Exercise 1 to section 4.5.[1]

Derive entropic inequality and constitutive equations for non-viscous (linear) fluid mixture. This fluid model is quite common in chemistry where viscosity effects are often negligible. In fact, we should remove $\mathbf{D}_\gamma$ from the set of the independent variables of the (linear) fluid mixture – see p. 173 in the book and cf. eqs. (3.129) and (3.130), and the text around eq. (3.181). Although this could be, in principle, realized on the results obtained for the mixture of the linear fluids, complete this exercise starting with appropriately simplified entropic inequality and with the corresponding general constitutive equations.

Try to answer before continuing reading.

We will start with the general local form of the entropy inequality or the Clausius-Duhem inequality, cf. (4.84) and (4.85):

$$T\Big(\sum_{\alpha=1}^{n}\rho_\alpha\grave{s}_\alpha+\sum_{\alpha=1}^{n}r_\alpha s_\alpha\Big)=-T\,\mathrm{div}(\mathbf{q}/T)+Q+T\sigma. \tag{1}$$

The term $\mathrm{div}(\mathbf{q}/T)$ is

$$\mathrm{div}(\mathbf{q}/T)=(1/T)\,\mathrm{div}\mathbf{q}-(1/T^2)\,\mathbf{q}.\mathrm{grad}T\equiv(1/T)\,\mathrm{div}\mathbf{q}-(1/T^2)\,\mathbf{q}.\mathbf{g}.$$

Eq. (1) is then modified:

$$T\Big(\sum_{\alpha=1}^{n}\rho_\alpha\grave{s}_\alpha+\sum_{\alpha=1}^{n}r_\alpha s_\alpha\Big)=-\mathrm{div}\mathbf{q}+(1/T)\,\mathbf{q}.\mathbf{g}+Q+T\sigma. \tag{2}$$

It follows from (4.82) in the book and upon combination with (2):

$$-\mathrm{div}\mathbf{q}+Q=\sum_{\alpha=1}^{n}\rho_\alpha\grave{u}_\alpha+\sum_{\alpha=1}^{n}r_\alpha u_\alpha-\sum_{\alpha=1}^{n}\mathrm{tr}\mathbf{T}_\alpha\mathbf{D}_\alpha+\sum_{\beta=1}^{n-1}\mathbf{k}_\beta.\mathbf{u}_\beta+$$
$$(1/2)\sum_{\beta=1}^{n-1}r_\beta\mathbf{u}_\beta^2=-(1/T)\,\mathbf{q}.\mathbf{g}-T\sigma+T\sum_{\alpha=1}^{n}\rho_\alpha\grave{s}_\alpha+T\sum_{\alpha=1}^{n}r_\alpha s_\alpha. \tag{3}$$

[1]Based on I. Samohýl: Irreversible Thermodynamics. Prague: University of Chemical Technology, 1998 (*in Czech*).

Introducing the specific partial free energy f_α (4.86) into (3) gives, cf. also the inequality in (4.84):

$$-T\sigma = \sum_{\alpha=1}^{n} \rho_\alpha \overset{\backslash}{f}_\alpha + \sum_{\alpha=1}^{n} \rho_\alpha s_\alpha \overset{\backslash\alpha}{T} + \sum_{\alpha=1}^{n} f_\alpha r_\alpha - \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{k}_\beta . \mathbf{u}_\beta +$$

$$(1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 + (1/T)\, \mathbf{q} . \mathbf{g} \leq 0. \tag{4}$$

