chemical potentials $\mu^J_\gamma$ themselves are only known to within functions of the form $\alpha_\gamma - T \beta_\gamma$.

The indeterminancy of $\mu^J_\gamma$, $\epsilon_1$, $\eta$ and $\Phi_j$ goes back to the fact that in a single body $\epsilon$ and $\eta$ are only known to within an additive constant from measurements of pressure and specific heat. This constant, of course, does not affect the balance of energy nor the entropy inequality of a single body and is thus irrelevant there. It is not clear at all, however, whether the indeterminancy $\sum_{\gamma=1}^{r} (q_\gamma / q) \alpha_\gamma$ in $\epsilon_1$ contributes to the balance of internal energy in a mixture and, indeed, it does, if there are chemical reactions. To derive the form of that contribution we must first realize that $q_1$ or $q_i$ too can only be known to within a function of the form $\sum_{a=1}^{r} q_a u_i^2 \alpha_a$, because it contains a term $\sum_{a=1}^{r} q_a \mathcal{E} u_i^2 \alpha_a$.

Thus in $\dot{\epsilon} + \partial q_i / \partial x_i$ the indeterminate parts of $\epsilon$ and $q_i$ will combine to give $\partial \left( \sum_{\gamma=1}^{r} \frac{q_\gamma}{q} x_\gamma \right) + \frac{\partial}{\partial x_i} \left( \sum_{\gamma=1}^{r} \frac{q_\gamma}{q} u_i^2 x_\gamma \right) = \sum_{\gamma=1}^{r} x_\gamma \epsilon_\gamma,$

where (2.1) and (2.4) have been used. We conclude that, in order to obtain a field equation from the balance of internal energy for a chemically reacting mixture, we must be given the constants $\alpha_\gamma$ of its constituents.

7. Evaluation of the Residual Entropy Inequality

With the knowledge of $A^\tau$, $A^{ae}$ and $A^{ae}$ by (6.1), (6.2) and with $\Phi_j$ given by (6.9) and $c_\alpha$ by (2.7) we may now write (4.8) in the form

$$
\begin{align*}
&\left( -\frac{1}{T} q^I_\gamma - \sum_{\gamma=1}^{r} T \frac{\partial}{\partial T} \left( \frac{\mu^I_\gamma}{T} \right) q_\gamma u_\gamma^I \right) \frac{\partial T}{\partial x_j} \\
&- \sum_{\beta=1}^{n} \left[ \sum_{\gamma=1}^{r} \gamma_\beta M_{\beta m} (\mu^I_\gamma + \frac{1}{2} u_\gamma^2) \right] A^a \\
&- \sum_{\gamma=1}^{r} \left( m_\gamma u_\gamma^I - c_\gamma v_\gamma^I \right) u_\gamma^I \geq 0.
\end{align*}
$$

A process in a reacting mixture is called an equilibrium, if i) the fields of temperature and velocities are uniform and time independent, ii) the velocities of all constituents are equal and iii) the reaction rate densities all vanish.

It is obvious that the left side of the inequality (7.1) which I denote by $\sigma$ has its minimum, namely zero, in equilibrium and hence follows by necessity that $***$

$$
\begin{align*}
\frac{\partial \sigma}{\partial T_j} \bigg|_E &= 0, & \frac{\partial \sigma}{\partial V_j^\gamma} \bigg|_E &= 0, & \frac{\partial \sigma}{\partial A^a} \bigg|_E &= 0.
\end{align*}
$$

The conditions (7.2) are trivially satisfied by the constitutive relations (3.8) and (7.2) yields the law of mass action

$$
\sum_{\beta=1}^{n} \gamma_\beta M_{\beta} \mu_{\beta} \bigg|_E = 0 \quad (a = 1, 2, \ldots, n)
$$

which furnishes $n$ relations between the $v$ densities $q_\alpha$.

