IRREVERSIBLE (RATIONAL) THERMODYNAMICS OF MIXTURES OF A SOLID SUBSTANCE WITH CHEMICALLY REACTING FLUIDS

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The method of rational thermodynamics of Truesdell's school (non-linear thermomechanics of continuum) has been applied to mixtures of a solid substance with chemically reacting fluids. The kinematics, balances, and stoichiometry in such mixtures are formulated, and constitutive equations are proposed involving the effects of diffusion, heat conduction, and long-term memory expressed by internal parameters. The final form of the constitutive equations has been obtained by applying the constitutive entropic principle of Coleman and Noll. The equilibrium in the mixture is discussed.

The present paper deals with both reversible and irreversible (transport) phenomena in mixtures of a solid with chemically reacting fluids (e.g. gases) with the aim to use the results in the description of heterogeneous catalysis[1]. We use the method of rational thermodynamics (non-linear mechanics of continuum) of Truesdell's school[2-7] and the results of our preceding works[8,9] about mixtures of a solid with non-reacting fluids. In contrast to the earlier thermodynamic analyses of such mixtures[6,10] we consider also the influence of internal (hidden) parameters modelling some memory effects, which may in heterogeneous catalysis represent, e.g., the influence of adsorption, desorption, or surface reaction[1].

Basic Concepts and Kinematics

As in the preceding work[8], vectors and tensors are denoted by small and capital bold type letters; Cartesian components and the summation rule are used in complicated expressions. These components are denoted by Latin superscripts: lower case for space (Euler) coordinates, upper case for reference (Lagrange) coordinates. The motion of a mixture of n constituents, of which the n-th is solid (or more precisely a substance of arbitrary symmetry) and the other are fluid, can be described as superposition of motions of the constituents $\alpha = 1, 2, \ldots, n$

$$\boldsymbol{x} = \chi_\alpha(\boldsymbol{X}_\alpha, t) \tag{1}$$

representing mapping of the particles $\mathbf{X}_\alpha$ (positions in the body of the constituent α in its reference configuration) into the point $\mathbf{x}$ in the mixture at the instant t (here exceptionally $\mathbf{X}_\alpha$ denotes vector; deviations from the notation of subscripts will occur below in stoichiometry). In actual configuration, all n particles $\mathbf{X}_\alpha$ of the constituent bodies hence occupy any point in the mixture at an instant t (compare[2−4,6]). We assume that the mapping (1) is invertible with respect to $\mathbf{X}_\alpha$, so that the deformation gradient $\mathbf{F}_\alpha$ defined as

$$\mathbf{F}_\alpha \equiv \operatorname{Grad} \chi_\alpha, \quad \text{or} \quad F_\alpha^{iJ} = \frac{\partial \chi_\alpha^i}{\partial X_\alpha^J} \tag{2}$$

is a regular tensor. Hence

$$E_\alpha \equiv \left|\det \mathbf{F}_\alpha\right| \neq 0. \tag{3}$$

The second deformation gradient is defined as

$$\mathbf{G}_\alpha \equiv \operatorname{Grad} \mathbf{F}_\alpha, \quad \text{i.e.} \quad G_\alpha^{iJK} = \partial F_\alpha^{iJ} / \partial X_\alpha^K. \tag{4}$$

We note that

$$\operatorname{Grad} E_\alpha = E_\alpha \operatorname{tr} \mathbf{F}_\alpha^{-1} \mathbf{G}_\alpha \quad \text{or} \quad \partial E_\alpha / \partial X_\alpha^K = E_\alpha F_\alpha^{-1\,Ji} G_\alpha^{iJK}, \tag{5}$$

where -1 denotes inversion. The velocity $\mathbf{v}_\alpha$ of constituent α is defined as

$$\mathbf{v}_\alpha \equiv \partial \chi_\alpha / \partial t \tag{6}$$

and the (spatial) velocity gradient $\mathbf{L}_\alpha$ is defined as

$$\mathbf{L}_\alpha \equiv \operatorname{grad} \mathbf{v}_\alpha \quad \text{i.e.} \quad L_\alpha^{ij} = \partial v_\alpha^i / \partial x^j \tag{7}$$

(the reference and spatial gradients are respectively denoted as Grad and grad). The diffusion velocity $\mathbf{u}_\alpha$ of constituent α (with respect to the solid constituent) is

$$\mathbf{u}_\alpha \equiv \mathbf{v}_\alpha - \mathbf{v}_n \tag{8}$$

and accordingly $\mathbf{u}_n = \mathbf{o}$. Hence, by the invertibility relation (1), we have for any quantity $\psi = \psi(\mathbf{x}, t)$ of the mixture also $\psi = \psi(\mathbf{X}_\alpha, t)$, and the time derivative of the latter function is denoted as material derivative, $\mathrm{D}_\alpha \psi / \mathrm{D}t$, for which we have

$$\mathrm{D}_\alpha \psi / \mathrm{D}t = \partial \psi / \partial t + \mathbf{v}_\alpha \cdot \operatorname{grad} \psi, \tag{9}$$

where $\partial \psi / \partial t$ is the time derivative of $\psi(\mathbf{x}, t)$. For the n-th constituent (solid), we shall

use the notation

$$D_n\psi/Dt \equiv \dot{\psi} \tag{10}$$

and accordingly

$$D_\alpha\psi/Dt = \dot{\psi} + \boldsymbol{u}_\alpha \, . \, \text{grad } \psi \, . \tag{11}$$

So, e.g. $\boldsymbol{v}_\alpha = D_\alpha\chi_\alpha/Dt$ or

$$\boldsymbol{L}_\alpha = (D_\alpha\boldsymbol{F}_\alpha/Dt) \, \boldsymbol{F}_\alpha^{-1} \, . \tag{12}$$

General Postulates

Here, we give the conservation laws and the second law of thermodynamics in local forms in the reacting mixture[2,10] (for derivation from postulated global balances see refs[6,7]).