Constitutive equations in non-viscous fluid mixture are given generally by the theorem on representation of linear isotropic functions, see pp. 173-174 in the book. They are $(\alpha, \gamma = 1, \ldots, n; \beta = 1, \ldots, n-1)$:

$$u_\alpha = \hat{u}_\alpha(\rho_\gamma, T), \tag{5}$$

$$s_\alpha = \hat{s}_\alpha(\rho_\gamma, T), \tag{6}$$

$$f_\alpha = \hat{f}_\alpha(\rho_\gamma, T), \tag{7}$$

$$r_\beta = \hat{r}_\beta(\rho_\gamma, T), \tag{8}$$

$$\mathbf{q} = -\lambda \mathbf{g} - \sum_{\delta=1}^{n-1} \tau_\delta \mathbf{u}_\delta + \sum_{\gamma=1}^{n} \chi_\gamma \mathbf{h}_\gamma, \tag{9}$$

$$\mathbf{k}_\beta = -\xi_\beta \mathbf{g} - \sum_{\delta=1}^{n-1} \nu_{\beta\delta} \mathbf{u}_\delta + \sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathbf{h}_\gamma, \tag{10}$$

$$\mathbf{T}_\alpha = -P_\alpha \mathbf{1}. \tag{11}$$

All coefficients, $\lambda, \tau_\delta, \chi_\gamma, \xi_\beta, \nu_{\beta\delta}, \omega_{\beta\gamma}, P_\alpha$, are functions of scalars ρ_α, T only. Compare these equations with the general constitutive equations of linear fluids mixture given in the book on pages 173-174 and 179-180. Let us substitute them into (4). From (7) we obtain

$$\overset{\backslash\alpha}{f}_\alpha \equiv \overset{\backslash}{f}_\alpha = \frac{\partial \hat{f}_\alpha}{\partial T} \overset{\backslash\alpha}{T} + \sum_{\gamma=1}^{n} \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \overset{\backslash\alpha}{\rho_\gamma}$$

and substituting this expression into (4):

$$-T\sigma = M_1 + M_2 + M_3 \leq 0 \tag{12}$$

where

$$M_1 = \sum_{\alpha=1}^{n} \left(\rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial T} + \rho_\alpha s_\alpha \right) \overset{\backslash\alpha}{T}, \tag{13}$$

$$M_2 = \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \overset{\backslash\alpha}{\rho_\gamma} + \sum_{\alpha=1}^{n} f_\alpha r_\alpha, \tag{14}$$

$$M_3 = (1/T)\, \mathbf{q}.\mathbf{g} - \sum_{\alpha=1}^{n} \mathrm{tr}\mathbf{T}_\alpha \mathbf{D}_\alpha + \sum_{\beta=1}^{n-1} \mathbf{k}_\beta.\mathbf{u}_\beta + (1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2. \tag{15}$$

M_1 is modified using the definition of the material derivative (4.3) and the diffusion velocity (4.24) which result in

$$\overset{\backslash\alpha}{T} = \frac{\partial T}{\partial t} + \mathbf{v}_\alpha.\mathbf{g} = \frac{\partial T}{\partial t} + \mathbf{u}_\alpha.\mathbf{g} + \mathbf{v}_n.\mathbf{g}$$

giving finally

$$M_1 = \sum_{\alpha=1}^{n} \rho_\alpha \Big(\frac{\partial \hat{f}_\alpha}{\partial T} + s_\alpha \Big) \frac{\partial T}{\partial t} + \sum_{\beta=1}^{n-1} \rho_\beta \Big(\frac{\partial \hat{f}_\beta}{\partial T} + s_\beta \Big) \mathbf{u}_\beta.\mathbf{g} +$$
$$\sum_{\alpha=1}^{n} \rho_\alpha \Big(\frac{\partial \hat{f}_\alpha}{\partial T} + s_\alpha \Big) \mathbf{v}_n.\mathbf{g}. \tag{16}$$

The partial derivative in M_2 can be modified using the definition of the material derivative (4.3), the diffusion velocity (4.24), and the mass balance (4.17); the latter can be written using (4.24) and (4.8) as:

$$\frac{\partial \rho_\gamma}{\partial t} + \rho_\gamma \mathrm{tr}\mathbf{D}_\gamma + \mathbf{u}_\gamma.\mathbf{h}_\gamma + \mathbf{v}_n.\mathbf{h}_\gamma = r_\gamma. \tag{17}$$