From (7.3) we conclude that the matrix

$$
\begin{align*}
\begin{bmatrix}
\alpha_\gamma \bigg|_E \\
\alpha_a \bigg|_E
\end{bmatrix}
&= - \left( \frac{1}{T} q^V_\gamma + \sum_{\gamma=1}^{r} \left( \delta_{\gamma \beta} - \frac{\partial q_\gamma}{\partial x_i} \right) \left[ q_\gamma \frac{\partial}{\partial T} \left( \frac{\mu^I_\gamma - \mu^I_\beta}{T} \right) + M_{\beta} \right] \right) \bigg|_E \\
&- \left( \frac{1}{T} q^V_a + \sum_{\gamma=1}^{r} \left( \delta_{\gamma \beta} - \frac{\partial q_\gamma}{\partial x_i} \right) \left[ q_\gamma \frac{\partial}{\partial T} \left( \frac{\mu^I_\gamma - \mu^I_\beta}{T} \right) + M_{\beta} \right] \right) \bigg|_E \\
&- \sum_{\gamma=1}^{r} \left( M_{\gamma} \left( \delta_{\gamma \beta} - \frac{\partial q_\gamma}{\partial x_i} \right) + M_{\beta} \left( \delta_{\gamma \beta} - \frac{\partial q_\gamma}{\partial x_i} \right) \right) \bigg|_E
\end{align*}
$$

** The dot denotes the material time derivative $\partial / \partial t + v_i \partial / \partial x_i$.

*** Note that $\sigma$ may be regarded as a function of $A^a (a = 1, 2, \ldots, n)$ and of $v - n$ densities $q_\alpha$. The index $E$ denotes equilibrium.
is positive semidefinite, while \((7.3)_2\) gives nothing simple here, where I have not written down explicit relations for the constitutive quantities \(A^\alpha\).

Diffusion can be derived from the balance of momenta of the constituents. I write these in the following form

\[
\varrho_\alpha \dot{v}_\alpha + \varrho_\alpha u_\alpha \frac{\partial v_\alpha}{\partial x_j} - \frac{\partial t_{ij}^\alpha}{\partial x_j} = m_i^\alpha - c_\alpha v_\alpha \quad (\alpha = 1, 2, \ldots, v). \tag{8.1}
\]

Division by \(\varrho_\alpha\) and substitution of the last equation from all others gives

\[
\dot{V}_\alpha^2 + \left( u_\alpha^2 \frac{\partial v_\alpha}{\partial x_j} - u_\alpha^r \frac{\partial v^r}{\partial x_j} \right) - \frac{1}{\varrho_\alpha} \frac{\partial t_{ij}^\alpha}{\partial x_j} + \frac{1}{\varrho_\alpha} \frac{\partial t_{ij}^r}{\partial x_j} = \sum_{\gamma=1}^{r-1} \left( \frac{1}{\varrho_\gamma} \frac{\partial q_{\gamma \gamma}}{\partial x_j} \right) (m_i^\gamma - c_\gamma v_\gamma) + \sum_{\alpha=1}^{r-1} c_\alpha V_j^2.
\]

In this relation I drop the acceleration term* and all products of quantities that vanish in equilibrium; furthermore I introduce the constitutive Eqs. (3.8)2 for \(t_{ij}^\gamma\) and solve for \(m_i^\beta - c_\beta v_\beta\):

\[
m_i^\beta - c_\beta v_\beta = \varrho_\beta \sum_{\alpha=1}^{r-1} \left( \delta_{\beta \alpha} - \frac{q_{\alpha \gamma}}{\varrho_\gamma} \right) \left( \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial x_i} - \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial x_i} \right), \quad \beta = 1, 2, \ldots, v - 1. \tag{8.2}
\]

With (6.10) one obtains

\[
m_i^\beta - c_\beta v_\beta = \varrho_\beta T \sum_{\alpha=1}^{r-1} \left( \delta_{\beta \alpha} - \frac{q_{\alpha \gamma}}{\varrho_\gamma} \right) \frac{\partial}{\partial x_i} \left( \frac{\mu_{\alpha I}^I - \mu_{\beta I}^I}{T} \right)
\]

\[+ \varrho_\beta \sum_{\alpha=1}^{r-1} \left( \delta_{\beta \alpha} - \frac{q_{\alpha \gamma}}{\varrho_\gamma} \right) \left( \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial T} \right) - \frac{\partial}{\partial x_i} \left( \frac{\mu_{\beta I}^I - \mu_{\beta I}^I}{T^2} \right) \frac{\partial T}{\partial x_i} \left( \beta = 1, 2, \ldots, v - 1 \right)
\]

and finally for the diffusion fluxes \(q_{\delta \gamma}\) with (3.8)4

\[
q_{\delta \gamma} u_\gamma = \sum_{\beta, \gamma=1}^{r-1} \left( \sum_{\alpha=1}^{r-1} F_{\delta \gamma} (\mathbb{M}^{-1})_{\gamma \beta} F_{\beta \alpha} T \right) \left[ \frac{\partial}{\partial x_i} \left( \frac{\mu_{\beta I}^I - \mu_{\gamma I}^I}{T} \right) \right]
\]

