G. M. KREMER
INGO MÜLLER

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Thermal Conductivity and Dynamic Pressure in Extended Thermodynamics of Chemically Reacting Mixture of Gases

by

G. M. KREMER

Departamento de Física, Universidade Federal do Paraná Caixa
Postal 19081 FAX: +41 267-4236 (Brazil) 81531-990 Curitiba, Brazil

and

Ingo MÜLLER

FB 6 - Thermodynamik Technische Universität Berlin,
Sekr. HF2, FAX +30 314-21021, 10623 Berlin, Germany

ABSTRACT. – While in a single non-relativistic gas the dynamic pressure vanishes, it is of order $\mathcal{O}(\frac{1}{c^2})$ in a relativistic gas. This was shown in a previous paper [1]. In the present paper we show that the dynamic pressure in a reacting gas is of $\mathcal{O}(1)$, i. e. even a non-relativistic mixture of gases has a non-vanishing bulk viscosity. The value of that viscosity is determined by the mass-defect M, or the heat of reaction Mc^2, and the thermal conductivity is also affected by the heat of reaction. In an example of dissociation of iodine the bulk viscosity can be as big as 50% of the shear viscosity and the thermal conductivity has twice the normal value. The results of the paper may be of interest to the cosmologist who is interested in the early universe. © Elsevier, Paris

Key words: Thermodynamics, relativity, mixtures, thermal conductivity, bulk viscosity.

RÉSUMÉ. – Tandis que dans un gaz non relativiste la pression dynamique est nulle, elle est de l'ordre de $\frac{1}{c^2}$ dans un gaz relativiste, comme il a été démontré dans un article précédent [1]. Ici nous montrons que la pression dynamique dans un gaz en réaction est de l'ordre de 1, c'est-à-dire, que

même un mélange non relativiste de gaz possède une viscosité de volume non-nulle. La valeur de cette viscosité est déterminée par le défaut de masse M, ou par la chaleur de réaction Mc^2 et la conductivité thermique est aussi affectée par la chaleur de réaction. Dans un exemple de dissociation de l'iode la viscosité de volume peut atteindre jusqu'a 50% de la viscosité de cisaillement et la conductivité thermique est le double de la valeur normale. Les résultats de ce papier peuvent intéresser les cosmologistes étudiant l'univers primordial. © Elsevier, Paris

1. PREVIEW AND DISCUSSION

In a mixture of reacting gases the transport coefficients depend on the heat of reaction Mc^2. It is true that the shear viscosity is not affected, but the thermal conductivity of a dissociating gas can be several times the normal value. This was already known to Nernst [2], who formulated a rough molecular argument to understand the effect, see also [3]. The bulk viscosity is affected most, because - in contrast to a non-reacting (non-relativistic) gas - it is non-zero in a reacting gas.

In this paper we calculate the shear viscosity μ, the bulk viscosity η and the thermal conductivity κ in a binary reacting gas mixture. For simplicity we consider a non-diffusive gas. The results for a non-relativistic gas are as follows

$$\mu = -\frac{1}{B_3}(n_1^E + n_2^E)kT, \tag{1.1}$$

$$\eta = \frac{-\frac{2}{3B_1^\pi}\left(\frac{Mc^2}{kT}\right)^2(n_1^E + n_2^E)kT}{\left(\frac{Mc^2}{kT}\right)^2 + 3(\gamma_1 + \gamma_2)\left(\frac{Mc^2}{kT}\right) - \frac{3}{4}\gamma_1\gamma_2\left(2\frac{m_1^2(n_1^E)^2 + m_2^2(n_2^E)^2}{m_1 m_2 n_1^E n_2^E} + 5\frac{m_1^2 + m_2^2}{m_1 m_2} - 6\right)}, \tag{1.2}$$

$$\kappa = \frac{1}{\hat{B}_4}\left\{\frac{5}{8}\frac{n_1^E n_2^E}{\frac{n_1^E}{\gamma_1} - \frac{n_2^E}{\gamma_2}}\frac{k^2 T}{m_1 m_2 \gamma_1 \gamma_2}\left[\left(2\frac{n_1^{E2} + n_2^{E2}}{n_1^E n_2^E} + 7\frac{m_1^2 + m_2^2}{m_1 m_2} - 10\right)\times\right.\right.$$

$$\left.\left.\times(m_1\gamma_1 - m_2\gamma_2) + 4(m_2 - m_1)\left(\frac{Mc^2}{kT}\right)\right]\right\}. \tag{1.3}$$

$1/B_3$, $1/B_1^\pi$ and $1/\hat{B}_4$ are the relaxation times of stress deviator, dynamic pressure and heat flux respectively; they are of the order of magnitude of

Table 1. – Effect of heat of reaction on bulk viscosity and thermal conductivity.

$T(K)$	K_p (atm)	$n_I^E(\mathrm{m}^{-3})$	$n_{I_2}^E(\mathrm{m}^{-3})$	α^E	V	R
800	3.16×10^{-5}	5.14×10^{22}	9.13×10^{24}	0.003	0.204	0.062
1000	3.16×10^{-3}	4.01×10^{23}	6.94×10^{24}	0.028	0.438	0.424
1200	7.08×10^{-2}	1.43×10^{24}	4.69×10^{24}	0.132	0.500	1.015
1400	6.17×10^{-1}	2.81×10^{24}	2.44×10^{24}	0.366	0.498	1.108
1500	1.51	3.36×10^{24}	1.53×10^{24}	0.523	0.490	0.932
1600	3.31	3.69×10^{24}	8.97×10^{23}	0.673	0.474	0.690
1800	11.2	3.77×10^{24}	3.11×10^{23}	0.858	0.420	0.311
2000	33.1	3.57×10^{24}	1.05×10^{23}	0.945	0.318	0.118
2200	75.9	3.29×10^{24}	4.28×10^{22}	0.975	0.204	0.050

the time of free flight of the molecules. m_{1_2} are the molecular masses of the constituents and γ_{1_2} are their stoichiometric coefficients. The particle densities $n_{1_2}^E$ are equilibrium values as determined by the law of mass-action.

By inspection of (1.2) we conclude that the bulk viscosity is determined by the heat of reaction Mc^2. In the limit of a single gas, i. e. for $n_1^E \to 0$ or $n_2^E \to 0$, the bulk viscosity vanishes as it ought to in a non-relativistic gas. In order to give an impression of the size of the bulk viscosity η in terms of the shear viscosity μ we have calculated the quantity $V = \eta B_1^\pi / \mu B_3$ as a function of temperature. Note that we assume that B_1^π and B_3 are comparable in size; after all, both are related to the collision frequency of molecules. V is represented in Table 1 which gives values - at $p = 1$ atm - for the dissociation of iodine

$$I_2 \to 2I. \tag{1.4}$$

K_p is the chemical constant taken from [4] and n_I^E, $n_{I_2}^E$ are the equilibrium densities calculated from the law of mass-action. α^E in the table is the extent of reaction

$$\alpha^E = \sqrt{\frac{K_p}{4p + K_p}}. \tag{1.5}$$

Inspection shows that, while V is small when one or the other constituent dominates at low and high temperature, it comes up to the value of 0.50 at

intermediate temperatures. Therefore we expect the bulk viscosity to reach up to 50% of the value of the shear viscosity.

Next we discuss the thermal conductivity. The equation (1.3) contains two terms, one with Mc^2 and one without. Thus it represents the dependence of the thermal conductivity κ upon the heat of reaction. The ratio R of these terms - the second one divided by the first - is represented in the last column of Table 1 as a function of T for the dissociating mixture of iodine.

Inspection of the table shows that in the temperature range, where the dissociation occurs, the thermal conductivity is more than doubled by the heat of reaction. In the nearly pure constituents at low and high temperatures the heat of reaction has no appreciable effect on the thermal conductivity.

The theory applies to chemical reactions and to nuclear reactions. It may also be useful to the cosmologist who is interested in the early universe .

In the following chapters the results (1.1) through (1.3) and some further minor results will be derived. The method used is relativistic extended thermodynamics, a powerful theory described in the monograph [5]. The field equations of relativistic extended thermodynamics are derived in full generality for non-degenerate gases but the specific results on the transport coefficients, viz. (1.1) through (1.3), are given only for the non-relativistic limit.

Previously it has been argued that extended thermodynamics can only do what the kinetic theory of gases can do better. With the present extension to chemically reacting mixtures this observation is no longer true; or at least we are unaware of any kinetic theory that could provide results as specific as the results (1.2), and (1.3) of extended thermodynamics.

2. FIELDS OF RELATIVISTIC EXTENDED THERMODYNAMICS OF CHEMICALLY REACTING NON-DIFFUSIVE MIXTURES

2.1. A Conventional Choice

We may say that it is the objective of extended thermodynamics of reacting, non-diffusive binary mixtures to determine the 15 fields

$$
\begin{cases}
\text{number densities } n_\alpha, & (\alpha = 1, 2), \\
\text{velocity } U^A, \\
\text{stress deviator } t^{\langle AB \rangle}, \\
\text{pressure } P, \\
\text{energy density } e, \\
\text{heat flux } q^A.
\end{cases} \tag{2.1}
$$

These fields determine the particle flux vectors A_α^A and the energy-momentum tensor A^{AB}. We have

$$A_\alpha^A = m_\alpha n_\alpha U^A,$$

$$A^{AB} = t^{\langle AB \rangle} + Ph^{AB} + \frac{1}{c^2}(U^A q^B + U^B q^A) + \frac{1}{c^2} eU^A U^B. \qquad (2.2)$$

$h^{AB} = \frac{1}{c^2} U^A U^B - g^{AB}$ is a projector.

