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 ν constituents let the following notation be introduced for every constituent α:

ϱ_α density of mass,
v_j^α velocity,
c_α density of mass production,
t_{ij}^α stress,
m_i^α density of momentum production,
ε_α specific internal energy,
q_i^α flux of internal energy,
l^α density of energy production.

These quantities are assumed to obey the equations of balance of mass, momentum and energy (see [4], or [5]):

$$\frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial \varrho_\alpha v_j^\alpha}{\partial x_j} = c_\alpha ,$$
$$\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j} (\varrho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha) = m_i^\alpha , \tag{2.1}$$
$$\frac{\partial \varrho_\alpha (\varepsilon_\alpha + \frac{1}{2} v_\alpha^2)}{\partial t} + \frac{\partial}{\partial x_j} \cdot (\varrho_\alpha (\varepsilon_\alpha + \tfrac{1}{2} v_\alpha^2) v_j^\alpha + q_j^\alpha - t_{ij}^\alpha v_i^\alpha) = l_\alpha ,$$

where the production densities are subject to the conditions

$$\sum_{\alpha=1}^{\nu} c_\alpha = 0 , \quad \sum_{\alpha=1}^{\nu} m_i^\alpha = 0 , \quad \sum_{\alpha=1}^{\nu} l_\alpha = 0 . \tag{2.2}$$

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

$$\begin{aligned}
\varrho &\equiv \sum_{\alpha=1}^{\nu} \varrho_\alpha, \\
v_i &\equiv \sum_{\alpha=1}^{\nu} \frac{\varrho_\alpha}{\varrho} v_i^\alpha , \\
t_{ij} &\equiv \sum_{\alpha=1}^{\nu} (t_{ij}^\alpha - \varrho_\alpha u_i^\alpha u_j^\alpha), \quad \text{where} \\
u_i^\alpha &\equiv v_i^\alpha - v_i \quad \text{diffusion velocity}, \\
\varepsilon &\equiv \sum_{\alpha=1}^{\nu} \frac{\varrho_\alpha}{\varrho} (\varepsilon_\alpha + \tfrac{1}{2} u_\alpha^2) , \\
q_i &\equiv \sum_{\alpha=1}^{\nu} (q_i^\alpha + \varrho_\alpha (\varepsilon_\alpha + \tfrac{1}{2} u_\alpha^2) u_i^\alpha - t_{ij}^\alpha u_j^\alpha)
\end{aligned} \tag{2.3}$$

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summation of the Eqs. (2.1) over all α 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])

$$\frac{\partial \varrho}{\partial t} + \frac{\partial \varrho\, v_j}{\partial x_j} = 0\,,$$
$$\frac{\partial \varrho\, v_i}{\partial t} + \frac{\partial}{\partial x_j}(\varrho\, v_i\, v_j - t_{ij}) = 0\,, \tag{2.4}$$
$$\frac{\partial \varrho\,(\varepsilon + \frac{1}{2} v^2)}{\partial t} + \frac{\partial}{\partial x_j} \cdot (\varrho\,(\varepsilon + \tfrac{1}{2} v^2)\, v_j + q_j - t_{ij}\, v_i) = 0.$$

Note that the diffusion velocities u_i^α, defined in $(2.3)_3$ obey the identity

$$\sum_{\alpha=1}^{\nu} \varrho_\alpha\, u_i^\alpha = 0\,. \tag{2.5}$$

Apart from the restriction $(2.2)_1$ on the c_α'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 Λ^a $(a = 1, 2, \ldots, n)$ be their reaction rate densities*; furthermore, let $\gamma_\alpha{}^a$ be the stochiometric coefficients of the constituent α in the reaction a and M_α the molecular weight of constituent α while m is the mass of a hydrogen atom. Then the equations

$$\sum_{\alpha=1}^{\nu} \gamma_\alpha{}^a\, M_\alpha\, m = 0 \qquad (a = 1, 2, \ldots, n) \tag{2.6}$$

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

$$c_\alpha = \sum_{a=1}^{n} (\gamma_\alpha{}^a\, M_\alpha\, m)\, \Lambda^a \tag{2.7}$$

holds, so that we have only n independent reaction rate densities rather than ν, or $\nu - 1$, mass production densities c_α.

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 ϱ_α and the velocities v_i^α of the constituents and of an empirical temperature ϑ of the mixture. For that one relies on the equations of balance of mass and momentum for the constituents and on the equation of balance of energy (or internal energy) for the mixture

$$\frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial \varrho_\alpha\, v_j^\alpha}{\partial x_j} = \sum_{a=1}^{n} (\gamma_\alpha{}^a\, M_\alpha\, m)\, \Lambda^a,$$
$$\frac{\partial \varrho_\alpha\, v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\varrho_\alpha\, v_i^\alpha\, v_j^\alpha - t_{ij}^\alpha) = m_i^\alpha, \tag{3.1}$$
$$\frac{\partial \varrho\, \varepsilon}{\partial t} + \frac{\partial}{\partial x_j}(\varrho\, \varepsilon\, v_j + q_j) = t_{ij}\, \frac{\partial v_i}{\partial x_j}\,.$$

In order to obtain field equations for ϱ_α, v_i^α and ϑ one must supplement these equations of balance by constitutive relations for Λ^a, t_{ij}^α, m_i^α, ε, and q_j whose form depends on the material. I shall consider *simple mixtures*** whose constitutive relations have the general form

$$\begin{aligned}
\Lambda^a &= \Lambda^a\ (\varrho_\alpha, v_i^\alpha, \vartheta, \vartheta_{|i})\,, && (a = 1, 2, \ldots, n)\\
t_{ij}^\alpha &= t_{ij}^\alpha\ (\text{---------})\,, && (\alpha = 1, 2, \ldots, \nu)\\
m_i^\alpha &= m_i^\alpha\ (\text{---------})\,, && \text{where } \sum_{\alpha=1}^{\nu} m_i^\alpha = 0\\
\varepsilon &= \varepsilon\ (\text{---------})\,, &&\\
q_i &= q_i\ (\text{---------})\,. &&
\end{aligned} \tag{3.2}$$

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:

$$\begin{aligned}
&[\varrho_\alpha (v_j^\alpha - v_j)\, e_j] = 0\,,\\
&[\varrho\, v_i (v_j - u_j)\, e_j] - [t_{ij}\, e_j] = K_i\,, \quad (\text{see }^+)\\
&[\varrho\,(\varepsilon + \tfrac{1}{2} v^2)(v_j - u_j)\, e_j]\\
&\qquad + [(q_j - t_{ij}\, v_i)\, e_j] = K_i\, u_i\,, \quad (\text{see }^+)
\end{aligned} \tag{3.3}$$

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 Λ^a, ε, q_i and t_{ij}^α transform as objective scalars, vectors

* The reaction rate density Λ^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.

** 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 ψ across the wall.

and tensors, m_i^α does not. However, the *interaction force* $m_i^\alpha - c_\alpha v_i^\alpha$ does transform as an objective vector ** and therefore we choose it, rather than m_i^α, as one of the constitutive quantities:

$$m_i^\alpha - c_\alpha v_i^\alpha = M_i(\varrho_\alpha, v_i^\alpha, \vartheta, \vartheta_{|i}) . \qquad (3.4)$$

The principle of material frame indifference with respect to Galilei transformations requires that the constitutive functions for Λ^a, t_{ij}^α, M_i^α, ε and q_i be the same ones in every Galileian frame and this implies that not all ν velocities v_i^α can occur as independent variables, but only the $\nu - 1$ combinations

$$V_i^\alpha \equiv v_i^\alpha - v_i^\nu . \qquad (3.5)$$

Therefore, the general form of the constitutive relations is

$$\begin{aligned} \Lambda^a &= \Lambda^a(\varrho_\beta, V_i^\beta, \vartheta, \vartheta_{|i}), \\ t_{ij}^\alpha &= t_{ij}^\alpha(\text{———}), \\ m_i^\alpha - c_\alpha v_i^\alpha &= M_i^\alpha(\text{———}), \\ \varepsilon &= \varepsilon\ (\text{———}), \\ q_i &= q_i\ (\text{———}) \end{aligned} \qquad (3.6)$$

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 $(2.3)_{4,5}$of ε and q_i suggests the decompositions

$$\varepsilon = \varepsilon_{\mathrm{I}}(\varrho_\alpha, V_i^\alpha, \vartheta, \vartheta_{|i}) + \sum_{\alpha=1}^{\nu} \frac{1}{2} \frac{\varrho_\alpha}{\varrho} u_\alpha^2 ,$$

$$q_i = q_i^{\mathrm{I}}(\text{———}) + \sum_{\alpha=1}^{\nu} \tfrac{1}{2} \varrho_\alpha u_\alpha^2 u_i^\alpha$$