\[+ \sum_{\beta, \gamma=1}^{r-1} F_{\delta \gamma} (\mathbb{M}^{-1})_{\gamma \beta} T^2 M_{\delta \beta} - \sum_{\alpha, \beta, \gamma=1}^{r-1} F_{\delta \gamma} (\mathbb{M}^{-1})_{\gamma \beta} F_{\beta \alpha} \left( \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial T} \right) - \frac{\partial}{\partial x_i} \left( \frac{\mu_{\beta I}^I - \mu_{\beta I}^I}{T^2} \right) \frac{\partial T}{\partial x_i} \left( \beta = 1, 2, \ldots, v - 1 \right)
\]

where the matrices \(F_{\delta \gamma}\) and \(\mathbb{M}_{\delta \gamma}\) have been introduced according to the definitions

\[
F_{\delta \gamma} = \varrho_\gamma \delta_{\gamma \delta} - \varrho_\gamma q_{\gamma \delta} \quad \text{and} \quad \mathbb{M}_{\delta \gamma} = M_{\gamma \gamma}. \tag{8.4}
\]

Equation (8.3) represents Fick's law, or rather a generalization of this law which is well known from linear irreversible thermodynamics (e.g. see 8), where the relation (8.3) is expressed in a suggestive manner in these words: The diffusion flux \(q_{\delta \gamma} u_\gamma\) is driven by the thermodynamic forces

\[
- \frac{\partial}{\partial x_i} \left( \frac{\mu_{\beta I}^I - \mu_{\gamma I}^I}{L} \right) \quad \text{and} \quad \frac{\partial}{\partial x_i} (1/T) \tag{8.5}
\]

Elimination of \(q_{\delta \gamma} u_\gamma\) between (8.3) and (8.6) and relabeling of indices leads to

\[
q_i = \sum_{\delta=1}^{r-1} \left( - \sum_{\alpha, \beta, \gamma=1}^{r-1} F_{\delta \gamma} (\mathbb{M}^{-1})_{\gamma \beta} F_{\beta \alpha} Q_\alpha \right) T - \frac{\partial}{\partial x_i} \left( \frac{\mu_{\gamma I}^I - \mu_{\gamma I}^I}{T} \right)
\]

\[+ \left( x T^2 - \sum_{\beta, \gamma=1}^{r-1} Q_\beta F_{\delta \gamma} (\mathbb{M}^{-1})_{\gamma \beta} T^2 M_{\delta \beta} - \sum_{\alpha, \beta, \gamma=1}^{r-1} Q_\alpha F_{\delta \gamma} (\mathbb{M}^{-1})_{\gamma \beta} F_{\beta \alpha} \left( \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial T} \right) - \frac{\partial}{\partial x_i} \left( \frac{\mu_{\beta I}^I - \mu_{\beta I}^I}{T^2} \right) \frac{\partial T}{\partial x_i} \right) \left( \beta = 1, 2, \ldots, v - 1 \right)
\]

\[
\left( \frac{\partial}{\partial x_i} (1/T) \right)
\]

* In 6 I have demonstrated that one can obtain a hyperbolic diffusion equation, if the acceleration is kept.
The dependence of $q_1$ on the gradients of the chemical potentials is called the diffusion-thermo-effect.

The Eqs. (8.3) and (8.7) are of the forms

$$q_\delta u_\delta = \sum_{\alpha=1}^{r-1} L_{\delta \alpha} \left[ - \frac{\partial}{\partial x_\alpha} \left( \frac{\mu_\alpha - \mu_\delta}{T} \right) \right] + L_{\nu \delta} \left[ \frac{\partial (1/T)}{\partial x_{\nu}} \right] ,$$

$$q_1 = \sum_{\delta=1}^{r-1} L_{\nu \delta} \left[ - \frac{\partial}{\partial x_\delta} \left( \frac{\mu_\delta - \mu_1}{T} \right) \right] + L_{\nu \nu} \left[ \frac{\partial (1/T)}{\partial x_{\nu}} \right] ,$$

where the definitions of the coefficients $L_{\delta \alpha}$, $L_{\delta \nu}$, $L_{\nu \delta}$ and $L_{\nu \nu}$ may be read off from the comparison of (8.8) with (8.3) and (8.7).