2.2. Absolute Temperature and Affinity

2.2.1. *Thermodynamics of a Single Gas*

In thermodynamics of a single gas we have just one particle density n and the energy density e as variables. But the natural variables of statistical mechanics are the fugacity [1] a and the absolute temperature T, because statistical mechanics provides the equilibrium pressure of an ideal gas in terms of a and T, viz. (e.g. see [5], p. 87)

$$p(a, T) = \exp\left(-\frac{m}{k}a\right) 4\pi y m^2 c(kT)^2 K_2\left(\frac{mc^2}{kT}\right). \qquad (2.3)$$

m is the molecular rest mass, k the Boltzmann constant, $K_2\left(\frac{mc^2}{kT}\right)$ the modified Bessel function of the second kind and y is related to the Planck constant: $y = 1/h^3$.

There is a one-to-one correspondence between the pair (n, e) and the pair (a, T) and this is furnished by the equations

$$n(a, T) = -\frac{1}{mT}\left(\frac{\partial p}{\partial a}\right)_T, \qquad e(a, T) = T^2\left(\frac{\partial}{\partial T}\left(\frac{p}{T}\right)\right)_a, \qquad (2.4)$$

or inversely

$$a = a(n, e), \qquad T = T(n, e). \qquad (2.5)$$

It is true that the inverse functions $a(n, e)$ and $T(n, e)$ cannot be expressed in analytical form, but they are known graphically or numerically.

Also statistical mechanics provides an explicit expression for the equilibrium entropy, viz.

$$h_E = \left(\frac{\partial p}{\partial T}\right)_a - \frac{a}{T}\left(\frac{\partial p}{\partial a}\right)_T. \qquad (2.6)$$

---

[1] a is equal to the chemical potential μ to within a factor $-1/T$: $a = -\mu/T$. This definition deviates slightly from the fugacity of chemical thermodynamics.

2.2.2. *Thermodynamics of a Binary Non-Reacting Mixture of Gases*

In thermodynamics of binary mixtures we have *two* densities n_α ($\alpha = 1, 2$) and the energy density e as variables. We may replace these by the fugacities a_α and the absolute temperature T, the variables which determine the partial pressures

$$p_\alpha(a_\alpha, T) = \exp\left(-\frac{m_\alpha}{k} a_\alpha\right) 4\pi y m_\alpha^2 c (kT)^2 K_2\left(\frac{m_\alpha c^2}{kT}\right). \qquad (2.7)$$

In analogy to (2.4) and (2.5) we have

$$n_\alpha(a_\alpha, T) = -\frac{1}{m_\alpha T}\left(\frac{\partial p_\alpha}{\partial a_\alpha}\right)_T, \qquad e(a_1, a_2, T) = \sum_\alpha T^2\left(\frac{\partial}{\partial T}\left(\frac{p_\alpha}{T}\right)\right)_{a_\alpha}, \qquad (2.8)$$

or inversely

$$a_\alpha = a_\alpha(n_1, n_2, e), \qquad T = T(n_1, n_2, T). \qquad (2.9)$$

The entropy reads, in terms of a_α and T

$$h_E = \sum_\alpha \left[\left(\frac{\partial p_\alpha}{\partial T}\right)_{a_\alpha} - \frac{a_\alpha}{T}\left(\frac{\partial p_\alpha}{\partial a_\alpha}\right)_T\right]. \qquad (2.10)$$

The densities n_α and e are independent.

2.2.3. *Thermodynamics of a Binary Reacting Mixture of Gases*

The equations (2.7) through (2.10) are also valid in a reacting mixture but there is a subtle difference: In equilibrium the two number densities are not independent because the law of mass action requires

$$\sum_\alpha \gamma_\alpha m_\alpha a_\alpha^E = 0, \qquad (2.11)$$

where the γ's are the stoichiometric coefficients. Close to equilibrium we may thus write in linear approximation, by virtue of a Taylor expansion

$$p_{\frac{1}{2}}(a_{\frac{1}{2}}, T) = p_{\frac{1}{2}}^E \pm \gamma_{\frac{1}{2}} m_{\frac{1}{2}} \dot{p}_{\frac{1}{2}}^E(a_{\frac{1}{2}} - a_{\frac{1}{2}}^E),$$

$$n_{\frac{1}{2}}(a_{\frac{1}{2}}, T) = \mp \frac{1}{T} \dot{p}_{\frac{1}{2}}^E \gamma_{\frac{1}{2}} - \frac{1}{T}\gamma_{\frac{1}{2}}^2 m_{\frac{1}{2}} \ddot{p}_{\frac{1}{2}}^E(a_{\frac{1}{2}} - a_{\frac{1}{2}}^E), \qquad (2.12)$$

$$e(a_1, a_2, T) = \sum_\alpha (p_\alpha'^E - p_\alpha^E) + [\![\gamma_\alpha m_\alpha(\dot{p}_\alpha'^E - \dot{p}_\alpha^E)(a_\alpha - a_\alpha^E)]\!],$$

$$h(a_1, a_2, T) = \frac{1}{T}\sum_\alpha (p_\alpha'^E - a\dot{p}_\alpha^E) + \frac{1}{T}[\![\gamma_\alpha m_\alpha(\ddot{p}_\alpha'^E - (a\dot{p}_\alpha^E)^\bullet)(a_\alpha - a_\alpha^E)]\!].$$

where

$$p_{\frac{1}{2}}^E = \exp\left(-\frac{m_{\frac{1}{2}}}{k} a_{\frac{1}{2}}^E\right) 4\pi y m_{\frac{1}{2}}^2 c(kT)^2 K_2\left(\frac{m_{\frac{1}{2}}c^2}{kT}\right). \qquad (2.13)$$

With the *mixture fugacity* (cf. (2.11))

$$a = \gamma_1 m_1 a_1^E = -\gamma_2 m_2 a_2^E, \qquad (2.14)$$

we may write

$$p_{\frac{1}{2}}^E(a, T) = \exp\left(\mp \frac{1}{k\gamma_{\frac{1}{2}}} a\right) 4\pi y m_{\frac{1}{2}}^2 c(kT)^2 K_2\left(\frac{m_{\frac{1}{2}}c^2}{kT}\right). \qquad (2.15)$$

The derivatives $\bullet$ and $'$ in (2.12) denote differentiation with respect to a and $\ln T$ respectively; $[\![f_\alpha]\!]$ stands for $f_1 - f_2$.

As long as we stick to situations close to equilibrium it is possible, and appropriate, to replace the two fugacities a_α by the mixture fugacity a, - characterizing equilibrium, cf. (2.14) - and the *chemical affinity*

$$\Delta = \sum_\alpha \gamma_\alpha m_\alpha a_\alpha, \qquad (2.16)$$

which represents a "driving force" toward equilibrium. By (2.11) we have $\Delta = 0$ in equilibrium.

In order to obtain a_α in terms of Δ we need an additional equation, supplementary to (2.16). This additional equation results from the entropy $(2.12)_4$. Indeed, since the entropy must be a maximum in equilibrium, it cannot depend linearly on $(a_\alpha - a_\alpha^E)$ and therefore the last term in $(2.12)_4$ must vanish:

$$\gamma_1 m_1 (\dot{p}_1'^E - (a\dot{p}_1^E)^\bullet)(a_1 - a_1^E) - \gamma_2 m_2 (\dot{p}_2'^E - (a\dot{p}_2^E)^\bullet)(a_2 - a_2^E) = 0. \quad (2.17)$$

Between (2.16) and (2.17) we have a linear algebraic system for the determination of a_α from which we obtain

$$a_1 = \frac{1}{\gamma_1 m_1}\left(a + \underbrace{\frac{(\dot{p}_2'^E - (a\dot{p}_2^E)^\bullet)}{(\dot{p}_1'^E - (a\dot{p}_1^E)^\bullet) + (\dot{p}_2'^E - (a\dot{p}_2^E)^\bullet)}}_{A_1} \Delta\right),$$

$$a_2 = \frac{1}{\gamma_2 m_2}\left(-a + \underbrace{\frac{(\dot{p}_1'^E - (a\dot{p}_1^E)^\bullet)}{(\dot{p}_1'^E - (a\dot{p}_1^E)^\bullet) + (\dot{p}_2'^E - (a\dot{p}_2^E)^\bullet)}}_{-A_2}\Delta\right). \qquad (2.18)$$

These relations replace the two fugacities a_α by a and Δ. Also, by $(2.12)_{2,3}$, $n_\alpha(a_\alpha, T)$ and $e(a_1, a_2, T)$ now become explicit functions of a, T which are linear in Δ. The advantage of the new variables a, Δ over the old ones a_1, a_2 is that in the former set equilibrium is characterized by the vanishing of one variable, viz. Δ.