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 Λ^a, t_{ij}^α, $m_i^\alpha - c_\alpha v_i^\alpha$ and the intrinsic quantities ε_{I}, q_i^{I}, just defined, do not depend on V_i^β and $\vartheta_{|i}$ nonlinearly. The isotropy of the constitutive functions then implies the following representations

$$\begin{aligned} \Lambda^a &= \Lambda^a(\varrho_\beta, \vartheta), \quad (a = 1, 2, \dots, n) \\ t_{ij}^\alpha &= -p_\alpha(\varrho_\beta, \vartheta), \quad (\alpha = 1, 2, \dots, \nu) \\ \varepsilon_{\mathrm{I}} &= \varepsilon_{\mathrm{I}}(\varrho_\beta, \vartheta), \\ m_i^\alpha - c_\alpha v_i^\alpha &= M_\vartheta^\alpha(\varrho_\beta, \vartheta)\, \vartheta_{|i} + \sum_{\gamma=1}^{\nu-1} M_{V_\gamma}^\alpha(\varrho_\beta, \vartheta)\, V_i^\gamma, \\ &\quad (\alpha = 1, 2, \dots, \nu - 1) \quad (\text{see } ***) \\ q_i^{\mathrm{I}} &= -\varkappa(\varrho_\beta, \vartheta)\, \vartheta_{|i} + \sum_{\gamma=1}^{\nu-1} q_{V_\gamma}(\varrho_\beta, \vartheta)\, V_i^\gamma . \end{aligned} \qquad (3.8)$$

p_α is called the pressure of component α and $\varkappa$ 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 defiinitions of V_i^α and u_i^α and which permits the calculation of one of these sets of relative velocities from the other. We have

$$u_i^\alpha = \sum_{\gamma=1}^{\nu-1} (\delta_{\alpha\gamma} - \varrho_\gamma/\varrho)\, V_i^\gamma \quad (\alpha = 1, 2, \dots, \nu) . \qquad (3.9)$$

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

$$\frac{\partial \varrho \eta}{\partial t} + \frac{\partial}{\partial x_j}(\varrho \eta v_j + \Phi_j) \geqq 0 \qquad (4.1)$$

holds. The specific entropy η is an objective scalar and the nonconvective entropy flux Φ_j 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

$$[\varrho \eta (v_j - u_j) e_j] + [\Phi_j e_j] = 0 ,$$
$$\text{if} \quad [\vartheta] = 0 \quad \text{and} \quad \varepsilon_{ijk} e_j v_k^\alpha = 0 . \qquad (4.2)$$

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 $\varrho \eta (v_i - u_i) e_i$ 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 Φ_i, the heat flux q_i and

++ For motivation of this statement see[6], p. 12.

*** Note that

$$m_i^\nu - c_\nu v_i^\nu = -\sum_{\alpha=1}^{r=1} [(m_i^\alpha - c_\alpha v_i^\alpha) + c_\alpha V_i^\alpha] .$$

* I assume that the wall has no tangential velocity.

diffusion velocities u_i^α; 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 η and the non-convective entropy flux are given by constitutive relations of the form

$$\eta = \eta(\varrho_\beta, V_i^\beta, \vartheta, \vartheta_{|i}),$$
$$\Phi_i = \Phi_i(\qquad\qquad), \tag{4.3}$$

where both functions must be isotropic with respect to Galilei transformations. Here again I wish to exclude non-linear dependence on V_i^α and $\vartheta_{|i}$ and therefore we have

$$\eta = \eta(\varrho_\beta, \vartheta),$$
$$\Phi_i = \varphi_\vartheta(\varrho_\beta, \vartheta)\,\vartheta_{|i} + \sum_{\gamma=1}^{\nu-1} \varphi_{V_\gamma}(\varrho_\beta, \vartheta)\, V_i^\gamma. \tag{4.4}$$

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

$$\begin{aligned}\frac{\partial \varrho\eta}{\partial t} &+ \frac{\partial}{\partial x_j}(\varrho\eta v_j + \Phi_j) - \sum_{\alpha=1}^{\nu} \Lambda^{\varrho_\alpha}\left(\frac{\partial \varrho_\alpha}{\partial t} + \frac{\partial \varrho_\alpha v_j^\alpha}{\partial x_j} - c_\alpha\right) \\ &- \sum_{\alpha=1}^{\nu} \Lambda^{v_i^\alpha}\left(\frac{\partial \varrho_\alpha v_i^\alpha}{\partial t} + \frac{\partial}{\partial x_j}(\varrho_\alpha v_i^\alpha v_j^\alpha - t_{ij}^\alpha) - m_i^\alpha\right) \\ &- \Lambda^\varepsilon\left(\frac{\partial \varrho\varepsilon}{\partial t} + \frac{\partial}{\partial x_j}(\varrho\varepsilon v_j + q_j) - t_{ij}\frac{\partial v_i}{\partial x_j}\right) \geqq 0\end{aligned} \tag{4.5}$$

holds for all analytic fields ϱ_α, v_i^α and ϑ. The factors Λ^{ϱ_α}, $\Lambda^{v_i^\alpha}$ and Λ^ε are called Lagrange multipliers by Liu and they may be functions of the variables $\varrho_\alpha, v_i^\alpha, \vartheta, \vartheta_{|i}$.

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

$$\frac{\partial\vartheta}{\partial t}, \frac{\partial^2\vartheta}{\partial t\,\partial x_k}, \frac{\partial^2\vartheta}{\partial x_i\,\partial x_k}, \frac{\partial\varrho_\beta}{\partial t}, \frac{\partial\varrho_\beta}{\partial x_k}, \frac{\partial v_i^\beta}{\partial t}, \frac{\partial v_i^\beta}{\partial x_k}.$$

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

$$\Gamma^A \equiv \frac{\partial\eta}{\partial A} - \Lambda^\varepsilon\frac{\partial\varepsilon}{\partial A} \quad\text{and}\quad \Delta_j^A \equiv \frac{\partial\Phi_j}{\partial A} - \Lambda^\varepsilon\frac{\partial q_j}{\partial A}, \tag{4.6}$$

we obtain from this argument the following conditions:

$$\varrho\,\Gamma^{\varrho_\beta} - \Lambda^{\varrho_\beta} = 0, \quad (\beta = 1, 2, \dots, \nu) \tag{4.7$_1$}$$

$$\varrho\,\Gamma^{V_i^\beta} - \Lambda^{v_i^\beta}\varrho_\beta = 0, \quad (\beta = 1, 2, \dots, \nu-1) \tag{4.7$_2$}$$

$$-\sum_{\beta=1}^{\nu-1}\varrho\,\Gamma^{V_i^\beta} - \Lambda^{v_i^\nu}\varrho_\nu = 0, \tag{4.7$_3$}$$

$$\Gamma^\vartheta = 0, \tag{4.7$_4$}$$

$$\Gamma^{\vartheta_{|i}} = 0, \tag{4.7$_5$}$$

$$\Delta_j^{\varrho_\beta} - \varrho\,\Gamma^{\varrho_\beta} u_j^\beta + \sum_{\alpha=1}^{\nu}\Lambda^{v_k^\alpha}\frac{\partial t_{kj}^\alpha}{\partial\varrho_\beta} + \Lambda^\varepsilon t_{ij}\frac{1}{\varrho}u_i^\beta = 0, \quad (\beta = 1, 2, \dots, \nu) \tag{4.7$_6$}$$

$$\Delta_j^{V_i^\beta} - \varrho\,\Gamma^{V_i^\beta} u_j^\beta + \sum_{\alpha=1}^{\nu}\Lambda^{v_k^\alpha}\frac{\partial t_{kj}^\alpha}{\partial V_i^\beta} - \Lambda^{\varrho_\beta}\varrho_\beta\delta_{ij} + \Lambda^\varepsilon t_{ij}\frac{\varrho_\beta}{\varrho} = 0, \quad (\beta = 1, 2, \dots, \nu-1) \tag{4.7$_7$}$$

$$-\sum_{\beta=1}^{\gamma-1}\left(\Delta_j^{V_i^\beta} - \varrho\,\Gamma^{V_i^\beta}u_j^\beta + \sum_{\alpha=1}^{\nu}\Lambda^{v_k^\alpha}\frac{\partial t_{kj}^\alpha}{\partial V_i^\beta}\right) - \Lambda^{\varrho_\nu}\varrho_\nu\delta_{ij} + \Lambda^\varepsilon t_{ij}\frac{\varrho_\nu}{\varrho} = 0, \tag{4.7$_8$}$$

$$\Delta_{(j)}^{\vartheta_{(i)}} = 0 \qquad (\text{see } **). \tag{4.7$_9$}$$

There remains the inequality

$$\Delta_j^\vartheta\,\vartheta_{,j} + \sum_{\alpha=1}^{\nu}\Lambda^{\varrho_\alpha}c_\alpha + \sum_{\alpha=1}^{\nu}\Lambda^{v_i^\alpha}(m_i^\alpha - c_\alpha v_i^\alpha) \geqq 0. \tag{4.8}$$