The balances of the constituent masses are

$$D_\alpha\varrho_\alpha/Dt + \varrho_\alpha \, \text{div } \boldsymbol{v}_\alpha = r_\alpha \, , \quad \alpha = 1 \, , \dots, n \, , \tag{13}$$

where ϱ_α denotes density (mass concentration) of constituent α in the mixture and r_α is the production of its mass per unit time in unit volume due to chemical reactions. The balances (13) can, with respect to Eq. (9), be rewritten in the form

$$\partial\varrho_\alpha/\partial t + \text{div } \varrho_\alpha\boldsymbol{v}_\alpha = r_\alpha \, . \tag{14}$$

From this we derive the (spatial) gradient

$$\partial\boldsymbol{h}_\alpha/\partial t + (\text{grad } \boldsymbol{h}_\alpha) \, \boldsymbol{v}_\alpha + \varrho_\alpha \, \text{div } \boldsymbol{L}_\alpha^T + \boldsymbol{h}_\alpha\boldsymbol{L}_\alpha + \boldsymbol{h}_\alpha \, \text{tr } \boldsymbol{L}_\alpha = \text{grad } r_\alpha \, , \tag{15}$$

where div $\boldsymbol{L}_\alpha^T$ is in the component form $\partial L_\alpha^{ij}/\partial x^i$ (T denotes transposition) and the density gradient is

$$\boldsymbol{h}_\alpha \equiv \text{grad } \varrho_\alpha \, , \quad \alpha = 1, \dots, n \, . \tag{16}$$

If we set by definition[10]

$$\gamma_\alpha \equiv E_\alpha\varrho_\alpha \tag{17}$$

then the mass balance of constituent α (13) can be written as

$$D_\alpha\gamma_\alpha/Dt = E_\alpha r_\alpha \, , \tag{18}$$

where use was made of the Euler equation

$$D_\alpha E_\alpha/Dt = E_\alpha \, \text{div } \boldsymbol{v}_\alpha \, . \tag{19}$$

We shall concentrate on the case where the n-th constituent (solid) does not react

$$r_n \equiv 0 \tag{20}$$

(however, it can have an influence on the reaction velocity as a heterogeneous catalyst[1]). For this constituent, the mass balance can be obtained by integration of Eq. (18) in the form

$$\gamma_n = \varrho_n E_n = \varrho_n |\det F_n| = \varrho_n^* \tag{21}$$

where ϱ_n^* is the density in reference configuration of component n, considered as known (as the field $\varrho_n^*(X_n)$). The mass balance of the mixture is given by

$$\sum_{\alpha=1}^{n} r_\alpha = \sum_{\beta=1}^{n-1} r_\beta = 0 . \tag{22}$$

The momentum balance of constituent α is

$$\varrho_\alpha \, D_\alpha v_\alpha / Dt = \text{div } T_\alpha + \varrho_\alpha (b_\alpha + i_\alpha) + k_\alpha , \tag{23}$$

where T_α is the (partial) stress tensor of constituent α, k_α is the interaction volume force acting on constituent α (originating from the other constituents), b_α is the external volume force acting on it (e.g. gravitation), and i_α is the apparent force acting on it (only in non-inertial reference systems).

The momentum balance of the mixture is

$$\sum_{\alpha=1}^{n} (k_\alpha + r_\alpha v_\alpha) = \mathbf{o} \tag{24}$$

and the balance of the moment of momentum of constituent α is

$$M_\alpha = T_\alpha - T_\alpha^T , \tag{25}$$

where M_α denotes the moment of forces (in unit volume) acting on it and originating from the other constituents (directly, i.e. not mediated by the moments of forces from the balance (23)). For $M_\alpha \equiv \mathbf{O}$ the tensors T_α are symmetrical.

The balance of the moment of momentum of the mixture has the form

$$\sum_{\alpha=1}^{n} M_\alpha = \mathbf{O} \tag{26}$$

and the balance of the energy of the mixture is

$$\sum_{\alpha=1}^{n} \varrho_\alpha \, D_\alpha u_\alpha / Dt + \sum_{\alpha=1}^{n} r_\alpha u_\alpha = \sum_{\alpha=1}^{n} \text{tr } T_\alpha^T L_\alpha - \text{div } q +$$

$$+ Q - \sum_{\alpha=1}^{n} \boldsymbol{k}_\alpha \cdot \boldsymbol{u}_\alpha - \tfrac{1}{2} \sum_{\alpha=1}^{n} r_\alpha u_\alpha^2 \,, \tag{27}$$

where u_α is the (partial) internal energy of constituent α, $\boldsymbol{q}$ is the heat flux, and Q denotes the heat source (e.g. by radiation). The second law of thermodynamics in the local form corresponds to the Clausius–Duhem inequality

$$\sigma \equiv \sum_{\alpha=1}^{n} \varrho_\alpha \, \mathrm{D}_\alpha s_\alpha / \mathrm{D}t + \sum_{\alpha=1}^{n} r_\alpha s_\alpha + \mathrm{div}\,(\boldsymbol{q}/T) - Q/T \geqq 0 \,, \tag{28}$$