It is useful and customary to decompose the pressure P in $(2.2)_2$ into an equilibrium part $\sum_\alpha p_\alpha^E$ and a *dynamic pressure* π such that

$$P = \sum_\alpha p_\alpha^E + \pi. \qquad (2.19)$$

3. FIELDS EQUATIONS

3.1. Balance Laws

We may now rephrase the objective of extended thermodynamics by saying that we wish to determine the 15 fields

$$a, \Delta, T, U^A, t^{\langle AB \rangle}, \pi, q^A, \qquad (3.1)$$

which determine the particle flux vectors A_α^A and the energy-momentum tensor A^{AB}. We have

$$A_\alpha^A = m_\alpha n_\alpha(a, T, \Delta)U^A,$$

$$A^{AB} = t^{\langle AB \rangle} + \left(\sum_\alpha p_\alpha^E + \pi\right)h^{AB} + \frac{1}{c^2}(U^A q^B + U^B q^A) + \qquad (3.2)$$

$$+ \frac{1}{c^2}\sum_\alpha \left[(p_\alpha'^E - p_\alpha^E) + (\dot{p}_\alpha'^E - \dot{p}_\alpha^E)A_\alpha\Delta\right]U^A U^B.$$

The necessary field equations for the fields (3.1) are the equations of balance of masses, and energy-momentum and the flux balance, viz.

$$A_{\alpha,A}^A = \gamma_\alpha m_\alpha \ell, \qquad (\alpha = 1, 2),$$

$$A^{AB}_{,B} = 0, \qquad (3.3)$$

$$A^{ABC}_{,C} = I^{AB}, \qquad \left(I_A^A = \sum_\alpha c^2 \gamma_\alpha m_\alpha \ell, \quad A^{AB}_B = \sum_\alpha c^2 A_\alpha^A\right).$$

ℓ is the reaction rate density and the traceless tensor I^{AB} is the flux production. A^{ABC} is the flux tensor; it is fully symmetric and its trace is proportional to $\sum_\alpha A_\alpha^A$, so that $(3.3)_3$ represents only 9 equations, instead of 10.

A useful alternative form of the particle conservation laws $(3.3)_1$ reads

$$\left(\sum_\alpha m_\alpha n_\alpha U^A \right)_{,A} = \sum_\alpha \gamma_\alpha m_\alpha \ell, \tag{3.4}_1$$

$$\left(\left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2} \right) U^A \right)_{,A} = 0. \tag{3.4}_2$$

In this set only the first equation has a production which is governed by the *mass defect* of the reaction $M = \sum_\alpha \gamma_\alpha m_\alpha$; the second equation is a conservation law, representing the conservation of the number of atoms in the chemical reaction, or the conservation of nucleons in a nuclear reaction.

3.2. Constitutive theory

In order to close the system (3.3) we need constitutive equations for

- ℓ - the reaction rate density,
- A^{ABC} - the flux tensor,
- I^{AB} - the flux production.

In extended thermodynamics the constitutive equations have the generic form

$$\begin{aligned}
\ell &= \hat{\ell}(n_\alpha, U^M, A^{MN}) = \tilde{\ell}(a, T, \Delta, U^M, t^{\langle MN \rangle}, q^M, \pi), \\
A^{ABC} &= \hat{A}^{ABC}(n_\alpha, U^M, A^{MN}) = \tilde{A}^{ABC}(a, T, \Delta, U^M, t^{\langle MN \rangle}, q^M, \pi), \quad (3.5) \\
I^{AB} &= \hat{I}^{AB}(n_\alpha, U^M, A^{MN}) = \tilde{I}^{AB}(a, T, \Delta, U^M, t^{\langle MN \rangle}, q^M, \pi),
\end{aligned}$$

where $\hat{\ell}$, $\hat{A}$ and $\hat{I}$ are constitutive functions.

If the constitutive functions are known, the set (3.3), - or (3.4) and $(3.3)_{2,3}$ - represents a set of 15 equations for the 15 fields a, Δ, T, U^A, $t^{\langle AB \rangle}$, π, q^A. Every solution of this set is a *thermodynamic process*.

The constitutive functions are restricted by

- the entropy principle,
- the principle of relativity, and
- the requirement of convexity and causality.

3.3. Representations

The principle of relativity in the present context may be expressed by saying that $\tilde{\ell}$, $\tilde{A}^{ABC}$ and $\tilde{I}^{AB}$ are isotropic functions of their variables with respect to all space-time transformations. This means, if we restrict the attention to linear constitutive functions in the non-equilibrium quantities Δ, π, $t^{\langle AB \rangle}$, and q^A

$$\ell = \ell_\pi \pi + \ell_\Delta \Delta,$$
$$A^{ABC} = (C_1^0 + C_1^\pi \pi + C_1^\Delta \Delta)U^A U^B U^C +$$
$$+\frac{c^2}{6}(\sum_\alpha m_\alpha n_\alpha - C_1^0 - C_1^\pi \pi - C_1^\Delta \Delta)(g^{AB}U^C + g^{BC}U^A + g^{CA}U^B) +$$
$$+C_3(g^{AB}q^C + g^{BC}q^A + g^{CA}q^B) - \frac{6}{c^2}C_3(U^A U^B q^C + U^B U^C q^A + U^C U^A q^B) +$$
$$+C_5(t^{\langle AB \rangle}U^C + t^{\langle BC \rangle}U^A + t^{\langle CA \rangle}U^B), \tag{3.6}$$
$$I^{AB} = (B_1^\pi \pi + B_1^\Delta \Delta)g^{AB} - \frac{4}{c^2}(B_1^\pi \pi + B_1^\Delta \Delta)U^A U^B +$$
$$+B_3 t^{\langle AB \rangle} + \frac{1}{c^2}\hat{B}_4(q^A U^B + q^B U^A) + M\ell U^A U^B.$$

All coefficients may depend on a and T and, of course, n_α in $(3.6)_2$ is given by $(2.12)_2$, so that the term $\sum_\alpha m_\alpha n_\alpha$ contains a linear dependence on Δ.

These representations are formulated so as to satisfy the trace conditions indicated in $(3.3)_3$.

The entropy principle will turn out to determine all coefficients C in terms of the equation of state (2.15). This amazing definiteness of the entropy principle is the hallmark of extended thermodynamics, - and its redeeming feature. Because, indeed, were it not for its surprisingly specific results, nobody would undertake the task of following the complicated procedure of the evaluation of the entropy principle.

4. ENTROPY PRINCIPLE

4.1. Lagrange multipliers

The entropy principle states that the divergence of the entropy-entropy flux vector h^A - itself a constitutive quantity - be non-negative for all thermodynamic processes

$$h^A_{,A} \geq 0, \qquad h^A = \hat{h}^A(a, \Delta, U^M, A^{MN}). \tag{4.1}$$

Equivalent to this is the statement that the new inequality

$$h^A_{,A} + \lambda \left(\left(\sum_\alpha m_\alpha n_\alpha U^A \right)_{,A} - \sum_\alpha \gamma_\alpha m_\alpha \ell \right) + \Lambda \left(\left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2} \right) U^A \right)_{,A} +$$

$$+ \Lambda_A A^{AB}_{,B} + \Lambda_{AB}(A^{ABC}_{,C} - I^{AB}) \geq 0, \qquad (4.2)$$

holds for all fields n_α, U^A, A^{AB}. The lambdas are Lagrange multipliers, and Λ_{AB} may be taken to be traceless, because of $(3.3)_3$.

We introduce the vector potential

$$h'^A = h^A + \lambda \sum_\alpha m_\alpha n_\alpha U^A + \Lambda \left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2} \right) U^A + \Lambda_B A^{AB} + \Lambda_{BC} A^{ABC},$$

$$(4.3)$$

so that the inequality assumes the form

$$h'^A_{,A} - \sum_\alpha m_\alpha n_\alpha U^A \lambda_{,A} - \left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2} \right) U^A \Lambda_{,A} - A^{AB} \Lambda_{B,A} - A^{ABC} \Lambda_{BC,A} -$$

$$- \lambda \sum_\alpha \gamma_\alpha m_\alpha \ell - \Lambda_{AB} I^{AB} \geq 0. \qquad (4.4)$$

4.2. Lagrange multipliers as variables

Convexity and causality ensure that we may change variables

$$\text{from} \quad n_\alpha, U^A, A^{AB} \quad \text{to} \quad \Lambda, \lambda, \Lambda_A, \Lambda_{AB}, \qquad (4.5)$$

so that $n_\alpha, U^A, \ell, A^{AB}, A^{ABC}, I^{AB}$ is the new set of constitutive quantities.

This new shift of variables is one of the tricks by which extended thermodynamics manages to exploit the entropy inequality. Because in the new variables the inequality is easily evaluated. Indeed, we have

$$\left(\frac{\partial h'^A}{\partial \lambda} - \sum_\alpha m_\alpha n_\alpha U^A \right) \lambda_{,A} + \left(\frac{\partial h'^A}{\partial \Lambda} - \left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2} \right) U^A \right) \Lambda_{,A} +$$

$$+ \left(\frac{\partial h'^A}{\partial \Lambda_B} - A^{AB} \right) \Lambda_{B,A} + \left(\frac{\partial h'^A}{\partial \Lambda_{BC}} - A^{ABC} \right) \Lambda_{BC,A} - \lambda \sum_\alpha \gamma_\alpha m_\alpha \ell - \Lambda_{AB} I^{AB} \geq 0,$$

$$(4.6)$$

and, since this inequality must hold for all variable fields, we obtain

$$\frac{\partial h'^A}{\partial \lambda} = \sum_\alpha m_\alpha n_\alpha U^A, \quad \frac{\partial h'^A}{\partial \Lambda} = \left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2} \right) U^A, \quad \frac{\partial h'^A}{\partial \Lambda_B} = A^{AB},$$

$$\frac{\partial h'^A}{\partial \Lambda_{BC}} - \frac{1}{4} g^{BC} g_{MN} \frac{\partial h'^A}{\partial \Lambda_{MN}} = A^{ABC}, \qquad (4.7)$$

and there remains the residual inequality

$$-\lambda \sum_\alpha \gamma_\alpha m_\alpha \ell - \Lambda_{AB} I^{AB} \geq 0. \qquad (4.8)$$

We conclude that the quantities n_α, U^A, A^{AB}, and A^{ABC} in the new constitutive set are all given by derivatives of h'^A with respect to the new variables, the Lagrange multipliers; hence the name "vector potential" for h'^A. ℓ and I^{AB} are restricted by the residual inequality.