Then, the material derivative of the partial density is:

$$\overset{\backslash\alpha}{\rho_\gamma} \equiv \frac{\partial \rho_\gamma}{\partial t} + \mathbf{v}_\alpha.\mathbf{h}_\gamma = r_\gamma - \rho_\gamma \mathrm{tr}\mathbf{D}_\gamma + (\mathbf{u}_\alpha - \mathbf{u}_\gamma).\mathbf{h}_\gamma. \tag{18}$$

Further,

$$\rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} = \frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma} - f_\alpha \delta_{\alpha\gamma} \tag{19}$$

where $\delta_{\alpha\gamma}$ is Kronecker delta. Expressions (18) and (19) are substituted into (14):

$$M_2 = \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \Big(\frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma} - f_\alpha \delta_{\alpha\gamma} \Big) r_\gamma - \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \rho_\gamma \, \mathrm{tr}\mathbf{D}_\gamma +$$
$$\sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} (\mathbf{u}_\alpha - \mathbf{u}_\gamma).\mathbf{h}_\gamma + \sum_{\alpha=1}^{n} f_\alpha r_\alpha$$

and the next-to-last term can be modified using the Kronecker's delta defined as $\delta_{\beta\gamma} = 1$ for $\beta = \gamma = 1, \ldots, n-1$ and $\delta_{\beta\gamma} = 0$ for $\beta \neq \gamma$ including $\gamma = n$. The result is:

$$
\begin{aligned}
M_2 = & \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma} r_\gamma - \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \rho_\gamma \, \mathrm{tr} \mathbf{D}_\gamma + \\
& \sum_{\gamma=1}^{n} \sum_{\beta=1}^{n-1} \rho_\beta \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} \mathbf{u}_\beta . \mathbf{h}_\gamma - \sum_{\beta=1}^{n-1} \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \, \delta_{\beta\gamma} \mathbf{u}_\beta . \mathbf{h}_\gamma .
\end{aligned}
\tag{20}
$$

Finally, M_3 is modified substituting the constitutive equations (9)–(11):

$$
\begin{aligned}
M_3 = & \sum_{\alpha=1}^{n} P_\alpha \, \mathrm{tr} \mathbf{D}_\alpha - (1/T) \lambda \, \mathbf{g} . \mathbf{g} - \sum_{\delta=1}^{n-1} (1/T) \, \tau_\delta \, \mathbf{u}_\delta . \mathbf{g} + \sum_{\gamma=1}^{n} (1/T) \, \chi_\gamma \mathbf{h}_\gamma . \mathbf{g} - \\
& \sum_{\beta=1}^{n-1} \xi_\beta \, \mathbf{g} . \mathbf{u}_\beta - \sum_{\beta=1}^{n-1} \sum_{\delta=1}^{n-1} \nu_{\beta\delta} \, \mathbf{u}_\delta . \mathbf{u}_\beta + \sum_{\beta=1}^{n-1} \sum_{\gamma=1}^{n} \omega_{\beta\gamma} \mathbf{h}_\gamma . \mathbf{u}_\beta + \\
& (1/2) \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2 .
\end{aligned}
\tag{21}
$$

Substitution of relationships (16), (20), and (21) into (12) gives the following form of entropic inequality:

$$
\begin{aligned}
-T\sigma = & \sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma} r_\gamma + \sum_{\alpha=1}^{n} \rho_\alpha \Big(\frac{\partial \hat{f}_\alpha}{\partial T} + s_\alpha \Big) \frac{\partial T}{\partial t} + \\
& \sum_{\gamma=1}^{n} \Big(P_\gamma - \rho_\gamma \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \Big) \, \mathrm{tr} \mathbf{D}_\gamma + \\
& \sum_{\gamma=1}^{n} \sum_{\beta=1}^{n-1} \Big(\rho_\beta \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} - \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} \, \delta_{\beta\gamma} + \omega_{\beta\gamma} \Big) \mathbf{u}_\beta . \mathbf{h}_\gamma + \\
& \sum_{\gamma=1}^{n} (1/T) \, \chi_\gamma \mathbf{h}_\gamma . \mathbf{g} + \sum_{\alpha=1}^{n} \rho_\alpha \Big(\frac{\partial \hat{f}_\alpha}{\partial T} + s_\alpha \Big) \mathbf{v}_n . \mathbf{g} - \\
& \sum_{\beta=1}^{n-1} \Big((1/T) \, \tau_\beta + \xi_\beta - \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} - \rho_\beta s_\beta \Big) \mathbf{g} . \mathbf{u}_\beta - (1/T) \lambda \, \mathbf{g} . \mathbf{g} - \\
& \sum_{\beta=1}^{n-1} \sum_{\delta=1}^{n-1} \big(\nu_{\beta\delta} - (1/2) \, r_\beta \delta_{\beta\delta} \big) \mathbf{u}_\delta . \mathbf{u}_\beta \leq 0 .
\end{aligned}
\tag{22}
$$

This form can be simplified using the specific free energy of mixture f (4.92), the specific entropy of mixture s (4.91), and the specific chemical potential g_α (4.161); see also (4.160). We also introduce new symbols:

$$\vartheta_\beta = (1/T)\,\tau_\beta + \xi_\beta - \rho_\beta \frac{\partial \hat{f}_\beta}{\partial T} - \rho_\beta s_\beta;\ \beta = 1, \ldots, n-1 \tag{23}$$

and note that

$$\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} = \sum_{\alpha=1}^{n} \Big(\frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma} - \hat{f}_\alpha \delta_{\alpha\gamma} \Big) = g_\gamma - f_\gamma. \tag{24}$$

We can thus make following transformations. From the definition of g_α and f we have

$$g_\gamma = \frac{\partial \rho \hat{f}}{\partial \rho_\gamma} = \frac{\partial}{\partial \rho_\gamma} \rho \sum_{\alpha=1}^{n} w_\alpha f_\alpha = \frac{\partial}{\partial \rho_\gamma} \rho \sum_{\alpha=1}^{n} (\rho_\alpha/\rho) f_\alpha = \sum_{\alpha=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma}$$

and, consequently

$$\sum_{\alpha=1}^{n} \sum_{\gamma=1}^{n} \frac{\partial \rho_\alpha \hat{f}_\alpha}{\partial \rho_\gamma} r_\gamma = \sum_{\gamma=1}^{n} g_\gamma r_\gamma. \tag{25}$$

From similar sources we can derive[2]:

$$\frac{\partial \rho \hat{f}}{\partial T} \equiv \rho \frac{\partial \hat{f}}{\partial T} = \frac{\partial}{\partial T} \sum_{\alpha=1}^{n} \rho_\alpha f_\alpha \equiv \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial T}$$

and thus

$$\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial T} = \rho \frac{\partial \hat{f}}{\partial T}. \tag{26}$$

Further, combining

$$\rho_\beta \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} = \frac{\partial \rho_\beta \hat{f}_\beta}{\partial \rho_\gamma} - \hat{f}_\beta \delta_{\beta\gamma}$$

with (in which (24) was used)

$$-\sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma}\, \delta_{\beta\gamma} \equiv -\delta_{\beta\gamma} \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}_\alpha}{\partial \rho_\gamma} = -(g_\gamma - f_\gamma)\delta_{\beta\gamma} = -g_\gamma \delta_{\beta\gamma} + f_\gamma \delta_{\beta\gamma}$$

we have

$$\rho_\beta \frac{\partial \hat{f}_\beta}{\partial \rho_\gamma} - \sum_{\alpha=1}^{n} \rho_\alpha \frac{\partial \hat{f}}{\partial \rho_\gamma}\, \delta_{\beta\gamma} = \frac{\partial \rho_\beta \hat{f}_\beta}{\partial \rho_\gamma} - g_\gamma \delta_{\beta\gamma}. \tag{27}$$

[2] Note that $f = \sum_\alpha w_\alpha f_\alpha = (1/\rho) \sum_\alpha \rho_\alpha f_\alpha$.