where s_α is the partial entropy of constituent α, T absolute temperature, and σ denotes the production of entropy. Thus, we concentrate on the case where a single temperature T corresponds to all constituents of the mixture; therefore only the energy balance (27) for the mixture need be considered[2,4−7]. The partial free energy of constituent α is defined by the familiar relation

$$f_\alpha = u_\alpha - T s_\alpha \,, \quad \alpha = 1, \ldots, n \tag{29}$$

By eliminating $\boldsymbol{q}$ and Q from Eqs (27) and (28) and using Eq. (29) we obtain the reduced inequality

$$-T\sigma = \sum_{\alpha=1}^{n} \varrho_\alpha \, \mathrm{D}_\alpha f_\alpha / \mathrm{D}t + \sum_{\alpha=1}^{n} r_\alpha f_\alpha + \sum_{\alpha=1}^{n} \varrho_\alpha s_\alpha \, \mathrm{D}_\alpha T / \mathrm{D}t +$$

$$+ (\boldsymbol{q}/T) \cdot \boldsymbol{g} + \sum_{\alpha=1}^{n} \boldsymbol{k}_\alpha \cdot \boldsymbol{u}_\alpha - \sum_{\alpha=1}^{n} \mathrm{tr}\, \boldsymbol{T}_\alpha^{\mathrm{T}} \boldsymbol{L}_\alpha + \tfrac{1}{2} \sum_{\alpha=1}^{n} r_\alpha u_\alpha^2 \leqq 0 \,, \tag{30}$$

where

$$\boldsymbol{g} \equiv \mathrm{grad}\, T \tag{31}$$

is the temperature gradient.

Stoichiometry

As usual, we shall assume that all constituents of the mixture (chemical compounds) are composed of atomic substances (e.g. atoms of elements) which do not change during chemical reactions (so-called postulate of permanence of atomic substances), and we shall use the Bowen method[11] for the mathematical treatment (compare[2,6,7]). Let $T_{\sigma\alpha}$ denote the number of atoms of the type σ in the constituent α (there are at most z atoms of the type $\sigma = 1, \ldots, z$ in the mixture). Each atomic substance is characterized by its atomic mass $\mathscr{A}^\sigma$ (here it is preferable to use also superscripts), and accordingly the molar mass of each constituent can be expressed as

$$M_\alpha = \sum_{\sigma=1} \mathscr{A}^\sigma T_{\sigma\alpha} \,. \tag{32}$$

The postulate of permanence acquires the form

$$\sum_{\alpha=1}^{n} T_{\sigma\alpha} J^{\alpha} = 0, \quad \sigma = 1, \ldots, z, \tag{33}$$

where the rate of conversion J^{α} (in moles of constituent α per unit time in unit volume) is

$$J^{\alpha} = r_{\alpha}/M_{\alpha}. \tag{34}$$

Further it is necessary to know the rank, h, of the matrix of $T_{\sigma\alpha}$. Two cases may occur: for $h = n$ the mixture is non-reacting ($r_{\alpha} \equiv 0$ for any α), and for $h < n$ chemical reactions can proceed in the mixture. It can be shown[2,6,7,11] that the postulate of permanence can be equivalently expressed as follows: The abstract n-dimensional vectorial space (in which the vector of molar masses $\mathbf{M}$ or of chemical conversion rates $\mathbf{J}$ can be set up from the components M_{α} or J^{α}) can be decomposed to two subspaces, one of which (of dimension h) always contains the vector $\mathbf{M}$ and the other (so-called reaction subspace of dimension $n - h$) always contains the vector $\mathbf{J}$.

Each base of the $(n - h)$-dimensional reaction subspace corresponds to the choice of $n - h$ independent chemical reactions, and the components J_p of the vector $\mathbf{J}$ in this base express the rates of these reactions. The components J_p and J^{α} are uniquely interdependent, e.g.

$$J^{\alpha} = \sum_{p=1}^{n-h} J_p P^{p\alpha}, \quad \alpha = 1, \ldots, n, \tag{35}$$

where $P^{p\alpha}$ are stoichiometric coefficients of the constituent α in the p-th independent chemical reaction (the matrix of $P^{p\alpha}$ has the rank $n - h$).

Constitutive Equations

Starting from the so-called constitutive principles[2-7] and properties of reacting[6,7,10] and non-reacting mixtures[4,5,8], we shall propose the constitutive equations of a reacting fluid mixture and non-reacting solid substance for the following quantities:

$$\{f_{\alpha}, s_{\alpha}, T_{\alpha}, k_{\beta}, r_{\varphi}, \mathbf{q}, \dot{\beta}_q\} = \mathscr{F}(\mathbf{F}_n, \mathbf{G}_n, \varrho_{\delta}, \mathbf{h}_{\delta}, \mathbf{u}_{\delta}, T, \mathbf{g}, \beta_q) \tag{36}$$

$$\alpha = 1, \ldots, n; \quad \beta, \delta = 1, \ldots, n - 1; \quad \varphi = 1, \ldots, n - 2; \quad q = 1, \ldots, s$$

where $\mathscr{F}$ denotes the constitutive functions $\hat{f}_{\alpha}, \hat{s}_{\alpha}, \hat{\mathbf{T}}_{\alpha}, \hat{\mathbf{k}}_{\beta}, \hat{r}_{\varphi}, \hat{\mathbf{q}}$, and l_q of the independent variables given on the right-hand side. Thus, e.g. the constitutive equations for the material derivatives of the internal parameters $\dot{\beta}_q$ (which are s in number)