The conditions (4.7), (4.8) incorporate all restrictions implied by the entropy principle. Unfortunately these restrictions are largely formal. Indeed, since the Lagrange multipliers have no physical interpretation in their own right, we must convert the results (4.7) to statements on the physical quantities $n_\alpha, U^A, \ell, A^{AB}, A^{ABC}, I^{AB}$. This is a complicated process that can only be performed for near-equilibrium processes.

5. LAGRANGE MULTIPLIERS

5.1. Determination of the Lagrange Multipliers

In equilibrium the productions ℓ and I^{AB} must vanish, and therefore (4.8) implies that λ and Λ_{AB} also vanish:

$$\lambda^E = 0, \qquad \Lambda^E_{AB} = 0. \qquad (5.1)$$

This fact permits us to write the near-equilibrium representation of h'^A as a function of $\Lambda, \lambda, \Lambda_A, \Lambda_{AB}$. We include second order terms in λ and Λ_{AB} and obtain

$$h'_A = [\Gamma_0 + \Gamma_0^I \lambda + \Gamma_0^{II} \lambda^2 + \Gamma_{01} G_1 + \Gamma_{01}^I \lambda G_1 + \Gamma_{02} G_1^2 + \Gamma_{03} G_2 +$$

$$\Gamma_{04} H_2] \Lambda_A + [\Gamma_1 + \Gamma_1^I \lambda + \Gamma_{11} G_1] \Lambda_{AB} \Lambda^B + [\Gamma_2] \Lambda^2_{AB} \Lambda^B. \qquad (5.2)$$

Here the coefficients Γ may be functions of Λ and $G_0 = \Lambda_A \Lambda^A$ and we have defined

$$G_1 = \Lambda^A \Lambda_{AB} \Lambda^B, \qquad G_2 = \Lambda^A \Lambda^2_{AB} \Lambda^B, \qquad H_2 = \Lambda^{AB} \Lambda_{AB}. \qquad (5.3)$$

Insertion of (5.2) into (4.7) and linearization in λ and Λ_{AB} provides linear representations for

$$\sum_\alpha m_\alpha n_\alpha U^A, \quad \left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2}\right)U^A, \quad A^{AB}, \quad A^{ABC};$$

these, however, do not automatically satisfy the requirements that

- $\sum_\alpha m_\alpha n_\alpha U^A$ and $\left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2}\right)U^A$ are parallel,
- A^{AB} is symmetric (cf. $(2.2)_2$),   (5.4)
- $A^{AB}{}_B = c^2 \sum_\alpha m_\alpha n_\alpha U^A$ (cf. $(3.3)_3$).

For these requirements to be satisfied the Γ's must be interrelated. Summarizing a cumbersome calculation we may write

$$h'_A = \left[\Gamma_0 + \Gamma_0^I\lambda + \Gamma_0^{II}\lambda^2 + \frac{\partial\Gamma_1}{\partial G_0}G_1 + \frac{\partial\Gamma_1^I}{\partial G_0}\lambda G_1 + \frac{1}{2}\frac{\partial^2\Gamma_2}{\partial G_0^2}G_1^2 + \frac{\partial\Gamma_2}{\partial G_0}G_2 \right.$$

$$\left. + \frac{1}{4}\Gamma_2 H_2\right]\Lambda_A + \left[\Gamma_1 + \Gamma_1^I\lambda + \frac{\partial\Gamma_2}{\partial G_0}G_1\right]\Lambda_{AB}\Lambda^B + [\Gamma_2]\Lambda_{AB}^2\Lambda^B. \quad (5.5)$$

This ensures the symmetry of A^{AB}. The trace condition $(5.4)_3$ requires

$$\frac{\partial G_0^3\Gamma_1}{\partial G_0} = c^2 G_0^2\Gamma_0^I, \quad \frac{\partial G_0^4\Gamma_2}{\partial G_0} = c^2 G_0^3\Gamma_1^I, \quad \frac{\partial G_0^3\Gamma_1^I}{\partial G_0} = 2c^2 G_0^2\Gamma_0^{II}, \quad (5.6)$$

and finally the condition for parallelism $(5.4)_1$ requires

$$\Gamma_0^I = Q\frac{\partial\Gamma_0}{\partial\Lambda}, \quad \frac{\partial\Gamma_1^I}{\partial G_0} = Q\frac{\partial^2\Gamma_1}{\partial\Lambda\partial G_0}, \quad 2\Gamma_0^{II} = Q\frac{\partial\Gamma_0^I}{\partial\Lambda}, \quad \Gamma_1^I = Q\frac{\partial\Gamma_1}{\partial\Lambda},$$
$$(5.7)$$

where Q is given by

$$Q = \frac{\sum_\alpha m_\alpha n_\alpha}{\left(\frac{n_1}{\gamma_1} - \frac{n_2}{\gamma_2}\right)}. \quad (5.8)$$

Insertion of h'_A from (5.5) into (4.7)$_{1,2,3}$ gives linear relations of the form

$$-\frac{1}{T}[\![m_\alpha\gamma_\alpha\dot{p}^E_\alpha + m_\alpha\gamma_\alpha\ddot{p}^E_\alpha A_\alpha\Delta]\!]U^A = \left(\Gamma^I_0 + 2\Gamma^{II}_0\lambda + \frac{\partial\Gamma^I_1}{\partial G_0}G_1\right)\Lambda^A + \Gamma^I_1\Lambda^{AB}\Lambda_B,$$

$$-\frac{1}{T}\left[\sum_\alpha\dot{p}^E_\alpha + \sum_\alpha\ddot{p}^E_\alpha A_\alpha\Delta\right]U^A = \left(\frac{\partial\Gamma_0}{\partial\Lambda} + \frac{\partial\Gamma^I_0}{\partial\Lambda}\lambda + \frac{\partial^2\Gamma_1}{\partial\Lambda\partial G_0}G_1\right)\Lambda^A + \frac{\partial\Gamma_1}{\partial\Lambda}\Lambda^{AB}\Lambda_B,$$

$$t^{\langle AB\rangle} + \left[\sum_\alpha p^E_\alpha + \pi\right]h^{AB} + \frac{1}{c^2}(U^Aq^B + U^Bq^A) + \qquad\qquad (5.9)$$

$$+ \frac{1}{c^2}\left[\sum_\alpha(p'^E_\alpha - p^E_\alpha) + \sum_\alpha(\dot{p}'^E_\alpha - \dot{p}^E_\alpha)A_\alpha\Delta\right]U^AU^B =$$

$$= \left(\Gamma_0 + \Gamma^I_0\lambda + \frac{\partial\Gamma_1}{\partial G_0}G_1\right)g^{AB} + \Gamma_1\Lambda^{AB} + 2\left(\frac{\partial\Gamma_0}{\partial G_0} + \frac{\partial\Gamma^I_0}{\partial G_0}\lambda + + \frac{\partial^2\Gamma_1}{\partial G^2_0}G_1\right)\Lambda^A\Lambda^B +$$

$$+ 2\frac{\partial\Gamma_1}{\partial G_0}(\Lambda^B\Lambda^{AC}\Lambda_C + \Lambda^A\Lambda^{BC}\Lambda_C).$$

From this set of equations we may, in principle, determine the Lagrange multipliers in terms of $a, T, \Delta, U^A, t^{\langle AB\rangle}, q^A, \pi$. In practice this is impossible, except in equilibrium and in linear approximation.

5.2. Lagrange multipliers in equilibrium

Sofar we have maintained a notation which emphasized the fact that n^E_α are derivatives of p^E_α as in (2.12). This notation becomes impractical now; we introduce

$$mn^E = \sum_\alpha m_\alpha n^E_\alpha, \quad \text{and} \quad p^E = \sum_\alpha p^E_\alpha, \qquad (5.10)$$

and use these quantities and their derivatives so as to provide always the most compact form of equations. Of course, the fact remains that $p^E_\alpha = p_\alpha(a, T)$ determines all these quantities. In equilibrium we have from (5.9)$_{1,2,3}$ and (5.6), (4.3)

$$mn^E U^E_A = \Gamma^I_0\Lambda_A, \qquad -\frac{1}{T}\dot{p}^E U^E_A = \frac{\partial\Gamma_0}{\partial\Lambda}\Lambda_A,$$

$$p^E h^E_{AB} + \frac{1}{c^2}e^E U^E_A U^E_B = \Gamma_0 g_{AB} + 2\frac{\partial\Gamma_0}{\partial G_0}\Lambda_A\Lambda_B, \qquad (5.11)$$

$$h^E_A = -\left[\Lambda\frac{\partial\Gamma_0}{\partial\Lambda} + 2\frac{\partial\Gamma_0}{\partial G_0}G_0\right]\Lambda_A.$$

Thus we conclude

$$p^E = -\Gamma_0, \quad p^E + e^E = 2G_0 \frac{\partial \Gamma_0}{\partial G_0}, \tag{5.12}_1$$

$$-\frac{1}{T}\dot{p}^E = \frac{\sqrt{G_0}}{c}\frac{\partial \Gamma_0}{\partial \Lambda}, \quad U_A^E = \frac{c}{\sqrt{G_0}}\Lambda_A, \tag{5.12}_2$$

$$mn^E \frac{c}{\sqrt{G_0}} = \Gamma_0^I, \quad h^E = -\left[\Lambda \frac{\partial \Gamma_0}{\partial \Lambda} + 2\frac{\partial \Gamma_0}{\partial G_0}G_0\right]\frac{\sqrt{G_0}}{c}. \tag{5.13}$$

Combining these relations we obtain

$$e^E + h^E \frac{c}{\sqrt{G_0}} + p^E = -\frac{c}{\sqrt{G_0}}\frac{\Lambda}{\gamma_1 m_1}m_1 n_1^E + \frac{c}{\sqrt{G_0}}\frac{\Lambda}{\gamma_2 m_2}m_2 n_2^E, \tag{5.14}$$

and we compare this equation with a well-known thermodynamic relation which involves the absolute temperature T and the fugacities a_α

$$e^E - Th^E + p^E = -T\sum_\alpha a_\alpha^E m_\alpha n_\alpha^E. \tag{5.15}$$

The comparison shows that we have to set (recall (2.14))

$$\frac{\sqrt{G_0}}{c} = -\frac{1}{T}, \quad \Lambda = -a; \tag{5.16}$$

a being the mixture fugacity.