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 $\Gamma^{V_i^\beta}$ results from the kinetic energy of the diffusive motion. Therefore, by use of (3.9) the Eqs. $(4.7)_{2,3}$ can be written as

$$\Lambda^{v_i^\beta} = -\Lambda^\varepsilon u_i^\beta. \tag{4.9}$$

Summation of all Eqs. $(4.7)_{7,8}$ and use of (4.9) lead to a restriction on Λ^{ϱ_β} of the form

$$\sum_{\alpha=1}^{\nu}\Lambda^{\varrho_\beta}\varrho_\beta = -\Lambda^\varepsilon\sum_{\alpha=1}^{\nu}p_\alpha. \tag{4.10}$$

The Eq. $(4.7)_5$ is identically satisfied for the simple constitutive class under consideration and $(4.7)_1$ and $(4.7)_4$ can be written in the form

** Round brackets indicate symmetrization.

$$\frac{\partial \eta}{\partial \vartheta} = \Lambda^\varepsilon \frac{\partial \varepsilon_{\mathrm{I}}}{\partial \vartheta},$$

$$\frac{\partial \eta}{\partial \varrho_\beta} = \Lambda^\varepsilon \frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\beta} + \frac{1}{\varrho} \Lambda^{\varrho_\beta} + \Lambda^\varepsilon \frac{1}{\varrho} \sum_{\alpha=1}^{\nu} \left(\delta_{\alpha\beta} - \frac{\varrho_\alpha}{\varrho}\right) \tfrac{1}{2} u_\alpha{}^2$$

$$(\beta = 1, 2, \ldots, \nu). \tag{4.11}$$

From $(4.11)_1$ it is obvious that Λ^ε is independent of $\boldsymbol{V}_i{}^\gamma$ and $\vartheta_{|i}$ and therefore it follows from $(4.11)_2$ that Λ^{ϱ_α} can be decomposed into a part independent of $\boldsymbol{V}_i{}^\gamma$ and $\vartheta_{|i}$ and another part whose dependence on the relative velocities is explicit:

$$\Lambda^{\varrho_\beta} = \Lambda_{\mathrm{I}}^{\varrho_\beta}(\varrho_\delta, \vartheta) - \Lambda^\varepsilon \sum_{\alpha=1}^{\nu} \left(\delta_{\alpha\beta} - \frac{\varrho_\alpha}{\varrho}\right) \frac{1}{2} u_\alpha{}^2. \tag{4.12}$$

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

$$\mathrm{d}\eta = \Lambda^\varepsilon \frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho} \mathrm{d}\vartheta + \sum_{\alpha=1}^{\nu} \left(\Lambda^\varepsilon \frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\alpha} + \frac{1}{\varrho} \Lambda_{\mathrm{I}}^{\varrho_\alpha}\right) \mathrm{d}\varrho_\alpha . \tag{4.13}$$

Division of $(4.7)_7$ by ϱ_β and of $(4.7)_8$ by ϱ_ν and subsequent subtraction leads to the relations

$$\frac{\partial \Phi_j}{\partial \boldsymbol{V}_i{}^\gamma} - \Lambda^\varepsilon \frac{\partial q_j}{\partial \boldsymbol{V}_i{}^\gamma} = \sum_{\beta=1}^{\nu} \left(\varrho_\gamma \delta_{\gamma\beta} - \frac{\varrho_\gamma \varrho_\beta}{\varrho}\right) \Lambda_{\mathrm{I}}^{\varrho_\beta} \delta_{ij},$$

$$(\gamma = 1, 2, \ldots, \nu - 1)$$

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 $(4.7)_9$ implies

$$\frac{\partial \Phi_j}{\partial \vartheta_{|i}} - \Lambda^\varepsilon \frac{\partial q_j}{\partial \vartheta_{|i}} = 0 .$$

By integration of the last two equations we obtain

$$\Phi_j = \Lambda^\varepsilon q_j{}^{\mathrm{I}} + \sum_{\beta=1}^{\nu} \Lambda_{\mathrm{I}}^{\varrho_\beta} \varrho_\beta u_j{}^\beta,$$

or, by (3.7) and (4.12)

$$\Phi_j = \Lambda^\varepsilon q_j + \sum_{\beta=1}^{\nu} \Lambda^{\varrho_\beta} \varrho_\beta u_j{}^\beta. \tag{4.14}$$

It remains to evaluate the conditions $(4.7)_6$. A careful and somewhat long calculation, which makes use of the results obtained so far, shows that $(4.7)_6$ is equivalent to

$$\frac{\partial \Lambda^\varepsilon}{\partial \varrho_\beta} q_j{}^{\mathrm{I}} + \sum_{\gamma=1}^{\nu} \left(\varrho_\gamma \frac{\partial \Lambda_{\mathrm{I}}{}^{\varrho_\gamma}}{\partial \varrho_\beta} + \Lambda^\varepsilon \frac{\partial p_\gamma}{\partial \varrho_\beta}\right) u_j{}^\gamma = 0$$

or with (3.8) and (3.9)

$$-\frac{\partial \Lambda^\varepsilon}{\partial \varrho_\beta} \varkappa \vartheta_{|i} + \sum_{\delta=1}^{\nu-1} \left[\frac{\partial \Lambda^\beta}{\partial \varrho_\beta} q_{V_\delta} + \sum_{\gamma=1}^{\nu} \left(\varrho_\gamma \frac{\partial \Lambda_{\mathrm{I}}{}^{\varrho_\gamma}}{\partial \varrho_\beta} + \Lambda^\varepsilon \frac{\partial p_\gamma}{\partial \varrho_\beta}\right)\left(\delta_{\gamma\delta} - \frac{\varrho_\delta}{\varrho}\right)\right] \boldsymbol{V}_j{}^\delta = 0 .$$

This relation can obviously only be satisfied for all $\vartheta_{|j}$ and $\boldsymbol{V}_j{}^\delta$ if

$$\Lambda^\varepsilon = \Lambda^\varepsilon(\vartheta)$$

and

$$\frac{\partial (\Lambda_{\mathrm{I}}^{\varrho_\gamma} - \Lambda_{\mathrm{I}}^{\varrho_\nu})}{\partial \varrho_\beta} = -\Lambda^\varepsilon \left(\frac{1}{\varrho_\gamma} \frac{\partial p_\gamma}{\partial \varrho_\beta} - \frac{1}{\varrho_\nu} \frac{\partial p_\nu}{\partial \varrho_\beta}\right)$$

$$(\gamma, \beta = 1, 2, \ldots, \nu). \tag{4.15}$$

In particular we thus see that the Lagrange multiplier Λ^ε depends on ϑ only.

While the Eqs. (4.9) through (4.15) exhaust the conditions (4.7), they all still contain the multipliers Λ^{ϱ_α}, $\Lambda^{a_i{}^\alpha}$ and Λ^ε, 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 η:

$$\frac{\partial \frac{1}{\varrho} \Lambda_{\mathrm{I}}^{\varrho_\alpha}}{\partial \varrho_\beta} = \frac{\partial \frac{1}{\varrho} \Lambda_{\mathrm{I}}^{\varrho_\beta}}{\partial \varrho_\alpha},$$

$$\frac{\partial \Lambda_{\mathrm{I}}^{\varrho_\gamma} - \Lambda_{\mathrm{I}}^{\varrho_\nu}}{\partial \vartheta} = -\varrho \frac{\partial \Lambda^\varepsilon}{\partial \vartheta} \left(\frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\gamma} - \frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\nu}\right), \tag{4.16}$$

$$\frac{\partial \ln \Lambda^\varepsilon}{\partial \vartheta} = \left(\partial \sum_{\alpha=1}^{\nu} p_\alpha / \partial \vartheta \middle/ \sum_{\alpha=1}^{\nu} (\varrho \varrho_\alpha \partial \varepsilon_{\mathrm{I}} / \partial \varrho_\alpha - p_\alpha\right)$$

(see ***).