Linear irreversible thermodynamics contends that the coefficients in (8.8) obey the symmetry relations (see 8, p. 427)

$$L_{\delta \alpha} = L_{\alpha \delta} \quad \text{and} \quad L_{\delta \nu} = - L_{\nu \delta} \quad (8.9)$$

and Truesdell has shown in 3 that (8.9)1 can indeed be proved for mixtures that exhibit binary drags

The symmetry relations (8.9)2 then read

$$\sum_{\alpha, \beta, \gamma=1}^{r-1} F_{\gamma \alpha} (2\pi^{-1})_{\beta \gamma} F_{\beta \alpha} \left( \varepsilon_\alpha - \varepsilon_\beta + \frac{p_\alpha}{\varepsilon_\alpha} - \frac{p_\beta}{\varepsilon_\beta} \right) \frac{1}{T} \frac{\partial p_\alpha}{\partial T} = \sum_{\alpha, \beta, \gamma=1}^{r-1} F_{\gamma \alpha} (2\pi^{-1})_{\beta \gamma} F_{\beta \alpha} \left( \frac{1}{\varepsilon_\alpha} + \frac{p_\alpha}{\varepsilon_\alpha} \right) \frac{\partial p_\alpha}{\partial T} - \frac{1}{\varepsilon_\beta} \frac{\partial p_\beta}{\partial T} - \frac{1}{\varepsilon_\gamma} \frac{\partial p_\gamma}{\partial T} \left( \frac{\mu_\alpha}{T} - \frac{\mu_\beta}{T} \right) \right) T^2 .$$

Since I have already accepted the symmetry of $\mathfrak{M}$, it is obvious that (8.13) will be satisfied, if the two expressions

$$1 \frac{\partial p_\alpha}{\partial T} = \frac{\partial p_\alpha}{\partial T} - T^2 \frac{\partial}{\partial T} \left( \frac{\mu_\alpha}{T} \right) \quad \text{and} \quad \left( \varepsilon_\alpha + \frac{p_\alpha}{\varepsilon_\alpha} \right)$$

(8.14)

can be shown to be equal. Now, (6.7) can be rewritten as

$$d \left[ \frac{\partial (\varepsilon_\alpha - T \eta)}{T} \right] = \frac{\partial \varepsilon_\alpha}{T^2} d T + \sum_{\alpha=1}^{r} \frac{\mu_\alpha}{T} \cdot$$

whence follows as an integrability condition

$$\frac{\partial}{\partial T} \left( \frac{\mu_\alpha}{T} \right) = - \frac{1}{T^2} \frac{\partial \varepsilon_\alpha}{\partial \varepsilon_\alpha} .$$

Hence follows for the expression (8.14)1 with (6.4) and then with (6.12)

only, a restriction which imposes two conditions on the coefficients $M_{\nu \nu}$:

1) $M_{\nu \nu}$ does not depend on $\varphi_\delta$, if $\delta = \beta$ or $\gamma$,

2) $M_{\nu \nu} \to 0$, if $\varphi_\delta \to 0$. (8.10)

I proceed on the assumption that (8.9)1 indeed holds. This obviously implies that the matrix $\mathfrak{M}$ is symmetric and I now characterize a special case in which (8.9)2 can be proved:

i) The interaction force $m_\beta = c_\beta v_\beta$ is independent of the temperature gradient, i.e.

$$M_{\nu \nu} = 0 ,$$

(8.11)

ii) The flux of internal energy $q_1$ depends on the relative velocities only through the explicit terms

$$\sum_{\delta=1}^{r-1} \left( \varepsilon_\delta - \varepsilon_\nu + \frac{p_\delta}{\varepsilon_\delta} - \frac{p_\nu}{\varepsilon_\nu} \right) \frac{\partial q_\delta}{\partial T}$$

that go into its definition [see (2.3)]. By (8.6) this means

$$Q_\delta = \varepsilon_\delta - \varepsilon_\nu + \frac{p_\delta}{\varepsilon_\delta} - \frac{p_\nu}{\varepsilon_\nu} .$$

(8.12)

Thus the first of the two expressions in (8.14) is indeed equal to the second one. It has therefore been proved that the symmetry relations (8.9) hold in the special simple mixtures characterized by the conditions (8.10) through (8.12): In these mixtures the coefficients $L_{\nu \delta}$ of thermal diffusion are equal to the coefficients $L_{\nu \delta}$ of the diffusion-thermo-effect. This result provides an extension of the corresponding result in 9 where I considered the kinetic theory of a mixture of Maxwellian gases.

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