Therefore in equilibrium we have now identified all Lagrange multipliers. We have

$$\lambda = 0, \quad \Lambda = -a, \quad \Lambda_A = -\frac{1}{T}U_A^E, \quad \Lambda_{AB} = 0. \tag{5.17}$$

5.3. Linear Lagrange multipliers

We shall now use the equations (5.9) to calculate the Lagrange multipliers as linear functions of Δ, $t^{\langle AB\rangle}$, q^A and π. In order to linearize the system (5.9) we introduce

$$\Lambda = -a + \tilde{\Lambda},$$

$$\Lambda_A = -\frac{1}{T}U_A + \tau U_A + \tau_A, \tag{5.18}$$

$$\Lambda_{AB} = \sigma\left(h_{AB} + \frac{3}{c^2}U_A U_B\right) + \frac{1}{c^2}(U_A \sigma_B + U_B \sigma_A) + \sigma_{\langle AB\rangle},$$

and neglect products of $\tilde{\Lambda}$, τ, τ_A, σ, σ_A and $\sigma_{\langle AB\rangle}$. The vectors τ_A, σ_A and the traceless tensor $\sigma_{\langle AB\rangle}$ are space-like [2].

We obtain linear algebraic equations for the linear contributions to the Lagrange multipliers, viz.

$$
\begin{bmatrix}
-m\dot{n}^E & Tmn'^E & -Q^E m\dot{n}^E & -\frac{1}{T}\left(\frac{3}{2}\dot{\Gamma}_1'^E - 3\dot{\Gamma}_1^E\right)Q^E \\
\frac{1}{T}\ddot{p}^E & \dot{p}^E - \dot{p}'^E & -m\dot{n}^E & -\frac{1}{T}\left(\frac{3}{2}\dot{\Gamma}_1'^E - 3\dot{\Gamma}_1^E\right) \\
-\dot{p}^E & Tp'^E & Tmn^E & \left(\frac{3}{2}\Gamma_1'^E + \Gamma_1^E\right) \\
\dot{p}^E - \dot{p}'^E & T(p''^E - p'^E) & Tmn'^E & \frac{3}{2}\left(2\Gamma_1^E - 3\Gamma_1'^E + \Gamma_1''^E\right)
\end{bmatrix}
\begin{bmatrix}
\tilde{\Lambda} \\ \tau \\ \lambda \\ \sigma
\end{bmatrix} =
$$

$$
= \begin{bmatrix}
\sum_\alpha m_\alpha \dot{n}_\alpha^E A_\alpha \Delta \\
-\frac{1}{T}\sum_\alpha \ddot{p}_\alpha^E A_\alpha \Delta \\
\pi \\
\sum_\alpha (\dot{p}_\alpha'^E - \dot{p}_\alpha^E) A_\alpha \Delta
\end{bmatrix}, \tag{5.19}
$$

$$
\begin{bmatrix}
\dot{p}^E & \frac{1}{T}\dot{\Gamma}_1^E \\
-Tp'^E & (\Gamma_1^E - \Gamma_1'^E)
\end{bmatrix}
\begin{bmatrix}
\tau^A \\ \sigma^A
\end{bmatrix} =
\begin{bmatrix}
0 \\ q^A
\end{bmatrix}, \tag{5.20}
$$

$$
\sigma^{\langle AB\rangle} = \frac{1}{\Gamma_1^E} t^{\langle AB\rangle}. \tag{5.21}
$$

It ought to be emphasized that all coefficients in this set are explicitly related to the thermal equations of state (2.15). For Γ_1^E - and later Γ_2^E - this is true, because we obtain from (5.6)$_{1,2}$ by integration [3]

$$
\Gamma_1^E = 2c^2 T^6 \int \frac{mn^E}{T^6} dT, \qquad \Gamma_2^E = 4c^2 T^8 \int \frac{Q^E c^2}{T^3}\left(\int \frac{mn^E}{T^6} dT\right) dT. \tag{5.22}
$$

From the solutions of (5.19) through (5.21) we obtain the linear representations of the Lagrange multipliers

$$\lambda = \lambda_\pi \pi + \lambda_\Delta \Delta,$$

---

[2] Note that the Γ's in (5.9) have to be linearized in the deviations $\tilde{\Lambda}$ and $G_0 - \frac{c^2}{T^2} = -\frac{2c^2}{T}\tau$ of their variables Λ and G_0 from their equilibrium values. Thus for instance on the R.H.S. of (5.9)$_1$ we have set, cf. (5.13)$_1$, (5.16)

$$\Gamma_0^I = -Tmn^E + Tm\dot{n}^E \tilde{\Lambda} - T^2(mn'^E + mn^E)\tau,$$

and analogous expressions for the other Γ's and their derivatives.

[3] Constants of integration have been set equal to zero, since nobody sofar has found them to have physical significance.

$$\Lambda = -a + \Lambda_\pi \pi + \Lambda_\Delta \Delta,$$

$$\Lambda_A = -\frac{1}{T} U_A + (\tau_\pi \pi + \tau_\Delta \Delta) U_A + \tau_q q^A, \tag{5.23}$$

$$\Lambda_{AB} = (\sigma_\pi \pi + \sigma_\Delta \Delta)\left(h_{AB} + \frac{3}{c^2} U_A U_B \right) + \frac{1}{c^2}\sigma_q (U_A q_B + U_B q_A) + \frac{1}{\Gamma_1^E} t_{\langle AB \rangle},$$

where all coefficients are known functions of a and T given by the determinants of the matrices in (5.19), (5.20). We do not exhibit these functions, because they take up too much space.

6. FLUX TENSOR

The linear flux tensor follows from $(4.7)_4$ by insertion of the vector potential h'^A in (5.5) and removal of all non-linear terms. Thus

$$A^{ABC} = \left[\frac{\partial \Gamma_1}{\partial G_0} + \frac{\partial \Gamma_1^I}{\partial G_0}\lambda + \frac{\partial^2 \Gamma_2}{\partial G_0^2} G_1 \right] \Lambda^A \Lambda^B \Lambda^C +$$

$$+ \frac{1}{2}\left[\Gamma_1 + \Gamma_1^I \lambda + \frac{\partial \Gamma_2}{\partial G_0} G_1 \right] (g^{AB}\Lambda^C + g^{BC}\Lambda^A + g^{CA}\Lambda^B) +$$

$$+ \frac{1}{2}\Gamma_2 (g^{AB}\Lambda^{CD}\Lambda_D + g^{BC}\Lambda^{AD}\Lambda_D + g^{CA}\Lambda^{BD}\Lambda_D + \Lambda^{AB}\Lambda^C + \Lambda^{BC}\Lambda^A + \Lambda^{CA}\Lambda^B) +$$

$$+ \frac{\partial \Gamma_2}{\partial G_0}\left(\Lambda^A \Lambda^B \Lambda^{CD}\Lambda_D + \Lambda^B \Lambda^C \Lambda^{AD}\Lambda_D + \Lambda^C \Lambda^A \Lambda^{BD}\Lambda_D \right). \tag{6.1}$$

This is A^{ABC} expressed as a linear function of the Lagrange multipliers. Naturally, however, we want A^{ABC} as a function of the physical variables a, T, Δ, π, U^A, q^A, and $t^{\langle AB \rangle}$. In order to get that we introduce

$$\Gamma_1 = \Gamma_1^E - \dot{\Gamma}_1^E \tilde{\Lambda} + T\Gamma_1'^E \tau,$$

$$\frac{\partial \Gamma_1}{\partial G_0} = -\frac{T^2}{2c^2}\left(\Gamma_1'^E - \dot{\Gamma}_1'^E \tilde{\Lambda} + T(2\Gamma_1'^E + \Gamma_1''^E)\tau \right), \tag{6.2}$$

and replace all other Γ's by their equilibrium values. Thus

$$\Gamma_1^I = -Q^E \dot{\Gamma}_1^E, \qquad \frac{\partial \Gamma_1^I}{\partial G_0} = \frac{T^2}{2c^2}Q^E \dot{\Gamma}_1'^E, \qquad \Gamma_2 = \Gamma_2^E,$$

$$\frac{\partial \Gamma_2}{\partial G_0} = -\frac{T^2}{2c^2}\Gamma_2'^E, \qquad \frac{\partial^2 \Gamma_2}{\partial G_0^2} = \frac{T^4}{2c^4}\left(\frac{1}{2}\Gamma_2''^E + \Gamma_2'^E \right). \tag{6.3}$$