By use of the identity

$$\Lambda^{\varrho_\alpha} = \sum_{\gamma=1}^{\nu-1} \left(\delta_{\alpha\gamma} - \frac{\varrho_\gamma}{\varrho}\right)(\Lambda^{\varrho_\gamma} - \Lambda^{\varrho_\nu}) + \sum_{\gamma=1}^{\nu} \frac{\varrho_\gamma}{\varrho} \Lambda^{\varrho_\nu}$$

and (4.10), $(4.15)_2$ one can easily show that (4.16) is equivalent to

$$\frac{1}{\varrho_\alpha} \frac{\partial p_\alpha}{\partial \varrho_\beta} = \frac{1}{\varrho_\beta} \frac{\partial p_\beta}{\partial \varrho_\alpha} \quad (\alpha, \beta = 1, 2, \ldots, \nu.)$$

On the other hand the Eqs. $(4.15)_2$ imply integrability conditions for $\Lambda_{\mathrm{I}}^{\varrho_\gamma} - \Lambda_{\mathrm{I}}^{\varrho_\nu}$ and these come out as

$$\frac{1}{\varrho_\gamma{}^2} \left(\delta_{\gamma\alpha} \frac{\partial p_\gamma}{\partial \varrho_\beta} - \delta_{\gamma\beta} \frac{\partial p_\gamma}{\partial \varrho_\alpha}\right)$$

$$= \frac{1}{\varrho_\nu{}^2} \left(\delta_{\nu\alpha} \frac{\partial p_\nu}{\partial \varrho_\beta} - \delta_{\nu\beta} \frac{\partial p_\nu}{\partial \varrho_\alpha}\right) (\alpha, \beta, \gamma = 1, 2, \ldots, \nu).$$

Here we choose $\gamma = \alpha \neq \beta$ and obtain $\partial p_\alpha / \partial \varrho_\beta = 0$ for $\alpha \neq \nu$ and $\beta \neq \nu$, whereas, if $\alpha \neq \nu$ and $\beta = \nu$ we

*** Note that according to $(4.15)_1$ the expression on the right hand side of $(4.16)_3$ is independent of the densities ϱ_α and depends on ϑ only.

obtain

$$\frac{1}{\varrho_\alpha{}^2}\frac{\partial p_\alpha}{\partial \varrho_\nu} = -\frac{1}{\varrho_\nu{}^2}\frac{\partial p_\nu}{\partial \varrho_\alpha}$$

and that is incompatible with the above results

$$\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial \varrho_\beta} = \frac{1}{\varrho_\beta}\frac{\partial p_\beta}{\partial \varrho_\alpha}$$

unless both $\partial p_\alpha/\partial \varrho_\nu$ and $\partial p_\nu/\partial \varrho_\alpha$ vanish. Hence we have

$$p_\alpha = p_\alpha(\varrho_\alpha, \vartheta)\,, \tag{4.17}$$

or, in words, the *pressure of constituent* α *depends only on the density of that constituent*, and on ϑ 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

$$\frac{\partial\left[\Phi_j - \Lambda^\varepsilon\left(q_j^{\mathrm{I}} - \sum\limits_{\alpha=1}^{\nu} p_\alpha u_j{}^\alpha\right)\right]}{\partial \varrho_\beta} = \varrho\,\frac{\partial(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})}{\partial \varrho_\beta}\,u_j{}^\beta,$$

whence we obtain as an integrability condition for the square bracket

$$\frac{\partial(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})}{\partial \varrho_\beta} + \frac{\partial(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})}{\partial \varrho_\alpha} + \varrho\,\frac{\partial^2(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})}{\partial \varrho_\alpha\,\partial \varrho_\beta} = 0$$

or

$$\frac{\partial^2}{\partial \varrho_\alpha\,\partial \varrho_\beta}\left[\varrho(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})\right] = 0$$

for $\alpha \neq \beta$. The general solution of these differential equations restricts $\varrho(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})$ to be a sum of functions which depend on *one* density only. Now, by $(4.11)_1$ we have

$$\frac{\partial \varrho(\eta - \Lambda^\varepsilon \varepsilon_{\mathrm{I}})}{\partial \vartheta} = -\frac{\partial \Lambda^\varepsilon}{\partial \vartheta}\,\varrho\,\varepsilon_{\mathrm{I}}$$

so that $\varrho\,\varepsilon_{\mathrm{I}}$ and hence $\varrho\,\eta$ are also of this additive form and we may write

$$\varrho\,\varepsilon_{\mathrm{I}} = \sum_{\alpha=1}^{\nu} \varrho_\alpha\,\varepsilon_\alpha(\varrho_\alpha, \vartheta) \quad \text{and} \quad \varrho\,\eta = \sum_{\alpha=1}^{\nu} \varrho_\alpha\,\eta_\alpha(\varrho_\alpha, \vartheta)\,, \tag{4.18}$$

* See[6]. There I have shown that neither (4.17) nor (4.18) below need to hold, if the constitutive quantities are allowed to depend on the gradients of densities.

where, of course, we now interpret ε_α and η_α as the specific internal energy and the specific entropy of constituent α and we note that these depend only the density of that constituent.

The integrability conditions for $\Lambda_{\mathrm{I}}^{\varrho_\gamma} - \Lambda_{\mathrm{I}}^{\varrho_\nu}$ that are implied by $(4.15)_2$ and $(4.16)_2$ read

$$\frac{\partial}{\partial \vartheta}\left(\Lambda^\varepsilon\left(\frac{1}{\varrho_\gamma}\frac{\partial p_\gamma}{\partial \varrho_\beta} - \frac{1}{\varrho_\nu}\frac{\partial p_\nu}{\partial \varrho_\beta}\right)\right) = \frac{\partial \Lambda^\varepsilon}{\partial \vartheta}\frac{\partial}{\partial \varrho_\beta}\left(\varrho\left(\frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\gamma} - \frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\nu}\right)\right)$$

and, by use of (4.17) and (4.18), this can be written as

$$\frac{\partial}{\partial \varrho_\gamma}\left(\varrho_\gamma{}^2\frac{\partial \varepsilon_\gamma}{\partial \varrho_\gamma} - p_\gamma - \frac{1}{\partial \ln \Lambda^\varepsilon/\partial \vartheta}\frac{\partial p_\gamma}{\partial \vartheta}\right) = 0\,. \tag{4.19}$$

For a single fluid results corresponding to (4.9) through (4.16) may be obtained by setting $\nu = 1$ and one gets

$$\Lambda^{v_i} = 0\,, \qquad \Lambda^\varrho\,\varrho = -\Lambda^\varepsilon p\,; \tag{4.20}$$

there should be an index 1 on Λ^{v_i}, Λ^ϱ, ϱ and p, but that may be dropped when only one constituent is present. For $\nu = 1$ the equation (4.13), by virtue of $(4.20)_2$ reduces to

$$\mathrm{d}\eta = \Lambda^\varepsilon\left[\frac{\partial \varepsilon}{\partial \vartheta}\,\mathrm{d}\vartheta + \left(\frac{\partial \varepsilon}{\partial \varrho} - \frac{p}{\varrho^2}\right)\mathrm{d}\varrho\right] \tag{4.21}$$

and, of course, there is no distinction between ε and ε_{I} in a single body. The entropy flux (4.14) becomes

$$\Phi_i = \Lambda^\varepsilon q_i \tag{4.22}$$

and Λ^ε is a function of ϑ only by $(4.15)_1$. The Eqs. $(4.15)_2$ and $(4.16)_{1,2}$ are identically satisfied while $(4.16)_3$ gives

$$\frac{\partial \ln \Lambda^\varepsilon}{\partial \vartheta} = \frac{\partial p/\partial \vartheta}{\varrho^2\,\partial \varepsilon/\partial \varrho - p}\,. \tag{4.23}$$

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

$$u_i = v_i^{\alpha} = v_i \tag{5.1}$$

on either side. I eliminate the force K_i from $(3.3)_{2,3}$ and obtain

$$[q_i\, e_i] = 0 \tag{5.2}$$

whereas (4.2) in the present case becomes

$$[\Phi_i\, e_i] = 0 \quad \text{if} \quad [\vartheta] = 0\,. \tag{5.3}$$

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

$$\Lambda_{\mathrm{I}}{}^{\varepsilon}(\vartheta) = \Lambda_{\mathrm{II}}{}^{\varepsilon}(\vartheta)\,, \tag{5.4}$$

that is to say: *$\Lambda^{\varepsilon}(\vartheta)$ is a universal function of ϑ.* 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 $\Lambda^{\varepsilon}(\vartheta)$ is the absolute temperature $T(\vartheta)$*,

$$\Lambda^{\varepsilon}(\vartheta) = 1/T(\vartheta)\,, \tag{5.5}$$

because in thermodynamics of single bodies the absolute temperature is defined as *the* integrating denominator of the expression $d\varepsilon - (p/\varrho^2)\, d\varrho$ that is a universal function of the temperature alone.