with respect to the n-th constituent (compare Eq. (10))* are

$$\dot{\beta}_q = l_q(\boldsymbol{F}_n, \boldsymbol{G}_n, \varrho_1, \ldots, \varrho_{n-1}, \boldsymbol{h}_1, \ldots, \boldsymbol{h}_{n-1}, \boldsymbol{u}_1, \ldots, \boldsymbol{u}_{n-1}, T, \boldsymbol{g}, \beta_1, \ldots, \beta_s)$$

$$q = 1, \ldots, s \, . \tag{37}$$

By the definitions (29), (34), (35), and $(38)-(40)$ it can be seen that the same type of constitutive equations applies for J^x, J_p, u_α, f, s, and g_α; similarly the quantities r_n, r_{n-1} and $\boldsymbol{k}_n$ can be obtained from Eqs (20), (22), and (23). The constitutive equations (36) hence express that the n-th constituent is solid (or of any symmetry) and others are fluid (deformations exert an influence only through the densities[5-7,12]) and obey, among others, the constitutive principles of equipresence (independent variables are in all constitutive equations the same) and objectivity (all variables are independent of the choice of the reference system; we shall not deal with isotropicity of the constitutive functions, leading to further reduction of their form, since the tensor character of β_q is not known, not to speak about other reasons).

The most important restrictions referring to the constitutive equations (1) follow from the principle of dissipation (or admissibility)[13,14], to which the rest of the present work is devoted (see also[2-8,10]). According to this principle, the Clausius––Duhem inequality (28) is satisfied for all processes obeying the balances in the material with constitutive equations (36) (so-called admissible thermodynamic processes). For all such processes the reduced inequality (30) must be satisfied, whence follow aditional restrictions referring to the constitutive equations (36).

We introduce the free energy of the mixture, f

$$\varrho f = \sum_{\alpha=1}^{n} \varrho_\alpha f_\alpha \tag{38}$$

the entropy of the mixture, s

$$\varrho s = \sum_{\alpha=1}^{n} \varrho_\alpha s_\alpha \tag{39}$$

and chemical potential, g_α, of the constituent α

$$g_\alpha = \partial \varrho \hat{f} / \partial \varrho_\alpha \quad \alpha = 1, \ldots, n \, , \tag{40}$$

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* We use this derivative owing to the special function of the n-th constituent in our model. However, it may be that a constitutive equation of the type (37) could be used for $\mathrm{D}_\alpha \beta_q / \mathrm{D}t$ with $\alpha \neq n$. Yet such model is generally different, as can be seen when $\dot{\beta}_q$ is recalculated to $\mathrm{D}_\alpha \beta_q / \mathrm{D}t$ for $\alpha \neq n$ (by Eq. (11)): in fact, owing to grad β the constitutive equations for $\mathrm{D}_\alpha \beta_q / \mathrm{D}t$ are not functions of the type (37), but functionals depending also on the history (past values) of the dependent variables.

where ϱ is the density of the mixture

$$\varrho = \sum_{\alpha=1}^{n} \varrho_\alpha \tag{41}$$

(note that f, s, and g_α are given by a constitutive equation of the type (36)). By introducing the constitutive equations (36) into Eq. (30) we obtain after rearrangement (particularly of the term $D_\alpha f_\alpha / Dt$) using Eqs (9), (11), (14) (to express $\partial \varrho_\delta / \partial t$), (15) (to express $\partial h_\alpha / \partial t$), and $(38)-(40)$ finally the following inequality:

$$
\begin{aligned}
-T\sigma &= \sum_{\alpha=1}^{n} g_\alpha r_\alpha + \sum_{\varphi=1}^{n-2} \left[(\partial \hat{f} / \partial h_\varphi^i) - (\partial \hat{f} / \partial h_{n-1}^i) \right] \left[(\partial \hat{r}_\varphi / \partial F_n^{jJ}) G_n^{jJK} F_n^{-1\,Ki} + \right. \\
&\quad + (\partial \hat{r}_\varphi / \partial G_n^{jJK} (\mathrm{Grad}\, \mathbf{G}_n)^{jJKL} F_n^{-1\,Li} + \sum_{\delta=1}^{n-1} (\partial \hat{r}_\varphi / \partial \varrho_\delta)\, h_\delta^i + \\
&\quad + \sum_{\delta=1}^{n-1} (\partial \hat{r}_\varphi / \partial h_\delta^j)\,(\mathrm{grad}\, \mathbf{h}_\delta)^{ji} + \sum_{\delta=1}^{n-1} (\partial \hat{r}_\varphi / \partial u_\delta^j)\,(L_\delta^{ji} - L_n^{ji}) + \\
&\quad + (\partial \hat{r}_\varphi / \partial T)\, g^i + (\partial \hat{r}_\varphi / \partial g^j)\,(\mathrm{grad}\, \mathbf{g})^{ji} + \sum_{q=1}^{s} (\partial \hat{r}_\varphi / \partial \beta_q)\,(\mathrm{grad}\, \beta_q)^i \Big] + \\
&\quad + \sum_{\delta=1}^{n-1} \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial \mathbf{h}_\delta) . (\mathrm{grad}\, \mathbf{h}_\delta)\, \mathbf{u}_\alpha - \sum_{\delta=1}^{n-1} \varrho(\partial \hat{f} / \partial \mathbf{h}_\delta) . (\mathrm{grad}\, \mathbf{h}_\delta)\, \mathbf{u}_\delta - \\
&\quad - \sum_{\delta=1}^{n-1} \varrho(\partial \hat{f} / \partial \mathbf{h}_\delta)\, \varrho_\delta . \mathrm{grad}\, \mathrm{tr}\, \mathbf{L}_\delta - \sum_{\delta=1}^{n-1} \varrho(\partial \hat{f} / \partial \mathbf{h}_\delta) . \mathbf{h}_\delta \mathbf{L}_\delta - \\
&\quad - \sum_{\delta=1}^{n-1} \varrho(\partial \hat{f} / \partial \mathbf{h}_\delta) . \mathbf{h}_\delta\, \mathrm{tr}\, \mathbf{L}_\delta + \sum_{\delta=1}^{n-1} \varrho(\partial \hat{f} / \partial \mathbf{u}_\delta) . (\partial \mathbf{v}_\delta / \partial t) - \sum_{\delta=1}^{n-1} \varrho(\partial \hat{f} / \partial \mathbf{u}_\delta) . \dot{\mathbf{v}}_n + \\
&\quad + \varrho(\partial \hat{f} / \partial F_n^{iJ})\, F_n^{jJ} L_n^{ij} - \sum_{\alpha=1}^{n} \sum_{\delta=1}^{n-1} \varrho_\alpha (\partial \hat{f}_\alpha / \partial u_\delta^i)\, u_\alpha^j L_n^{ij} - T_n^{ij} L_n^{ij} + \\
&\quad + \sum_{\delta=1}^{n-1} \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial u_\delta^i)\, v_\alpha^j L_\delta^{ij} - \sum_{\delta=1}^{n-1} T_\delta^{ij} L_\delta^{ij} - \sum_{\delta=1}^{n-1} \sum_{\alpha=1}^{n} \varrho_\delta \varrho_\alpha (\partial \hat{f}_\alpha / \partial \varrho_\delta)\, \delta^{ij} L_\delta^{ij} + \\
&\quad + \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial F_n^{iJ})\, u_\alpha^j G_n^{iJK} F_n^{-1\,Kj} + \sum_{\delta=1}^{n-1} \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial \varrho_\delta)\,(\mathbf{u}_\alpha - \mathbf{u}_\delta) . \mathbf{h}_\delta + \\
&\quad + (\partial \hat{f} / \partial G_n^{iJK})\, \dot{G}_n^{iJK} + \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial G_n^{iJK})\, u_\alpha^j (\mathrm{Grad}\, \mathbf{G}_n)^{iJKL} F_n^{-1\,Lj} + \\
&\quad + \varrho((\partial \hat{f} / \partial T) + s)\,(\partial T / \partial t) + \sum_{\alpha=1}^{n} \varrho_\alpha ((\partial \hat{f}_\alpha / \partial T) + s_\alpha)\, \mathbf{v}_\alpha . \mathbf{g} + \\
&\quad + \varrho(\partial \hat{f} / \partial \mathbf{g}) . (\partial \mathbf{g} / \partial t) + \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial g^i)\,(\mathrm{grad}\, \mathbf{g})^{ij}\, v_\alpha^j + \sum_{q=1}^{s} \varrho(\partial \hat{f} / \partial \beta_q)\, \dot{\beta}_q + \\
&\quad + \sum_{q=1}^{s} \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial \beta_q)\, \mathbf{u}_\alpha . \mathrm{grad}\, \beta_q + (1/T)\, \mathbf{q} . \mathbf{g} + \sum_{\delta=1}^{n-1} \mathbf{k}_\delta . \mathbf{u}_\delta + \\
&\quad + \sum_{\alpha=1}^{n} (1/2)\, r_\alpha \mathbf{u}_\alpha^2 \leq 0 .
\end{aligned}
\tag{42}
$$

As already mentioned, according to the dissipation principle the entropic inequality (28) and hence also the reduced inequality (30) must be satisfied for all admissible thermodynamic processes, i.e. for all fields of motion (deformations), temperature, density, and internal parameters and the corresponding responses of the constitutive equations (36), which satisfy all balances (13)−(27). The energy balance (27) or the momentum balance of the constituent (23) are satisfied by suitable Q or $\boldsymbol{b}_\alpha$ (or $\boldsymbol{b}_\alpha + \boldsymbol{i}_\alpha$), since these fields can essentially be determined from the outside of the mixture. The balances of momentum (24) and mass (22) of the mixture are satisfied by suitable $\boldsymbol{k}_n$ or r_{n-1}. Hence, according to the mentioned principle the inequality (42) must also be satisfied for all fields of motion, densities, and internal parameters chosen in the material with constitutive equations (36) so that the mass balances of the constituents (13) or (18) be also satisfied. Particularly, the inequality (42) must be satisfied for the following fields in a mixture where $\boldsymbol{y}$ is an arbitrary point with particles $\boldsymbol{Y}_\alpha$ of all constituents $\alpha = 1, \ldots, n$ at any instant τ and $\boldsymbol{x}$ is an arbitrary point with particles $\boldsymbol{X}_\alpha$ of all constituents at a certain instant t:

The field of motion for n-th constituent

$$
\begin{aligned}
y^i = \chi_n^i(\boldsymbol{Y}_n, \tau) = {} & x^i + v_n^i(\tau - t) + F_n^{iJ}(Y_n^J - X_n^J) + \tfrac{1}{2}G_n^{iJK}(Y_n^J - X_n^J)(Y_n^K - X_n^K) + \\
& + L_n^{ij}F_n^{jJ}(Y_n^J - X_n^J)(\tau - t) + \tfrac{1}{2}\dot{v}_n^i(\tau - t)^2 + \\
& + \tfrac{1}{6}(\operatorname{Grad}\boldsymbol{G}_n)^{iJKL}(Y_n^J - X_n^J)(Y_n^K - X_n^K)(Y_n^L - X_n^L) + \tfrac{1}{2}G_n^{iJK}(Y_n^J - X_n^J)\cdot \\
& \cdot (Y_n^K - X_n^K)(\tau - t),
\end{aligned}
\tag{43}
$$

where use was made of Eq. (12) for $\boldsymbol{F}_n$.