Also we introduce (5.18) - always neglecting non-linear terms in Δ, π, q^A, and $t^{\langle AB \rangle}$. A lengthy calculation provides the result

$$A^{ABC} = -\frac{1}{T} \left\{ \frac{1}{c^2} \left[-\frac{1}{2}\Gamma_1'^E + \frac{1}{2}\dot{\Gamma}_1'^E \tilde{\Lambda} + \left(\frac{1}{2}\Gamma_1''^E - \frac{1}{2}\Gamma_1'^E \right)(-T\tau) + \frac{1}{2}Q^E \dot{\Gamma}_1'^E \lambda + \right. \right.$$

$$\left. + 3\left(\frac{1}{4}\Gamma_2''^E - \Gamma_2'^E + 2\Gamma_2^E \right)\sigma \right] U^A U^B U^C + \left[\frac{1}{2}\Gamma_1^E - \frac{1}{2}\dot{\Gamma}_1^E \tilde{\Lambda} + \right.$$

$$\left(\frac{1}{2}\Gamma_1^E - \frac{1}{2}\Gamma_1'^E \right)(-T\tau) -$$

$$\left. -\frac{1}{2}Q^E \dot{\Gamma}_1^E \lambda + \left(\Gamma_2^E - \frac{3}{4}\Gamma_2'^E \right)\sigma \right] (g^{AB}U^C + g^{BC}U^A + g^{CA}U^B) +$$

$$+ \frac{T}{2c^2}\Gamma_1'^E [U^A U^B \tau^C + U^B U^C \tau^A + U^C U^A \tau^B] +$$

$$+ \frac{1}{c^2}\left(\Gamma_2^E - \frac{1}{2}\Gamma_2'^E \right)[U^A U^B \sigma^C + U^B U^C \sigma^A + U^C U^A \sigma^B] -$$

$$-\frac{T}{2}\Gamma_1^E [g^{AB}\tau^C + g^{BC}\tau^A + g^{CA}\tau^B] + \frac{1}{2}\Gamma_2^E [g^{AB}\sigma^C + g^{BC}\sigma^A + g^{CA}\sigma^B] +$$

$$+ \frac{1}{2}\Gamma_2^E \left[\sigma^{\langle AB \rangle}U^C + \sigma^{\langle BC \rangle}U^A + \sigma^{\langle CA \rangle}U^B \right] \right\}. \tag{6.4}$$

This expression is far from being explicit in the variables a, T, Δ, π, U^A, q^A, and $t^{\langle AB \rangle}$, mainly because it still contains the Lagrange multipliers $\tilde{\Lambda}$, λ, τ, σ, τ^A, σ^A, and $\sigma^{\langle AB \rangle}$. These Lagrange multipliers may be calculated from the algebraic system (5.19) through (5.21) and thus results A^{ABC} in the form (3.6)$_2$ with coefficients C which have the forms

$$C_1^0 = \frac{1}{2Tc^2}\Gamma_1'^E, \tag{6.5}$$

$$C_1^\pi \pi + C_1^\Delta \Delta = -\frac{3}{Tc^2}\left[\dot{\Gamma}_1^E \tilde{\Lambda} + \left(\Gamma_1'^E - \Gamma_1^E \right)(-T\tau) + Q^E \dot{\Gamma}_1^E \lambda + \left(\frac{3}{2}\Gamma_2'^E - 2\Gamma_2^E \right)\sigma \right], \tag{6.6}$$

$$C_3 = -\frac{1}{2T} \frac{\begin{bmatrix} \dot{p} & -\dot{\Gamma}_1^E \\ \Gamma_1^E & \Gamma_2^E \end{bmatrix}}{\begin{bmatrix} \dot{p} & -\dot{\Gamma}_1^E \\ p' & \Gamma_1^E - \Gamma_1'^E \end{bmatrix}}, \qquad C_5 = -\frac{1}{2T}\frac{\Gamma_2^E}{\Gamma_1^E}. \tag{6.7}$$

Note that $\tilde{\Lambda}$, τ, λ and σ in (6.6) may be calculated from (5.19) as linear functions of π and Δ. Thus C_1^π and C_1^Δ can be determined in terms of p^E, Γ_1^E, Γ_2^E. The explicit result is too complicated to be written down in this paper.

7. PRODUCTIONS

We insert the representations $(3.6)_{1,3}$ for the reaction rate density and the flux production into the residual inequality (4.8). Also we introduce the calculated expressions $(5.23)_{1,4}$ into that inequality. Thus we obtain

$$[\pi \quad \Delta] \begin{bmatrix} 12\sigma_\pi B_1^\pi - M\lambda_\pi \ell_\pi & 12\sigma_\pi B_1^\Delta - M\lambda_\pi \ell_\Delta \\ 12\sigma_\Delta B_1^\pi - M\lambda_\Delta \ell_\pi & 12\sigma_\Delta B_1^\Delta - M\lambda_\Delta \ell_\Delta \end{bmatrix} \begin{bmatrix} \pi \\ \Delta \end{bmatrix} -$$

$$- \frac{2}{c^2}\sigma_q \hat{B}_4 q_B q^B - \frac{1}{\Gamma_1^E} B_3 t_{\langle AB \rangle} t^{\langle AB \rangle} \geq 0. \qquad (7.1)$$

and it follows that we must have

$$\begin{bmatrix} 12\sigma_\pi B_1^\pi - M\lambda_\pi \ell_\pi & 12\sigma_\pi B_1^\Delta - M\lambda_\pi \ell_\Delta \\ 12\sigma_\Delta B_1^\pi - \frac{M}{12}\lambda_\Delta \ell_\pi & 12\sigma_\Delta B_1^\Delta - M\lambda_\Delta \ell_\Delta \end{bmatrix} - \text{pos. def.,}$$

$$\sigma_q \hat{B}_4 \geq 0, \ \frac{B_3}{\Gamma_1^E} \leq 0. \qquad (7.2)$$

These are rather weak restrictions on the signs of the coefficients ℓ_π, ℓ_Δ, B_1^π, B_1^Δ, $\hat{B}_4$ and B_3. There is no more to be had on these coefficients from extended thermodynamics, nor from any other macroscopic theory. However, we shall proceed on the assumption that the leading terms of these coefficients are "classical", i. e. of $\mathcal{O}(1)$. After all, they are due to intermolecular collisions and therefore they are expected to be of the order of magnitude of the collision frequency.

8. RESULTS

8.1. Linear Field Equations of Relativistic Extended Thermodynamics

We summarize the results of the preceding sections by writing the linearized forms of the field equations. There are four scalar equations, two vectorial ones and a tensor equation. We have

$$\begin{bmatrix} m\dot{n}^E & mn'^E & mn^E & 0 & 0 & 0 \\ \ddot{p}^E & \dot{p}'^E - \dot{p}^E & \dot{p}^E & 0 & X_1 & 0 \\ \dot{p}'^E - \dot{p}^E & p''^E - p'^E & p'^E & 0 & X_2 & 1 \\ \frac{\dot{\Gamma}_1'^E - 3\dot{\Gamma}_1^E}{2T} & \frac{\Gamma_1''^E - 4\Gamma_1'^E + 3\Gamma_1^E}{2T} & \frac{\Gamma_1'^E - \Gamma_1^E}{2T} & \frac{c^2}{2}C_1^\pi & \frac{c^2}{2}C_1^\Delta & -5C_3 \end{bmatrix} \begin{bmatrix} \frac{da}{d\tau} \\ \frac{d\ln T}{d\tau} \\ U^A_{,A} \\ \frac{d\pi}{d\tau} \\ \frac{d\Delta}{d\tau} \\ q^A_{,A} \end{bmatrix} =$$

$$
= \begin{bmatrix} \sum_\alpha \gamma_\alpha m_\alpha \ell \\ 0 \\ 0 \\ \frac{1}{c^2} I_{AB} U^A U^B \end{bmatrix} = \begin{bmatrix} M(\ell_\pi \pi + \ell_\Delta \Delta) \\ 0 \\ 0 \\ -3(B_1^\pi \pi + B_1^\Delta \Delta) + M(\ell_\pi \pi + \ell_\Delta \Delta)c^2 \end{bmatrix}, \quad (8.1)
$$

$$
\begin{bmatrix} \dot{p}^E & p'^E & 1 & \sum_\alpha \dot{p}_\alpha^E A_\alpha & 1 & p'^E & 1 \\ -\frac{\dot{\Gamma}_1^E}{2T} & -\frac{\Gamma_1'^E - \Gamma_1^E}{2T} & -\frac{c^2}{6} C_1^\pi & -\frac{c^2}{6} C_1^\Delta & -C_5 & -\frac{\Gamma_1'^E - \Gamma_1^E}{2T} & 5C_3 \end{bmatrix} \times
$$

$$
\times \begin{bmatrix} h^{AB} a_{,B} \\ h^{AB} (\ln T)_{,B} \\ h^{AB} \pi_{,B} \\ h^{AB} \Delta_{,B} \\ t^{\langle AB \rangle}_{\quad ,B} \\ \frac{1}{c^2} \frac{dU^A}{d\tau} \\ \frac{1}{c^2} \frac{dq^A}{d\tau} \end{bmatrix} = \begin{bmatrix} 0 \\ -\frac{\hat{B}_4}{c^2} q^A \end{bmatrix}, \quad (8.2)
$$

$$
-\frac{\Gamma_1^E}{T} h^{E\langle A} h^{B\rangle D} U_{\langle D, E \rangle} + 2C_3 h^{E\langle A} h^{B\rangle D} q_{\langle D, E \rangle} + C_5 \frac{dt^{\langle AB \rangle}}{d\tau} = B_3 t^{\langle AB \rangle}.
$$

$$(8.3)$$

In (8.1) $X_1 = \sum_\alpha A_\alpha \ddot{p}_\alpha^E$ and $X_2 = \sum_\alpha A_\alpha (\dot{p}_\alpha'^E - \dot{p}_\alpha^E)$. These are fully general results in the linear approximation. In particular, they are valid for a relativistic non-degenerate mixture of gases at arbitrarily high temperatures. The only unknown cofeficients are ℓ_π, ℓ_Δ, B_1^π, B_1^Δ, $\hat{B}_4$ and B_3 [4].