$\Lambda^{\varepsilon}(\vartheta)$ can be calculated from (4.23) by integration, if only p and $\partial\varepsilon/\partial\varrho$ are known as functions of ϱ and ϑ for any *single* body—as they are for an ideal gas for instance. Thus $\Lambda^{\varepsilon}(\vartheta)$ can now be considered as a known function of ϑ. In fact, it is found that $T(\vartheta)$ is a monotonically increasing function of ϑ 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 ϱ_{α}, T, $T_{|i}$ and V_i^{α}, tacitly replacing ϑ by T in what follows.

For the following argument we shall have to suppose that the functions $\varepsilon(\varrho, T)$ and $\eta(\varrho, T)$ are also known in single fluids. Indeed, $\partial\varepsilon/\partial\varrho$ is known from (4.23), after $p(\varrho, T)$ has been determined experimentally, and all that is needed in addition for the determination of $\varepsilon(\varrho, T)$ can be obtained from measurements of the specific heat $\partial\varepsilon/\partial T$ for a fixed ϱ as a function of T. Thus $\varepsilon(\varrho, T)$ follows by integration to within a constant and $\eta(\varrho, T)$ 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 γ (say). Here too, we represent that wall by a singular surface, however, now that surface is not material. Instead we have

$$u_i = v_i^{\alpha} \quad (\alpha \neq \gamma) \quad \text{and} \quad v_i = u_i + (\varrho_{\gamma}/\varrho)(v_i^{\gamma} - u_i) \tag{5.6}$$

at the surface. Elimination of K_i from $(3.3)_{2,3}$ leads to

$$[q_i\, e_i] - \left[\frac{t_{ij}\, e_i\, e_j}{\varrho} - \varepsilon - \tfrac{1}{2}(v_k - u_k)(v_k - u_k)\right] \cdot \varrho\,(v_l - u_l)\, e_l = 0\,,$$

where $(3.3)_1$ has also been used. With (3.7) and $(3.8)_2$ one obtains after some calculation

$$[q_i^{\mathrm{I}}\, e_i] + \left[\frac{\sum\limits_{\beta=1}^{\nu} p_{\beta}}{\varrho} + \varepsilon_{\mathrm{I}} + \tfrac{1}{2}(v_k^{\gamma} - u_k)(v_k^{\gamma} - u_k)\right] \times \varrho\,(v_l - u_l)\, e_l = 0\,, \tag{5.7}$$

whereas for the entropy flux we have from (4.2):

$$[\Phi_i\, e_i] + [\eta]\,\varrho\,(v_l - u_l)\, e_l = 0, \ \text{if} \ [\vartheta] = 0\,. \tag{5.8}$$

Now Φ_j is equal to

$$(1/T)\, q_j + \sum_{\beta=1}^{\nu} \Lambda_{\mathrm{I}}^{\varrho_{\beta}}\, \varrho_{\beta}\, u_j{}^{\beta}$$

by (4.14), so that (5.8) may be written as

$$[q_i^{\mathrm{I}}\, e_i] + T\left[\eta + \sum_{\beta=1}^{\nu}\left(\delta_{\gamma\beta} - \frac{\varrho_{\beta}}{\varrho}\right)\Lambda_{\mathrm{I}}^{\varrho_{\beta}}\right] \times \varrho\,(v_l - u_l)\, e_l = 0\,, \tag{5.9}$$

since T is continuous because ϑ is and because $T(\vartheta)$ is a universal function.

Elimination of $[q_i^{\mathrm{I}}\, e_i]$ from (5.7) and (5.8) leads to

$$\left[\varepsilon_{\mathrm{I}} - T\eta + \tfrac{1}{2}(v_k^{\gamma} - u_k)(v_k^{\gamma} - u_k) + \sum_{\beta=1}^{\nu} p_{\beta}/\varrho - T\sum_{\beta=1}^{\nu}(\delta_{\gamma\beta} - \varrho_{\beta}/\varrho)\,\Lambda_{\mathrm{I}}^{\varrho_{\beta}}\right] = 0\,, \tag{5.10}$$

or with (4.10) and (5.5)

$$[\varepsilon_{\mathrm{I}} - T\eta + \tfrac{1}{2}(v_k^{\gamma} - u_k)(v_k^{\gamma} - u_k) - T\Lambda_{\mathrm{I}}^{\varrho_{\gamma}}] = 0\,. \tag{5.11}$$

We conclude that the quantity in brackets is continuous; it is called the *chemical potential of consistuent* γ and we denote it by μ_{γ}:

$$\mu_{\gamma} = \varepsilon_{\mathrm{I}} - T\eta + \tfrac{1}{2}(v_k^{\gamma} - u_k)(v_k^{\gamma} - u_k) - T\Lambda_{\mathrm{I}}^{\varrho_{\gamma}}\,. \tag{5.12}$$

We see that μ_{γ} depends on the velocity $v_k^{\gamma} - u_k$ in an explicit manner and I find it useful to introduce the *intrinsic chemical potential*

$$\mu_\gamma{}^{\mathrm{I}} \equiv \mu_\gamma - \tfrac{1}{2}(v_k{}^\gamma - u_k)(v_k{}^\gamma - u_k) \qquad (5.13)$$

which may depend on ϱ_β and ϑ only.
Multiplication of (5.12) by ϱ_γ/ϱ and summation over all γ leads to

$$\sum_{\beta=1}^{\nu} (\varrho_\beta/\varrho)\, \mu_\beta{}^{\mathrm{I}} = \varepsilon_{\mathrm{I}} - T\eta + \sum_{\beta=1}^{\nu} p_\beta/\varrho\,, \qquad (5.14)$$

because of (4.10). Elimination of $\varepsilon_{\mathrm{I}} - T\eta$ from (5.12) and (5.14) gives the equation

$$\Lambda_{\mathrm{I}}^{\varrho_\gamma} = -\frac{1}{T}\left(\sum_{\beta=1}^{\nu}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\mu_\beta{}^{\mathrm{I}} + \sum_{\beta=1}^{\nu} p_\beta/\varrho\right). \quad (5.15)$$

We draw the obvious conclusion that the Lagrange multipliers Λ^{ϱ_β} can be calculated, if the pressure $\sum_{\beta=1}^{\nu} p_\beta$ of the mixture and the chemical potentials $\mu_\gamma{}^{\mathrm{I}}$ of all constituents have been measured as functions of $\varrho_1, \varrho_2, \ldots, \varrho_\nu, T$. 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 γ and which separates the pure constituent γ from a mixture of ν constituents which, of course, include γ. At that surface we have by (5.11) and (5.12)

$$\{\mu_\gamma{}^{\mathrm{I}}(\varrho_1, \ldots, \varrho_\nu, T) + \tfrac{1}{2}(v_k{}^\gamma - u_k)(v_k{}^\gamma - u_k)\}_{\text{mixture}}$$
$$= \{\varepsilon(\varrho, T) - T\eta(\varrho, T) + \tfrac{1}{2}(v_k{}^\gamma - u_k)(v_k{}^\gamma - u_k) + p(\varrho, T)/\varrho\}_{\text{pure constituent } \gamma}\,.$$

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

$$\varrho_1, \quad \ldots, \varrho_\nu, T, v_i{}^\gamma - u_i$$

in the mixture, the density ϱ and the velocity $v_k{}^\gamma - u_k$ of the pure constituent are measured, *one* value of $\mu_\gamma{}^{\mathrm{I}}$ results. When we repeat this for different values of $\varrho_1, \ldots, \varrho_\nu, T, v_i{}^\gamma - u_i$, eventually we obtain the function $\mu_\gamma{}^{\mathrm{I}}(\varrho_1, \ldots, \varrho_\nu, T)$ to within a linear function of T, since $\varepsilon(\varrho, T)$ and $\eta(\varrho, T)$ in the pure constituent are only known to within a constant. From (5.15) we may therefore conclude that the Lagrange multipliers Λ^{ϱ_γ} can be calculated to within functions of the form

$$\sum_{\beta=1}^{\nu} (\delta_{\gamma\beta} - \varrho_\beta/\varrho)(\alpha_\beta - T\eta_\beta)\,, \qquad (5.16)$$

where α_β and β_β are the unknown additive constants in the specific internal energy and the specific entropy of the pure constituent β.