An analogous field can be chosen for the chemically reacting constituents, $\beta = 1, \ldots, n - 1$; their references are chosen so that in the point $\boldsymbol{x}$ and instant t

$$
\boldsymbol{F}_\beta = \boldsymbol{1}, \quad \boldsymbol{G}_\beta = \boldsymbol{O}, \quad \operatorname{Grad}\boldsymbol{G}_\beta = \boldsymbol{O}
\tag{44}
$$

and use is made of Eqs (9) and (10)

$$
\begin{aligned}
y^i = \chi_\beta^i(\boldsymbol{Y}_\beta, \tau) = {} & x^i + v_\beta^i(\tau - t) + \delta^{iJ}(Y_\beta^J - X_\beta^J) + L_\beta^{ij}\delta^{jJ}(Y_\beta^J - X_\beta^J)(\tau - t) + \\
& + \tfrac{1}{2}(\partial v_\beta^i/\partial t + v_\beta^j L_\beta^{ij})(\tau - t)^2 + \tfrac{1}{2}(\operatorname{grad}\boldsymbol{L}_\beta)^{ijk}\delta^{kK}\delta^{jJ}(Y_\beta^J - X_\beta^J)(Y_\beta^K - X_\beta^K)(\tau - t),
\end{aligned}
\tag{45}
$$

where δ^{iJ} are shifters[15] (or Kronecker delta symbols, when the space and reference coordinates coincide).

The temperature field is chosen as follows:

$$
\begin{aligned}
T(\boldsymbol{y}, \tau) = {} & T + (\partial T/\partial t)(\tau - t) + g^i(y^i - x^i) + \tfrac{1}{2}(\operatorname{grad}\boldsymbol{g})^{ij}(y^i - x^i)(y^j - x^j) + \\
& + (\partial g^i/\partial t)(y^i - x^i)(\tau - t).
\end{aligned}
\tag{46}
$$

In the fields above, all the quantities

$$\mathbf{v}_{\alpha}, \mathbf{G}_n, \mathbf{F}_n, \dot{\mathbf{v}}_n, \text{Grad } \mathbf{G}_n, \dot{\mathbf{G}}_n, \partial \mathbf{v}_{\beta}/\partial t, \text{grad } \mathbf{L}_{\beta}, \mathbf{L}_{\alpha}, \tag{47}$$

$$T, \partial T/\partial t, \mathbf{g}, \text{grad } \mathbf{g}, \partial \mathbf{g}/\partial t \quad \alpha = 1, \dots, n; \quad \beta = 1, \dots, n-1 \tag{48}$$

are taken at the point $\mathbf{x}$ with particles $\mathbf{X}_{\alpha}$ at the instant t.

Let us further consider the field of the quantities γ_{β} (17) in a body with particles $\mathbf{Y}_{\beta}$, but at a chosen instant t (in contrast to (43), (45), and (46))

$$\gamma_{\beta}(\mathbf{Y}_{\beta}, t) = \gamma_{\beta} + (\text{Grad } \gamma_{\beta})^{\text{J}} (Y_{\beta}^{\text{J}} - X_{\beta}^{\text{J}}) +$$
$$+ \tfrac{1}{2}(\text{Grad} (\text{Grad } \gamma_{\beta}))^{\text{JK}} (Y_{\beta}^{\text{J}} - X_{\beta}^{\text{J}})(Y_{\beta}^{\text{K}} - X_{\beta}^{\text{K}}) = \varrho_{\beta} +$$
$$+ h_{\beta}^{i}\delta^{i\text{J}}(Y_{\beta}^{\text{J}} - X_{\beta}^{\text{J}}) + \tfrac{1}{2}(h_{\beta}^{i}h_{\beta}^{j}\delta^{i\text{K}}\delta^{j\text{L}} + \tag{49}$$
$$+ (\text{grad } h_{\beta})^{ij} \delta^{i\text{K}}\delta^{j\text{L}})(Y_{\beta}^{\text{K}} - X_{\beta}^{\text{K}})(Y_{\beta}^{\text{L}} - X_{\beta}^{\text{L}}).$$

In the second expression, use was made of the definitions (4), (5), (16), and (44).

Finally, let us consider the field of internal parameters β_q in the mixture at the point $\mathbf{y}$ but again only at the chosen instant t

$$\beta_q(\mathbf{Y}_n, t) = \beta_q + (\text{grad } \beta_q)^{i} F_n^{i\text{J}}(Y_n^{\text{J}} - X_n^{\text{J}}) \quad q = 1, \dots, s. \tag{50}$$

Here again, the quantities $F_n^{i\text{J}}$ and

$$\varrho_{\beta}, \mathbf{h}_{\beta}, \text{grad } \mathbf{h}_{\beta} \quad \beta = 1, \dots, n-1 \tag{51}$$

$$\beta_q, \text{grad } \beta_q \quad q = 1, \dots, s \tag{52}$$

are taken at the point $\mathbf{x}$ in chosen particles $\mathbf{X}_{\alpha}$ and at a chosen instant t.