Substituting (25) to (27), inequality (22) is simplified to:

$$-T\sigma = \sum_{\gamma=1}^{n} g_\gamma r_\gamma + \rho\Big(\frac{\partial \hat{f}}{\partial T} + s\Big)\frac{\partial T}{\partial t} + \sum_{\gamma=1}^{n}[P_\gamma - \rho_\gamma(g_\gamma - f_\gamma)]\,\mathrm{tr}\mathbf{D}_\gamma +$$
$$\sum_{\gamma=1}^{n}(1/T)\,\chi_\gamma \mathbf{h}_\gamma.\mathbf{g} + \sum_{\gamma=1}^{n}\sum_{\beta=1}^{n-1}\Big(\frac{\partial \rho_\beta \hat{f}_\beta}{\partial \rho_\gamma} - g_\gamma \delta_{\beta\gamma} + \omega_{\beta\gamma}\Big)\mathbf{u}_\beta.\mathbf{h}_\gamma +$$
$$\rho\Big(\frac{\partial \hat{f}}{\partial T} + s\Big)\mathbf{v}_n.\mathbf{g} - \sum_{\beta=1}^{n-1}\vartheta_\beta\,\mathbf{g}.\mathbf{u}_\beta - (1/T)\lambda\,\mathbf{g}.\mathbf{g} -$$
$$\sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1}\big(\nu_{\beta\delta} - (1/2)\,r_\beta \delta_{\beta\delta}\big)\mathbf{u}_\delta.\mathbf{u}_\beta \le 0. \tag{28}$$

All quantities in this inequality

$$g_\gamma, r_\gamma, f, s, P_\gamma, f_\gamma, \omega_{\beta\gamma}, \chi_\gamma, \vartheta_\beta, \lambda, \nu_{\beta\delta}$$

are functions of scalars ρ_γ, T only. Following variables are mutually independent and can be selected arbitrarily:

$$\rho_\gamma, \mathbf{h}_\gamma.\mathbf{u}_\beta, \mathbf{v}_n, \mathrm{tr}\mathbf{D}_\gamma, T, \partial T/\partial t, \mathbf{g}. \tag{29}$$

We can apply Lemma A.5.1 on page 296 in the book. The independent variables ρ_γ, T are fixed at arbitrarily selected values and then suitable quantities from (29), playing the role of X in Lemma A.5.1, are also fixed at proper values.

In this way we find that

$$\frac{\partial \hat{f}}{\partial T} = -s \tag{30}$$

and

$$P_\gamma = \rho_\gamma(g_\gamma - f_\gamma); \quad \gamma = 1, \ldots, n \tag{31}$$

for $X = \partial T/\partial t$ and $X = \mathrm{tr}\mathbf{D}_\gamma$, respectively. Choosing $X = \mathbf{h}_\gamma$ with $\mathbf{g} = \mathbf{o}$, $\mathbf{u}_\beta \neq \mathbf{o}$ we see that

$$\omega_{\beta\gamma} = g_\gamma \delta_{\beta\gamma} - \frac{\partial \rho_\beta \hat{f}_\beta}{\partial \rho_\gamma}; \quad \gamma = 1, \ldots, n; \beta = 1, \ldots, n-1. \tag{32}$$

Similarly, choosing $X = \mathbf{h}_\gamma$ with $\mathbf{g} \neq \mathbf{o}$, $\mathbf{u}_\beta = \mathbf{o}$:

$$\chi_\gamma = 0; \quad \gamma = 1, \ldots, n \tag{33}$$

Consequently, (28) is modified to:

$$T\sigma = -\sum_{\gamma=1}^{n} g_\gamma r_\gamma + \sum_{\beta=1}^{n-1} \vartheta_\beta\, \mathbf{g}.\mathbf{u}_\beta + (1/T)\lambda\, \mathbf{g}.\mathbf{g} +$$
$$\sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1} \big(\nu_{\beta\delta} - (1/2)\, r_\beta \delta_{\beta\delta}\big)\mathbf{u}_\delta.\mathbf{u}_\beta \geq 0 \qquad (34)$$