6. Results in Terms of Absolute Temperature and Chemical Potentials

As I have demonstrated, it is possible to relate the Lagrange multipliers Λ^ε and Λ^{ϱ_β} to the absolute temperature T and the chemical potentials μ_γ which may be measured—to within functions $\alpha_\gamma - T\beta_\gamma$—by measurements of the pressure and the specific heat of the pure constituents and of the pressure $\sum_{\beta=1}^{\nu} p_\beta$ of the mixture. We have by (5.5) and (5.15):

$$\Lambda^\varepsilon = 1/T\,, \qquad (6.1)$$
$$\Lambda_{\mathrm{I}}^{\varrho_\gamma} = -(1/T)\left(\sum_{\gamma=1}^{\nu} (\delta_{\gamma\beta} - \varrho_\beta/\varrho)\,\mu_\beta{}^{\mathrm{I}} + \sum_{\beta=1}^{\nu} p_\beta/\varrho\right)$$

and I remark that by (4.9) the Lagrange multipliers $\Lambda^{v_i{}^\beta}$ too are now determined:

$$\Lambda^{v_i{}^\beta} = -(1/T)\, u_i{}^\beta. \qquad (6.2)$$

I shall now rewrite the results of Section 4, which were derived from the entropy inequality, in terms of T and $\mu_\beta{}^{\mathrm{I}}$ rather than Λ^ε and $\Lambda_{\mathrm{I}}^{\varrho_\beta}$. First of all. I recall from (4.17) that

$$p_\alpha = p_\alpha(\varrho_\alpha, T) \qquad (6.3)$$

holds, while by (4.18) we have

$$\varrho\,\varepsilon_{\mathrm{I}} = \sum_{\alpha=1}^{\nu} \varrho_\alpha\,\varepsilon_\alpha(\varrho_\alpha, T) \quad \text{and} \quad \varrho\,\eta = \sum_{\alpha=1}^{\nu} \varrho_\alpha\,\eta_\alpha(\varrho_\alpha, T). \qquad (6.4)$$

Equation (4.10) and the definition (5.12) and (5.13) of $\mu_\gamma{}^{\mathrm{I}}$ imply

$$\varepsilon_{\mathrm{I}} - T\eta = \sum_{\gamma=1}^{\nu} \frac{\varrho_\gamma}{\varrho}\,\mu_\gamma{}^{\mathrm{I}} - \frac{\sum_{\gamma=1}^{\nu} p_\gamma}{\varrho} \qquad (6.5)$$

which indicates that $\varepsilon_{\mathrm{I}} - T\eta$ of the mixture is known to within a function of the form

$$\sum_{\gamma=1}^{\nu} (\varrho_\gamma/\varrho)(\alpha_\gamma - T\beta_\gamma)\,,$$

since the chemical potentials are known to within functions $\alpha_\gamma - T\beta_\gamma$.

The equation (4.13) now reads

$$\mathrm{d}\eta = \frac{1}{T}\frac{\partial \varepsilon_{\mathrm{I}}}{\partial T}\,\mathrm{d}T + \frac{1}{T}\sum_{\gamma=1}^{\nu} \left(\frac{\partial \varepsilon_{\mathrm{I}}}{\partial \varrho_\gamma} - \frac{\sum_{\beta=1}^{\nu} p_\beta}{\varrho^2} - \sum_{\beta=1}^{\nu}\left(\frac{1}{\varrho}\,\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho^2}\right)\mu_\beta{}^{\mathrm{I}}\right)\mathrm{d}\varrho_\gamma \tag{6.6}$$

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

$$\mathrm{d}[\varrho(\varepsilon_{\mathrm{I}} - T\eta)] = -\varrho\,\eta\,\mathrm{d}T + \sum_{\gamma=1}^{\nu}\mu_\gamma{}^{\mathrm{I}}\,\mathrm{d}\varrho_\gamma \tag{6.7}$$

and since we already know [see (6.4)] that $\varrho\,\varepsilon_{\mathrm{I}}$ and $\varrho\,\eta$ are sums of functions of only one density we conclude that

$$\partial\mu_\gamma{}^{\mathrm{I}}/\partial\varrho_\alpha = 0, \quad \text{unless} \quad \gamma = \alpha; \tag{6.8}$$

this means that the chemical potential of constituent γ 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:

$$\Phi_j = (1/T)\,q_j{}^{\mathrm{I}} - (1/T)\sum_{\gamma=1}^{\nu}\mu_\gamma{}^{\mathrm{I}}\,\varrho_\gamma\,u_j{}^\gamma \tag{6.9}$$

and we conclude that this relation is specific only to within a function of the form

$$\sum_{\gamma=1}^{\nu}(\alpha_\gamma/T - \beta_\gamma)\,\varrho_\gamma\,u_j{}^\gamma\,.$$

By use of (6.1), (6.3) and (6.8) we can reduce $(4.15)_2$ to

$$\partial p_\gamma/\partial\varrho_\gamma = \varrho_\gamma(\partial\mu_\gamma{}^{\mathrm{I}}/\partial\varrho_\gamma) \quad (\gamma = 1, 2, \ldots, \nu) \tag{6.10}$$

so that we are able to determine the partial pressures $p_\gamma(\varrho_\gamma, T)$ to within a function of T. It is interesting to see that (6.10) can be rewritten in the form

$$\frac{\partial p_\gamma}{\partial\varrho_\gamma} = \frac{\partial}{\partial\varrho_\gamma}\left(\varrho_\gamma{}^2\,\frac{\partial(\varepsilon_\gamma - T\,\eta_\gamma)}{\partial\varrho_\gamma}\right)$$

with the help of (6.7) and (6.4). Integration gives

$$p_\gamma = \varrho_\gamma{}^2\,\frac{\partial\varepsilon_\gamma - T\,\eta_\gamma}{\partial\varrho_\gamma} + f_\gamma(T)\,, \tag{6.11}$$

where the functions $f_\gamma(T)$ are arbitrary except that they must satisfy the requirement

$$\sum_{\gamma=1}^{\nu} f_\gamma(T) = 0$$

which follows from (6.5) by (6.7) and (6.4) again. Of course, p_γ ought to vanish when ϱ_γ tends to zero and then obviously $f_\gamma(T) = 0$ holds, if only $(\partial\varepsilon_\gamma - T\,\eta_\gamma)/\partial\varrho_\gamma$ is finite in that limit.

The integrability conditions (4.19) on integration lead to

$$\varrho_\gamma{}^2\,\frac{\partial\varepsilon_\gamma}{\partial\varrho_\gamma} - p_\gamma + T\,\frac{\partial p_\gamma}{\partial T} = g_\gamma(T)$$

where $g_\gamma(T)$ comes in as integration constant. Under the reasonable assumptions that $p_\gamma \equiv 0$ and $\partial\varepsilon_\gamma/\partial\varrho_\gamma$ finite for $\varrho_\gamma = 0$, we thus get

$$\frac{1}{T} = \frac{\partial p_\gamma/\partial T}{\varrho_\gamma{}^2\,(\partial\varepsilon_\gamma/\partial\varrho_\gamma) - p_\gamma} \tag{6.12}$$

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 $(4.16)_1$ are identically satisfied here* whereas the integrability conditions $(4.16)_{2,3}$ can be combined to read

$$\varrho\,\frac{\partial\varepsilon_{\mathrm{I}}}{\partial\varrho_\gamma} = \sum_{\beta=1}^{\nu}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\mu_\beta{}^{\mathrm{I}} + \frac{\sum_{\beta=1}^{\nu} p_\beta}{\varrho} - T\left(\sum_{\beta=1}^{\nu}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\frac{\partial\mu_\beta{}^{\mathrm{I}}}{\partial T} + \frac{1}{\varrho}\,\frac{\partial\sum_{\beta=1}^{\nu} p_\beta}{\partial T}\right) \tag{6.13}$$

and, if the specific heat $\partial\varepsilon_{\mathrm{I}}/\partial T$ of the mixture has been measured for one set of variables $\varrho_1, \ldots, \varrho_\nu$ as a function of T, integration of (6.12) will determine ε_{I} to within a function of the form

$$\sum_{\beta=1}^{\nu}(\varrho_\beta/\varrho)\,\alpha_\beta\,.$$

Equation (6.5) may then be used to determine η to within a function of the form

$$\sum_{\gamma=1}^{\nu}(\varrho_\gamma/\varrho)\,\beta_\gamma\,.$$

We thus conclude that the entropy principle in simple mixtures imposes restrictions on the constitutive relations which are summarized in the

* Note that $(4.16)_1$ was used to derive (6.3) and (6.4).

Eqs. (6.3) through (6.13). Some of these restrictions are in terms of $\mu_\gamma{}^{\mathrm{I}}$ and these are not quite specific as a consequence of the fact that the chemical potentials $\mu_\gamma{}^{\mathrm{I}}$ themselves are only known to within functions of the form $\alpha_\gamma - T\,\beta_\gamma$.