8.2. Linear Field Equations
of Non-Relativistic Extended Thermodynamics

In the non-relativistic limit the coefficients C can easily be calculated explicitly and we obtain

$$
C_1^0 = n_1^E m_1 + n_2^E m_2 + \mathcal{O}\left(\frac{1}{c^2}\right), \quad (8.4)_1
$$

$$
C_1^\pi = -\frac{6}{c^2} + \mathcal{O}\left(\frac{1}{c^4}\right), \quad (8.4)_2
$$

$$
C_1^\Delta = \mathcal{O}\left(\frac{1}{c^4}\right), \quad (8.4)_3
$$

---

[4] Note that the coefficients C_1^π, C_1^Δ, C_3 and C_5 on the L. H. S. of (8.1) through (8.3) occur only for brevity. Indeed, these coefficients - as well as $m\dot{n}^E$, $\ddot{p}^E$, etc. - are all determined by the equations of state (2.15), as was explained before.

$$C_3 = \frac{\frac{2}{5}\frac{(n_1^E)^2+(n_2^E)^2}{n_1^E n_2^E} + \frac{7}{5}\frac{m_1^2+m_2^2}{m_1 m_2} - 2}{\frac{\gamma_1+\gamma_2}{\gamma_1\gamma_2}\frac{Mc^2}{kT} - \left(\frac{(n_1^E)^2+(n_2^E)^2}{n_1^E n_2^E} + \frac{7}{2}\frac{m_1^2+m_2^2}{m_1 m_2} - 5\right)} + \mathcal{O}\left(\frac{1}{c^2}\right), \quad (8.4)_4$$

$$C_5 = 1 + \mathcal{O}\left(\frac{1}{c^2}\right). \tag{8.4_5}$$

Note that C_1^π and C_1^Δ had to be calculated including terms of $\mathcal{O}(\frac{1}{c^2})$, because - by (8.1) - these coefficients have an explicit factor c^2.

The formulation of the non-relativistic limit must be done carefully, since, because of the smallness of the mass defect $M = \sum_\alpha \gamma_\alpha m_\alpha$, the presence of the order parameter c^2 does not always indicate big terms. Indeed, Mc^2 is the *heat of reaction*, an entirely non-relativistic quantity, inasmuch as the conversion of mass into energy - which occurs in a chemical reaction - can be called non-relativistic.

The linear field equations of non-relativistic extended thermodynamics result by insertion of the coefficients C from (8.4) into the set (8.1) through (8.3). Also in that system we replace the other matrix elements according to the following list:

$$mn^E = m_1 n_1^E + m_2 n_2^E, \qquad m\dot{n}^E = -\frac{1}{k}\left(\frac{m_1 n_1^E}{\gamma_1} - \frac{m_2 n_2^E}{\gamma_2}\right), \tag{8.5_1}$$

$$mn'^E = \frac{c^2}{kT}\left[m_1^2 n_1^E\left(1 + \frac{3}{2}\frac{kT}{m_1 c^2}\right) + m_2^2 n_2^E\left(1 + \frac{3}{2}\frac{kT}{m_2 c^2}\right)\right]$$
$$+\mathcal{O}\left(\frac{1}{c^2}\right), \tag{8.5_2}$$

$$\dot{p}^E = -T\left(\frac{n_1^E}{\gamma_1} - \frac{n_2^E}{\gamma_2}\right), \qquad \ddot{p}^E = \frac{T}{k}\left(\frac{n_1^E}{\gamma_1^2} + \frac{n_2^E}{\gamma_2^2}\right), \tag{8.5_3}$$

$$p'^E = c^2\left[m_1 n_1^E\left(1 + \frac{5}{2}\frac{kT}{m_1 c^2} + \frac{15}{8}\left(\frac{kT}{m_1 c^2}\right)^2\right) + \right.$$

$$\left. +m_2 n_2^E\left(1 + \frac{5}{2}\frac{kT}{m_2 c^2} + \frac{15}{8}\left(\frac{kT}{m_2 c^2}\right)^2\right)\right] + \mathcal{O}\left(\frac{1}{c^4}\right), \tag{8.5_4}$$

$$\dot{p}'^E - \dot{p}^E = -\frac{c^2}{k}\left[\frac{m_1 n_1^E}{\gamma_1}\left(1 + \frac{3}{2}\frac{kT}{m_1 c^2}\right) - \frac{m_2 n_2^E}{\gamma_2}\left(1 + \frac{3}{2}\frac{kT}{m_2 c^2}\right)\right]$$

$$+\mathcal{O}\left(\frac{1}{c^2}\right), \tag{8.5_5}$$

$$p''^E - p'^E = \frac{c^4}{kT}\left[m_1^2 n_1^E\left(1 + 3\frac{kT}{m_1 c^2} + \frac{15}{2}\left(\frac{kT}{m_1 c^2}\right)^2\right) + \right.$$

$$\left. + m_2^2 n_2^E\left(1 + 3\frac{kT}{m_2 c^2} + \frac{15}{2}\left(\frac{kT}{m_2 c^2}\right)^2\right)\right] + \mathcal{O}\left(\frac{1}{c^2}\right), \tag{8.5$_6$}$$

$$\frac{\Gamma_1^E}{T} = 2kT\left(n_1^E + n_2^E\right) + \mathcal{O}\left(\frac{1}{c^2}\right), \tag{8.5$_7$}$$

$$\frac{\dot{\Gamma}_1^E}{2T} = -T\left[\frac{n_1^E}{\gamma_1}\left(1 + \frac{5}{2}\frac{kT}{m_1 c^2}\right) - \frac{n_2^E}{\gamma_2}\left(1 + \frac{5}{2}\frac{kT}{m_2 c^2}\right)\right] + \mathcal{O}\left(\frac{1}{c^4}\right), \tag{8.5$_8$}$$

$$\frac{\Gamma_1'^E - \Gamma_1^E}{2T} = c^2\left[m_1 n_1^E\left(1 + 5\frac{kT}{m_1 c^2} + \frac{25}{2}\left(\frac{kT}{m_1 c^2}\right)^2\right) + \right.$$

$$\left. + m_2 n_2^E\left(1 + 5\frac{kT}{m_2 c^2} + \frac{25}{2}\left(\frac{kT}{m_2 c^2}\right)^2\right)\right] + \mathcal{O}\left(\frac{1}{c^4}\right), \tag{8.5$_9$}$$

$$\frac{\dot{\Gamma}_1'^E - 3\dot{\Gamma}_1^E}{2T} = -\frac{c^2}{k}\left[\frac{m_1 n_1^E}{\gamma_1}\left(1 + 3\frac{kT}{m_1 c^2}\right) - \frac{m_2 n_2^E}{\gamma_2}\left(1 + 3\frac{kT}{m_2 c^2}\right)\right]$$

$$+ \mathcal{O}\left(\frac{1}{c^2}\right), \tag{8.5$_{10}$}$$

$$\frac{\Gamma_1''^E - 4\Gamma_1'^E + 3\Gamma_1^E}{2T} = \frac{c^4}{kT}\left[m_1^2 n_1^E\left(1 + \frac{9}{2}\frac{kT}{m_1 c^2} + \frac{135}{8}\left(\frac{kT}{m_1 c^2}\right)^2\right) + \right.$$

$$\left. + m_2^2 n_2^E\left(1 + \frac{9}{2}\frac{kT}{m_2 c^2} + \frac{135}{8}\left(\frac{kT}{m_2 c^2}\right)^2\right)\right] + \mathcal{O}\left(\frac{1}{c^2}\right), \tag{8.5$_{11}$}$$

$$\sum_\alpha \dot{p}_\alpha A_\alpha = \frac{(m_2 - m_1)n_1 n_2 T}{m_1 n_1 \gamma_2 - m_2 n_2 \gamma_1} +$$

$$+ \frac{n_1 n_2 (n_2 \gamma_1 - n_1 \gamma_2)[2a(m_1 \gamma_1 - m_2 \gamma_2)/k + 3\gamma_1 \gamma_2 (m_2 - m_1)]}{2\gamma_1 \gamma_2 (m_1 n_1 \gamma_2 - m_2 n_2 \gamma_1)^2}\frac{kT^2}{c^2}$$

$$+ \mathcal{O}\left(\frac{1}{c^4}\right). \tag{8.5$_{12}$}$$

All of these expressions have been restricted to *the* relativistic order that matters for non-relativistic equations.

8.3. Dynamic Pressure π and Reaction Rate Density ℓ

First we evaluate the scalar equations (8.1). It is useful to eliminate $\frac{da}{d\tau}$ and $\frac{d\ln T}{d\tau}$ between these equations and thus obtain expressions for the

reaction rate density ℓ and for the dynamic pressure π. With the definition

$$
D = \left(\frac{Mc^2}{kT}\right)^2 + 3(\gamma_1 + \gamma_2)\left(\frac{Mc^2}{kT}\right) -
$$
$$
-\frac{3}{4}\gamma_1\gamma_2\left(2\frac{m_1^2(n_1^E)^2 + m_2^2(n_2^E)^2}{m_1 m_2 n_1^E n_2^E} + 5\frac{m_1^2 + m_2^2}{m_1 m_2} - 6\right)
$$

(8.6)

we obtain to within terms of $\mathcal{O}\left(\frac{1}{c^2}\right)$

$$
\frac{kT}{D}\left(\frac{Mc^2}{kT}\right)^2\left[(n_1^E + n_2^E)U_{,A}^A - \frac{1}{kT}q_{,A}^A\right] = M\ell c^2,
$$

(8.7)

$$
-\frac{kT}{D}\left(\frac{Mc^2}{kT}\right)^2 (n_1^E + n_2^E)U_{,A}^A -
$$
$$
-\left\{\frac{1}{D}\left(\frac{Mc^2}{kT}\right)^2 + \frac{2\frac{(n_1^E)^2 + (n_2^E)^2}{n_1^E n_2^E} + 7\frac{m_1^2 + m_2^2}{m_1 m_2} - 10}{\frac{\gamma_1 + \gamma_2}{\gamma_1 \gamma_2}\frac{Mc^2}{kT} - \left(\frac{(n_1^E)^2 + (n_2^E)^2}{n_1^E n_2^E} + \frac{7}{2}\frac{m_1^2 + m_2^2}{m_1 m_2} - 5\right)}\right\}q_{,A}^A +
$$
$$
-3\frac{d\pi}{d\tau} = -3(B_1^\pi \pi + B_1^\Delta \Delta) + M\ell c^2.
$$

(8.8)

The equation (8.7) may be interpreted by saying that for a reaction to proceed we must have expansion $U_{,A}^A$, or heating $q_{,A}^A$, or both.