Summarizing: the (thermodynamic) constitutive equations in the discussed mixture are (5)–(7), $f = \hat{f}(\rho_\gamma, T)$, $s = \hat{s}(\rho_\gamma, T)$ and fulfill relationships (30) and (31). The partial stress tensor (11) is determined by the partial pressure $P_\alpha = \hat{P}_\alpha(\rho_\gamma, T)$ which appears in (31). The transport coefficients $\omega_{\beta\gamma}$ are also determined by thermodynamic quantities, cf. (32). The constitutive equations for the reaction rates are given by (8); r_n follows from the balance (4.20) in the book. Constitutive equations for (linear) transport phenomena are

$$\mathbf{q} = -\lambda \mathbf{g} - \sum_{\delta=1}^{n-1} \tau_\delta \mathbf{u}_\delta \qquad (35)$$

for the heat transport and (10) for the interactions (cross-effects); note that both contain the diffusion velocity, i.e. diffusion as another transport phenomenon. The result (33) tells that heat flow cannot arise from composition gradient. All coefficients λ, τ_δ, ξ_β, $\nu_{\beta\delta}$, $\omega_{\beta\gamma}$ are functions of scalars ρ_γ, T only. Those functions are generally non-linear but only $\omega_{\beta\gamma}$ are determined by thermodynamic quantities as (32) shows.

Equations (8) show that reaction rates are independent of $\mathbf{g}$ and $\mathbf{u}_\beta$. Choosing $\mathbf{g} = \mathbf{o}$ and $\mathbf{u}_\beta = \mathbf{o}$ it follows from (34) that the contribution of the reaction rates to the entropy change (entropy inequality) is non-negative:

$$\Pi_\mathrm{r} \equiv -\sum_{\gamma=1}^{n} g_\gamma r_\gamma \geq 0. \qquad (36)$$

Inequality (34) can be shortened:

$$T\sigma = \Pi_\mathrm{r} + \Pi_\mathrm{t} \geq 0 \qquad (37)$$

where Π_t is the contribution of the transport phenomena:

$$\Pi_\mathrm{t} \equiv \sum_{\beta=1}^{n-1} \vartheta_\beta\, \mathbf{g}.\mathbf{u}_\beta + (1/T)\lambda\, \mathbf{g}.\mathbf{g} + \sum_{\beta=1}^{n-1}\sum_{\delta=1}^{n-1} \big(\nu_{\beta\delta} - (1/2)\, r_\beta \delta_{\beta\delta}\big)\mathbf{u}_\delta.\mathbf{u}_\beta. \qquad (38)$$

For any selection of ρ_γ and T, Π_r is non-negative constant and Π_t is quadratic form with constant coefficients. Choosing all components of $\mathbf{g}$ and $\mathbf{u}_\beta$ sufficiently big, the form Π_t outweighs the constant Π_t. Consequently, also

$$\Pi_\mathrm{t} \geq 0. \tag{39}$$

This proof of (39) is more illustrative if the form (38) is transformed into the canonical form. We only remind that this form contains quadratic terms only (it is called also the diagonal form) and that law of inertia of quadratic forms says that all canonical forms of a quadratic form have the same number of positive, of negative, and of zero coefficients.

From Sylvester theorem on positive semi-definite quadratic forms and (38) follows:

$$\lambda \geq 0 \tag{40}$$

or

$$\nu_{\beta\beta} \geq (1/2)\, r_\beta. \tag{41}$$

The coefficient λ is thermal conductivity and (40) says that it cannot be negative. Relationship (41) expresses a limitation of reaction rates by diffusion (the coefficients $\nu_{\beta\beta}$ are closely related to diffusion coefficients). For example, in binary reaction mixture $\nu_{11} \geq (1/2)\, r_1$.