The indeterminancy of $\mu_\gamma{}^{\mathrm{I}}$, ε_{I}, η and Φ_j goes back to the fact that in a single body ε and η 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

$$\sum_{\gamma=1}^{\nu} (\varrho_\gamma/\varrho)\,\alpha_\gamma$$

in ε_{I} 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_i or $q_i{}^{\mathrm{I}}$ too can only be known to within a function of the form

$$\sum_{\alpha=1}^{\nu} \varrho_\alpha\, u_i{}^\alpha\, \alpha_\alpha\,,$$

because it contains a term

$$\sum_{\alpha=1}^{\nu} \varrho_\alpha\, \varepsilon_\alpha\, u_i{}^\alpha.$$

Thus in $\varrho\,\dot{\varepsilon} + \partial q_i/\partial x_i$ the indeterminate parts of ε and q_i will combine to give**

$$\varrho\left(\sum_{\gamma=1}^{\nu} \frac{\varrho_\gamma}{\varrho}\,\alpha_\gamma\right)^{\bullet} + \frac{\partial}{\partial x_i}\left(\sum_{\gamma=1}^{\nu} \varrho_\gamma\, u_i{}^\gamma\, \alpha_\gamma\right) = \sum_{\gamma=1}^{\nu} \alpha_\gamma\, c_\gamma\,,$$

where $(2.1)_1$ and $(2.4)_1$ 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 α_γ of its constituents.

7. Evaluation of the Residual Entropy Inequality

With the knowledge of Λ^ε, Λ^{ϱ_α} and $\Lambda^{v_i{}^\alpha}$ by (6.1), (6.2) and with Φ_j given by (6.9) and c_α by (2.7) we may now write (4.8) in the form

$$\begin{aligned}\left(-\frac{1}{T}\,q_j{}^{\mathrm{I}} - \sum_{\gamma=1}^{\nu} T\,\frac{\partial}{\partial T}\left(\frac{\mu_\gamma{}^{\mathrm{I}}}{T}\right)\varrho_\gamma\, u_j{}^\gamma\right)\frac{\partial T}{\partial x_j}&\\ -\sum_{a=1}^{n}\left[\sum_{\beta=1}^{\nu} \gamma_\beta{}^a\, M_\beta\, m\,(\mu_\beta{}^{\mathrm{I}} + \tfrac{1}{2}\,u_\beta{}^2)\right]\Lambda^a&\\ -\sum_{\gamma=1}^{\nu}(m_i{}^\gamma - c_\gamma\, v_i{}^\gamma)\,u_i{}^\gamma \geqq 0\,.&\end{aligned}\tag{7.1}$$

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 σ has its minimum, namely zero, in equilibrium and hence follows by necessity that***

$$\left.\frac{\partial\sigma}{\partial T_{,j}}\right|_{\mathrm{E}} = 0\,,\qquad \left.\frac{\partial\sigma}{\partial \boldsymbol{V}_j{}^\gamma}\right|_{\mathrm{E}} = 0\,,\qquad \left.\frac{\partial\sigma}{\partial \Lambda^a}\right|_{\mathrm{E}} = 0 \tag{7.2}$$

$$\left\|\begin{matrix}\left.\dfrac{\partial^2\sigma}{\partial T_{|i}\,\partial T_{|j}}\right|_{\mathrm{E}} & \left.\dfrac{\partial^2\sigma}{\partial T_{|i}\,\partial \boldsymbol{V}_j{}^\beta}\right|_{\mathrm{E}}\\ \left.\dfrac{\partial^2\sigma}{\partial \boldsymbol{V}_i{}^\alpha\,\partial T_{|j}}\right|_{\mathrm{E}} & \left.\dfrac{\partial^2\sigma}{\partial \boldsymbol{V}_i{}^\alpha\,\partial \boldsymbol{V}_j{}^\beta}\right|_{\mathrm{E}}\end{matrix}\right\| \text{positive semi-definite}$$

$$\left\|\frac{\partial^2\sigma}{\partial\Lambda^a\,\partial\Lambda^b}\right\|_{\mathrm{E}} \text{positive semi-definite} \tag{7.3}$$

The conditions $(7.2)_{1,2}$ are trivially satisfied by the constitutive relations (3.8) and $(7.2)_3$ yields the *law of mass action*

$$\sum_{\beta=1}^{\nu} \gamma_\beta{}^a\, M_\beta\, \mu_\beta{}^{\mathrm{I}}|_{\mathrm{E}} = 0 \qquad (a = 1, 2, \ldots, n) \tag{7.4}$$

which furnishes n relations between the ν densities ϱ_α.

From $(7.3)_1$ we conclude that the matrix

$$\left\|\begin{matrix}\varkappa|_{\mathrm{E}} & -\left.\left(\dfrac{1}{T}\,q_{\boldsymbol{V}^\alpha} + \displaystyle\sum_{\gamma=1}^{\nu-1}\left(\delta_{\gamma\alpha} - \frac{\varrho_\alpha}{\varrho}\right)\left[\varrho_\gamma\, T\,\frac{\partial}{\partial T}\left(\frac{\mu_\gamma{}^{\mathrm{I}} - \mu_\nu{}^{\mathrm{I}}}{T}\right) + M_\vartheta{}^\gamma\right]\right)\right|_{\mathrm{E}}\\ -\left.\left(\dfrac{1}{T}\,q_{\boldsymbol{V}^\beta} + \displaystyle\sum_{\gamma=1}^{\nu-1}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\left[\varrho_\gamma\, T\,\frac{\partial}{\partial T}\left(\frac{\mu_\gamma{}^{\mathrm{I}} - \mu_\nu{}^{\mathrm{I}}}{T}\right) + M_\vartheta{}^\gamma\right]\right)\right|_{\mathrm{E}} & -\left.\displaystyle\sum_{\gamma=1}^{\nu-1}\left(M^\gamma_{\boldsymbol{V}^\beta}\left(\delta_{\gamma\alpha} - \frac{\varrho_\alpha}{\varrho}\right) + M_{\boldsymbol{V}^\alpha}\left(\delta_{\gamma\beta} - \frac{\varrho_\beta}{\varrho}\right)\right)\right|_{\mathrm{E}}\end{matrix}\right\| \tag{7.5}$$

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

*** Note that σ may be regarded as a function of $\Lambda^a\,(a = 1, 2, \ldots, n)$ and of $\nu - n$ densities ϱ_α. 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 Λ^a.

8. Fick's Law, Thermal Diffusion and Diffusion-Thermo-Effect

Various considerations suggest that Fick's law diffusion can be derived from the balance of momenta of the constituents. I write these in the following form

$$\varrho_\alpha \dot{v}_i^\alpha + \varrho_\alpha u_j^\alpha \frac{\partial v_i^\alpha}{\partial x_j} - \frac{\partial t_{ij}^\alpha}{\partial x_j} = m_i^\alpha - c_\alpha v_i^\alpha \qquad (\alpha = 1, 2, \ldots, \nu). \tag{8.1}$$

Division by ϱ_α and substraction of the last equation from all others gives

$$\dot{V}_i^\alpha + \left(u_j^\alpha \frac{\partial v_i^\alpha}{\partial x_j} - u_j^\nu \frac{\partial v_i^\nu}{\partial x_j}\right) - \frac{1}{\varrho_\alpha}\frac{\partial t_{ij}^\alpha}{\partial x_j} + \frac{1}{\varrho_\nu}\frac{\partial t_{ij}^\nu}{\partial x_j} = \sum_{\gamma=1}^{\nu=1}\left(\frac{1}{\varrho_\gamma}\delta_{\alpha\gamma} + \frac{1}{\varrho_\nu}\right)(m_i^\gamma - c_\gamma v_i^\gamma) + \frac{1}{\varrho_\nu}\sum_{\alpha=1}^{\nu-1} c_\alpha V_i^\alpha .$$

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}^γ and solve for $m_i^\beta - c_\beta v_i^\beta$:

$$m_i^\beta - c_\beta v_i^\beta = \varrho_\beta \sum_{\alpha=1}^{\nu-1}\left(\delta_{\beta\alpha} - \frac{\varrho_\alpha}{\varrho}\right)\left(\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial x_i} - \frac{1}{\varrho_\nu}\frac{\partial p_\nu}{\partial x_i}\right), \quad \beta = 1, 2, \ldots, \nu - 1. \tag{8.2}$$