Now, if we choose the values of the quantitites (47), (48), (51), and (52) at an arbitrary point $\mathbf{x}$ (with particles $\mathbf{X}_{\alpha}$) and instant t arbitrarily and mutually independent, we obtain an admissible thermodynamic process. Indeed, such a choice generates the fields of motion (43) and (45) and temperature (46); the field of internal parameters is obtained by solving the differential equations (37) with the initial condition (50) and values (52) at the point $\mathbf{x}$ and instant t. Finally, it remains to satisfy the mass balance of the constituents $\beta = 1, \dots, n-1$ (the mass balance of n-th constituent (21) determines the field ϱ_n by motion (43), since the density of n-th constituent in the reference is conserved as given beforehand), which can be achieved by solving the differential equations (18) with initial conditions (49). According to the dissipation principle, also the inequality (42) must be fulfilled, i.e. it must hold good at a given point $\mathbf{x}$ (with particles $\mathbf{X}_{\alpha}$) and instant t with an arbitrary choice of the quantities (47), (48), (51), and (52). This leads to a restriction of the constitu-

tive equations (36) (and those for s, f, and g_α). Indeed, let us choose, at arbitrary $\boldsymbol{x}$ and t, some values of

$$\boldsymbol{F}_n, \boldsymbol{G}_n, \varrho_\delta, \boldsymbol{h}_\alpha, \boldsymbol{v}_\alpha, T, \boldsymbol{g}, \beta_q \tag{53}$$

for $\alpha = 1, \ldots, n$, $\delta = 1, \ldots, n-1$, $q = 1, \ldots, s$. Thus, the values of the responses (36) and hence of f, s, g_α are determined (compare Eqs (38), (39) and (41); Eq. (21) is used for ϱ_n). The remaining quantities (47), (48), (51), and (52)

$$\boldsymbol{L}_\alpha, \dot{\boldsymbol{v}}_n, \text{Grad } \boldsymbol{G}_n, \dot{\boldsymbol{G}}_n, \partial\boldsymbol{v}_\beta/\partial t, \text{grad } \boldsymbol{L}_\beta, \text{grad } \boldsymbol{g},$$
$$\partial\boldsymbol{g}/\partial t, \text{grad } \boldsymbol{h}_\beta, \text{grad } \beta_q, \partial T/\partial t \tag{54}$$

are fixed except for, e.g., the last one, $\partial T/\partial t$. Since the inequality (42) depends linearly on this quantity, the corresponding multiplicative term must be equal to zero

$$\partial\hat{f}/\partial T = -s \tag{55}$$

and this is an identity, since the quantities (53) are arbitrary. Analogously, by choosing a suitable grad $\boldsymbol{L}_\beta$ (e.g. with only one non-zero term $\partial L_\beta^{11}/\partial x^i$) with all other quantities (53) and (54) constant we obtain that the multiplicative term standing with grad tr $\boldsymbol{L}_\delta$ in the inequality (42) is equal to zero identically

$$\partial\hat{f}/\partial\boldsymbol{h}_\delta = \boldsymbol{o}, \quad \delta = 1, \ldots, n-1, \tag{56}$$

leading to a simplification of (42). Analogously, from the linearity of the dependence on $\partial\boldsymbol{v}_\delta/\partial t$ in (42) we obtain the identities

$$\partial\hat{f}/\partial\boldsymbol{u}_\delta = \boldsymbol{o}, \quad \delta = 1, \ldots, n-1 \tag{57}$$

and from the linearity in $\dot{G}_n^{iJK}$ follows the identity

$$\partial\hat{f}/\partial G_n^{iJK} = 0 \tag{58}$$

(according to the definition, this derivative has the same symmetry in J, K as G_n^{iJK}) and from the linearity of (42) in $\partial\boldsymbol{g}/\partial t$

$$\partial\hat{f}/\partial\boldsymbol{g} = \boldsymbol{o}. \tag{59}$$

Further we have the terms in (42) linear in $\boldsymbol{L}_\delta$, which by the same procedure lead to the identity for $\delta = 1, \ldots, n-1$

$$\sum_{\alpha=1}^n \varrho_\alpha(\partial\hat{f}_\alpha/\partial u_\delta^i) v_\alpha^j - T_\delta^{ij} - \sum_{\alpha=1}^n \varrho_\alpha\varrho_\delta(\partial\hat{f}_\alpha/\partial\varrho_\delta) \delta^{ij} = 0 \tag{60}$$

and terms linear in L_n give identically

$$- \sum_{\alpha=1}^{n} \sum_{\delta=1}^{n-1} \varrho_\alpha (\partial \hat{f}_\alpha / \partial u_\delta^i) \, u_\alpha^j - T_n^{ij} + \varrho (\partial \hat{f} / \partial F_n^{iJ}) \, F_n^{jJ} = 0 \, . \tag{61}$$

There is a term in (42) linear in the symmetric tensor grad $\boldsymbol{h}_\delta$ and therefore the tensor forming the product with it is antisymmetrical

$$\sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial h_\delta^i) \, u_\alpha^j + \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial h_\delta^j) \, u_\alpha^i = 0 \tag{62}$$

for $\delta = 1, ..., n - 1$, and for the same reason the tensor forming the product with the symmetrical tensor grad $\boldsymbol{g}$ in (42) is also antisymmetrical

$$\sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial g^i) \, v_\alpha^j + \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial g^j) \, v_\alpha^i = 0 \, . \tag{63}$$