The equations (8.7), (8.8) are equations of extended thermodynamics where π is a variable. The reader may be more used to ordinary thermodynamics, where π is a constitutive quantity, depending linearly on $U_{,A}^A$ and Δ. Such a constitutive quantity for π may be derived from (8.8) approximately. The approximation is suggested by the Maxwellian iteration of the kinetic theory of gases (e. g. see [6], [5]). This iteration is adapted to the present case by subtracting equation (8.7) from (8.8) and by replacing all quantities on the L. H. S. of the resulting equation by their equilibrium values, i. e. by setting q^A, π and Δ on the L. H. S. equal to zero and thus obtain a first iterate for π, viz.

$$
\pi = -\eta U_{,A}^A - \frac{B_1^\Delta}{B_1^\pi}\Delta,
$$

(8.9)

where

$$
\eta = -\frac{2}{3DB_1^\pi}\left(\frac{Mc^2}{kT}\right)^2 (n_1^E + n_2^E)kT,
$$

(8.10)

is the bulk viscosity.

Insertion of this expression for π into $\ell = \ell_\pi \pi + \ell_\Delta \Delta$ provides the constitutive relation of ordinary thermodynamics for the reaction rate density ℓ, viz.

$$\ell = \frac{2\ell_\pi}{3DB_1^\pi}\left(\frac{Mc^2}{kT}\right)^2 (n_1^E + n_2^E)U_{,A}^A + \left(\ell_\Delta - \ell_\pi \frac{B_1^\Delta}{B_1^\pi}\right)\Delta. \qquad (8.11)$$

The equations (8.9), (8.11) are the "phenomenological equations" of linear irreversible thermodynamics, linear relations between the

fluxes	and	forces
dynapic pressure π		divergence of velocity $U_{,A}^A$
reaction rate density		affinity Δ

Among the "phenomenological coefficients" relating forces and fluxes the most important one is the bulk viscosity η given in (8.10). The main purpose of this paper is the determination of the bulk viscosity η and its "relativistic order", its dependence on n_1^E, n_2^E and on the mass defect M, or the heat of reaction Mc^2. We are now in a position to discuss η and we itemize its salient features

- The bulk viscosity is proportional to $1/B_1^\pi$ which - by (8.8) - is the relaxation time for the dynamic pressure. We know that in gases relaxation times are of the order of magnitude of times of free flight of the molecules. Therefore $1/B_1^\pi$ is of relativistic order $\mathcal{O}(1)$.

- Consequently the bulk viscosity η in a reacting binary mixture is of relativistic order $\mathcal{O}(1)$. That means that a mixture of relativistic gases - *and of non-relativistic gases* - has a bulk viscosity.

- The bulk viscosity η depends on the mass-defect M, or the heat of reaction Mc^2, explicitly. Without mass defect there would be no bulk viscosity; nor would there be a reaction rate, as we have seen.

- If we proceed to the limit of a single gas by letting n_2^E (say) tend to zero, the bulk viscosity in (8.9) vanishes. This agrees with the observation that non-relativistic gases have no bulk viscosity while the bulk viscosity of relativistic gases has terms of $\mathcal{O}\left(\frac{1}{c^2}\right)$ and of smaller order, see [1].

- Table 1 in chapter 1 shows for the dissociating gas mixture consisting of molecular and atomic iodine how the bulk viscosity depends on the temperature. In that case we have $Mc^2 = -148.7 \times 10^3 \text{J/mol}$, see [4].

8.4. Viscosity and thermal conductivity

Complex equations of the type (8.2) and (8.3) for q^A and $t^{\langle AB\rangle}$ are known in the kinetic theory of gases and they are boiled down to the "phenomenological relations" of Fourier and Navier-Stokes by the first step of an iterative scheme due to Maxwell. In that step all non-equilibrium quantities on the L. H. S.'s of (8.2) and (8.3) are neglected so that equations for q^A and $t^{\langle AB\rangle}$ result which serve as first iterates, viz. , without terms of $\mathcal{O}\left(\frac{1}{c^2}\right)$

$$\begin{bmatrix} \dot{p}^E & p'^E & p'^E \\ -\frac{\dot{\Gamma}_1^E}{2T} & -\frac{\Gamma_1'^E-\Gamma_1^E}{2T} & -\frac{\Gamma_1'^E-\Gamma_1^E}{2T} \end{bmatrix} \begin{bmatrix} h^{AB}a_{,B} \\ h^{AB}(\ln T)_{,B} \\ \frac{1}{c^2}\frac{dU^A}{d\tau} \end{bmatrix} = \begin{bmatrix} 0 \\ -\frac{\hat{B}_4}{c^2}q^A \end{bmatrix}, \quad (8.12)$$

$$-\frac{\Gamma_1^E}{T}h^{E\langle A}h^{B\rangle D}U_{\langle D,E\rangle} = B_3 t^{\langle AB\rangle}. \quad (8.13)$$

The homogeneous equation in (8.12) may be used to eliminate $h^{AB}a_{,B}$ from the non-homogeneous one and we obtain

$$\left[\frac{\dot{\Gamma}_1^E}{2T}\frac{p'^E}{\dot{p}^E} - \frac{\Gamma_1'^E-\Gamma_1^E}{2T}\right]h^{AB}\left[(\ln T)_{,B} + \frac{1}{c^2}\frac{dU^A}{d\tau}\right] = -\frac{\hat{B}_4}{c^2}q^A. \quad (8.14)$$

Comparison of (8.13) and (8.14) with the classical equations of Navier-Stokes and Fourier provides a definition of the shear viscosity μ and the thermal conductivity κ, viz.

$$\mu = -\frac{1}{2T}\frac{1}{B_3}\Gamma_1^E, \qquad \text{or}$$

$$\mu = -\frac{1}{B_3}(n_1^E + n_2^E)kT + \mathcal{O}\left(\frac{1}{c^2}\right), \quad (8.15)$$

$$\kappa = \frac{c^2}{\hat{B}_4}\left[\frac{\dot{\Gamma}_1^E}{2T^2}\frac{p'^E}{\dot{p}^E} - \frac{\Gamma_1'^E-\Gamma_1^E}{2T^2}\right], \qquad \text{or}$$

$$\kappa = \frac{1}{\hat{B}_4}\left\{\frac{5}{8}\frac{n_1^E n_2^E}{\frac{n_1^E}{\gamma_1} - \frac{n_2^E}{\gamma_2}}\frac{k^2 T}{m_1 m_2 \gamma_1 \gamma_2}\left[\left(2\frac{(n_1^E)^2 + (n_2^E)^2}{n_1^E n_2^E} + 7\frac{m_1^2 + m_2^2}{m_1 m_2} - 10\right) \times \right.\right.$$

$$\left.\left. \times(m_1\gamma_1 - m_2\gamma_2) + \frac{4}{kT}(m_2 - m_1)Mc^2\right]\right\} + \mathcal{O}\left(\frac{1}{c^2}\right). \quad (8.16)$$

$1/B_3$ and $1/\hat{B}_4$ are the relaxation times of stress and heat flux and they are of the order of magnitude of the time of free flight of the molecules of the gas.

There is nothing remarkable about the viscosity (8.15). It looks exactly as it does in a single fluid, at least in the given approximation of $\mathcal{O}(1)$.

The thermal conductivity is more interesting. Indeed, it contains a term that is proportional to the mass-defect M. Such an effect has been observed, and as early as 1904 Nernst [2] developed a crude molecular model to explain it.

Since the influence of the heat of reaction on the thermal conductivity κ emerges here as a natural consequence of the systematic application of extended thermodynamics, we make an estimate of the size of this effect by forming the ratio R of the first and second terms in (8.16):

$$R = 4\frac{Mc^2}{kT}\frac{(m_2 - m_1)}{\left(2\frac{(n_1^E)^2 + (n_2^E)^2}{n_1^E n_2^E} + 7\frac{m_1^2 + m_2^2}{m_1 m_2} - 10\right)(m_1\gamma_1 - m_2\gamma_2)}. \qquad (8.17)$$

Table 1 in Chapter 1 represents specific values of R as a function of temperature for the dissociation of iodine $I_2 \rightarrow 2I$. The value of R a function of temperature is discussed in chapter 1.

In the limit of a single gas, i. e. for $n_2^E \rightarrow 0$ the thermal conductivity becomes

$$\kappa = -\frac{1}{\hat{B}_4}\frac{5}{2}\frac{n_1^E kT}{m_1} + \mathcal{O}\left(\frac{1}{c^2}\right), \qquad (8.18)$$

which agrees with the result given in [5], and - incidentally - to the result of the kinetic theory of gases, see [7].

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