With (6.10) one obtains

$$\begin{aligned} m_i^\beta - c_\beta v_i^\beta = {} & \varrho_\beta T \sum_{\alpha=1}^{\nu-1}\left(\delta_{\beta\alpha} - \frac{\varrho_\alpha}{\varrho}\right)\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{T}\right) \\ & + \varrho_\beta \sum_{\alpha=1}^{\nu-1}\left(\delta_{\beta\alpha} - \frac{\varrho_\alpha}{\varrho}\right)\left(\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\nu}\frac{\partial p_\nu}{\partial T} - T\frac{\partial}{\partial T}\left(\frac{\mu_\alpha^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{T}\right)\right)\frac{\partial T}{\partial x_i} \quad (\beta = 1, 2, \ldots, \nu - 1) \end{aligned}$$

and finally for the diffusion fluxes $\varrho_\delta u_i^\delta$ with $(3.8)_4$

$$\begin{aligned} \varrho_\gamma u_i^\delta = {} & \sum_{\alpha=1}^{\nu-1}\left\{-\sum_{\beta,\gamma=1}^{\nu-1} F_{\delta\gamma}(\mathfrak{M}^{-1})_{\gamma\beta} F_{\beta\alpha} T\right\}\left[-\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{T}\right)\right] \\ & + \left\{\sum_{\beta,\gamma=1}^{\nu-1} F_{\delta\gamma}(\mathfrak{M}^{-1})_{\gamma\beta} T^2 M_\vartheta^\beta - \sum_{\alpha,\beta,\gamma=1}^{\nu-1} F_{\delta\gamma}(\mathfrak{M}^{-1})_{\gamma\beta} F_{\beta\alpha}\left(\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\nu}\frac{\partial p_\nu}{\partial T} - T\frac{\partial}{\partial T}\left(\frac{\mu_\alpha^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{T}\right)T^2\right\}\left[\frac{\partial(1/T)}{\partial x_i}\right] \end{aligned} \tag{8.3}$$

where the matrices $F_{\delta\gamma}$ and $\mathfrak{M}_{\delta\gamma}$ have been introduced according to the definitions

$$F_{\delta\gamma} = \varrho_\delta \delta_{\delta\gamma} - \varrho_\delta \varrho_\gamma/\varrho \quad \text{and} \quad \mathfrak{M}_{\delta\gamma} = M_{V^\gamma}^\beta . \tag{8.4}$$

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 $\varrho_\delta u_i^\delta$ is driven by the *thermodynamic forces*

$$-\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{L}\right) \quad \text{and} \quad \frac{\partial(1/T)}{\partial x_i}; \tag{8.5}$$

that the diffusion flux depends on the temperature gradient is known as the thermo-diffusion-effect.

In linear irreversible thermodynamics it is also customary to express the flux of internal energy in terms of the thermodynamic forces (8.5). From $(3.8)_5$ we have

$$q_i^{\mathrm{I}} = \sum_{\delta=1}^{\nu-1} Q_\delta \varrho_\delta u_i^\delta + \varkappa T^2 \frac{\partial(1/T)}{\partial x_i},$$

where

$$Q_\delta \equiv \sum_{\gamma=1}^{\nu-1}\left(\frac{1}{\varrho_\delta}\delta_{\delta\gamma} + \frac{1}{\varrho_\nu}\right) q_{V^\gamma} . \tag{8.6}$$

Elimination of $\varrho_\delta u_i^\delta$ between (8.3) and (8.6) and relabeling of indices leads to

$$\begin{aligned} q_i^{\mathrm{I}} = {} & \sum_{\delta=1}^{\nu-1}\left\{-\sum_{\alpha,\beta,\gamma=1}^{\nu-1} F_{\delta\gamma}(\mathfrak{M}^{-1})_{\beta\gamma} F_{\beta\alpha} Q_\alpha T\right\} - \left[\frac{\partial}{\partial x_i}\left(\frac{\mu_\delta^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{T}\right)\right] \\ & + \left\{\varkappa T^2 + \sum_{\beta,\gamma,\delta=1}^{\nu-1} Q_\delta F_{\delta\gamma}(\mathfrak{M}^{-1})_{\gamma\beta} T^2 M_\vartheta^\beta - \sum_{\alpha,\beta,\gamma,\delta=1}^{\nu-1} Q_\delta F_{\delta\gamma}(\mathfrak{M}^{-1})_{\gamma\beta} F_{\beta\alpha} \right. \\ & \left. \cdot\left(\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\nu}\frac{\partial p_\nu}{\partial T} - T\frac{\partial}{\partial T}\left(\frac{\mu_\alpha^{\mathrm{I}} - \mu_\nu^{\mathrm{I}}}{T}\right)T^2\right\}\left[\frac{\partial(1/T)}{\partial x_i}\right]. \end{aligned} \tag{8.7}$$

* In[6] I have demonstrated that one can obtain a hyperbolic diffusion equation, if the acceleration is kept.

The dependence of q_i^{I} on the gradients of the chemical potentials is called the diffusion-thermo-effect.

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

$$\varrho_\delta u_i^\delta = \sum_{\alpha=1}^{\nu-1} L_{\delta\alpha}\left[-\frac{\partial}{\partial x_i}\left(\frac{\mu_\alpha^{\mathrm{I}}-\mu_\nu^{\mathrm{I}}}{T}\right)\right] + L_{\delta\nu}\left[\frac{\partial(1/T)}{\partial x_i}\right],$$

$$q_i^{\mathrm{I}} = \sum_{\delta=1}^{\nu-1} L_{\nu\delta}\left[-\frac{\partial}{\partial x_i}\left(\frac{\mu_\delta^{\mathrm{I}}-\mu_\nu^{\mathrm{I}}}{T}\right)\right] + L_{\nu\nu}\left[\frac{\partial(1/T)}{\partial x_i}\right], \tag{8.8}$$

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)

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

and Truesdell has shown in [3] that $(8.9)_1$ can indeed be proved for mixtures that exhibit binary drags only, a restriction which imposes two conditions on the coefficients $M^{\beta}_{V\gamma}$:

1) $M^{\beta}_{V\gamma}$ does not depend on ϱ_δ, if $\delta \neq \beta$ or γ,

2) $M^{\beta}_{V\gamma} \to 0$, if $\varrho_\beta \to 0$. (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 $m_i^\beta - c_\beta v_i^\beta$ is independent of the temperature gradient, i.e.

$$M_\vartheta{}^\beta = 0\,, \tag{8.11}$$

ii) The flux of internal energy q_i^{I} depends on the relative velocities only through the explicit terms

$$\sum_{\delta=1}^{\nu-1}\left(\varepsilon_\delta - \varepsilon_\nu + \frac{p_\delta}{\varrho_\delta} - \frac{p_\nu}{\varrho_\nu}\right)\varrho_\delta u_i^\delta$$

that go into its definition [see $(2.3)_5$]. By (8.6) this means

$$Q_\delta = \varepsilon_\delta - \varepsilon_\nu + \frac{p_\delta}{\varrho_\delta} - \frac{p_\nu}{\varrho_\nu}\,. \tag{8.12}$$

The symmetry relations $(8.9)_2$ then read

$$\sum_{\alpha,\beta,\gamma=1}^{\nu-1} F_{\delta\gamma}(\mathfrak{M}^{-1})_{\beta\gamma} F_{\beta\alpha}\left(\varepsilon_\alpha - \varepsilon_\nu + \frac{p_\alpha}{\varrho_\alpha} - \frac{p_\nu}{\varrho_\nu}\right) T = \sum_{\alpha,\beta,\gamma=1}^{\nu-1} F_{\delta\gamma}(\mathfrak{M}^{-1})_{\gamma\beta} F_{\beta\alpha}\left(\frac{1}{\varrho_\alpha}\frac{\partial p_\alpha}{\partial T} - \frac{1}{\varrho_\nu}\frac{\partial p_\nu}{\partial T} - T\frac{\partial}{\partial T}\right)\frac{\mu_{\alpha;} - \mu_{\nu;}}{T}\Bigg)\Bigg) T^2 \,\cdot \tag{8.13}$$

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

$$\frac{1}{\varrho_\alpha} T\frac{\partial p_\alpha}{\partial T} - T^2\frac{\partial}{\partial T}\left(\frac{\mu_\alpha^{\mathrm{I}}}{T}\right) \quad \text{and} \quad \left(\varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha}\right) \tag{8.14}$$

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

$$\mathrm{d}\left[\frac{\varrho(\varepsilon_{\mathrm{I}} - T\eta)}{T}\right] = -\frac{\varrho\,\varepsilon_{\mathrm{I}}}{T^2}\mathrm{d}T + \sum_{\alpha=1}^{\nu}\frac{\mu_\alpha^{\mathrm{I}}}{T}\mathrm{d}\varrho_\alpha$$

whence follows as an integrability condition

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

Hence follows for the expression $(8.14)_1$ with (6.4) and then with (6.12)

$$\frac{1}{\varrho_\alpha} T\frac{\partial p_\alpha}{\partial T} - T^2\frac{\partial}{\partial T}\left(\frac{\mu_\alpha^{\mathrm{I}}}{T}\right) = \frac{1}{\varrho_\alpha} T\frac{\partial p_\alpha}{\partial T} + \varepsilon_\alpha + \varrho_\alpha\frac{\partial\varepsilon_\alpha}{\partial\varrho_\alpha} = \varepsilon_\alpha + \frac{p_\alpha}{\varrho_\alpha}\,.$$

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 $L_{\delta\nu}$ 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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