Now, we have a term in (42) linear in the arbitrary Grad $\boldsymbol{G}_n$ and again this expression must cancel out. Then, with respect to symmetry of $(\text{Grad } \boldsymbol{G}_n)^{iJKL}$ in the superscripts J, K, L (only 30 components out of 81 are independent), the tensor D^{iJKL} of the 4th order

$$D^{iJKL} \equiv \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial G_n^{iJK}) \, F_n^{-1 \, Lj} u_\alpha^j \tag{64}$$

satisfies the relations[6,16]

$$D^{\mathbf{iJJJ}} = 0 \, , \quad D^{\mathbf{iJJK}} + D^{\mathbf{iJKJ}} + D^{\mathbf{iKJJ}} = 0 \, ,$$

$$D^{\mathbf{i}123} + D^{\mathbf{i}312} + D^{\mathbf{i}231} + D^{\mathbf{i}132} + D^{\mathbf{i}213} + D^{\mathbf{i}321} = 0 \, , \quad \mathbf{i, J, K, L} = 1, 2, 3 \, , \tag{65}$$

where the bold type superscripts are excluded from the summation rule.

At last, we have a term in (42) that depends linearly on grad β_q; this is, however, arbitrary (compare Eq. (50)), hence

$$\sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial \beta_q) \, \boldsymbol{u}_\alpha = \boldsymbol{o} \, , \quad q = 1, ..., s \tag{66}$$

and so the inequality (42) is reduced to

$$- T\sigma = \sum_{\alpha=1}^{n} g_\alpha r_\alpha + \sum_{\alpha=1}^{n} \varrho_\alpha (\partial \hat{f}_\alpha / \partial F_n^{iJ}) \, u_j^\alpha G_n^{iJK} F_n^{-1 \, Kj} +$$

$$+ \sum_{\alpha=1}^{n} \sum_{\delta=1}^{n-1} \varrho_\alpha (\partial \hat{f}_\alpha / \partial \varrho_\delta) \, (\boldsymbol{u}_\alpha - \boldsymbol{u}_\delta) \, . \, \boldsymbol{h}_\delta + \sum_{\alpha=1}^{n} \varrho_\alpha ((\partial \hat{f}_\alpha / \partial T) + s_\alpha) \, \boldsymbol{v}_\alpha \, . \, \boldsymbol{g} +$$

$$+ \sum_{q=1}^{s} \varrho (\partial \hat{f} / \partial \beta_q) \, \dot{\beta}_q + (1/T) \, \boldsymbol{q} \, . \, \boldsymbol{g} + \sum_{\delta=1}^{n-1} \boldsymbol{k}_\delta \, . \, \boldsymbol{u}_\delta + \tfrac{1}{2} \sum_{\alpha=1}^{n} r_\alpha u_\alpha^2 \leqq 0 \, . \tag{67}$$

With the aid of the results (8), (55), (57), and (59) the expressions (60), (63), and (67) can further be rearranged as follows. From Eq. (60) we obtain

$$T_\delta^{ij} + \sum_{\alpha=1}^{n} \varrho_\alpha \varrho_\delta (\partial \hat{f}_\alpha / \partial \varrho_\delta)\, \delta^{ij} - \sum_{\beta=1}^{n-1} \varrho_\beta (\partial \hat{f}_\beta / \partial u_\delta^i)\, u_\beta^j = 0 \tag{68}$$

for $\delta = 1, \ldots, n-1$, and from Eq. (63)

$$\sum_{\alpha=1}^{n} \left(\varrho_\alpha (\partial \hat{f}_\alpha / \partial g^i)\, u_\alpha^j + \varrho_\alpha (\partial \hat{f}_\alpha / \partial g^j)\, u_\alpha^i \right) = 0 \tag{69}$$

and finally the inequality (67) can be rewritten as

$$-T\sigma = \tfrac{1}{2} \sum_{\beta=1}^{n-1} r_\beta u_\beta^2 + \sum_{p=1}^{n-h} J_p A^p + \sum_{\beta=1}^{n-1} \boldsymbol{p}_\beta \cdot \boldsymbol{u}_\beta + \boldsymbol{m} \cdot (\boldsymbol{g}/T) + \varrho \sum_{q=1}^{s} a_q \dot{\beta}_q \lesseqgtr 0 , \tag{70}$$

where the affinity a_q for the internal parameter is given as

$$a_q \equiv \partial \hat{f} / \partial \beta_q , \quad q = 1, \ldots, s , \tag{71}$$

the chemical affinity of p-th chemical reaction, A^p (differing in sign from the classical definition) is defined as

$$A^p \equiv \sum_{\alpha=1}^{n} g_\alpha M_\alpha P^{p\alpha} , \quad p = 1, \ldots, n-h , \tag{72}$$

where $g_\alpha M_\alpha$ is the molar chemical potential; further we define

$$\boldsymbol{m} \equiv \boldsymbol{q} + \sum_{\alpha=1}^{n} \varrho_\alpha ((\partial \hat{f}_\alpha / \partial T) + s_\alpha)\, \boldsymbol{u}_\alpha , \tag{73}$$

$$p_\beta^j \equiv k_\beta^j - g_\beta h_\beta^j + \sum_{\delta=1}^{n-1} (\partial \varrho_\beta \hat{f}_\beta / \partial \varrho_\delta)\, h_\delta^j + (\partial \varrho_\beta \hat{f}_\beta / \partial F_n^{iJ})\, G_n^{iJK} F_n^{-1\,Kj} ,$$

$$\beta = 1, \ldots, n-1 . \tag{74}$$

Finally it can be seen from Eqs $(56)-(59)$ that the constitutive equations for f and hence also for s according to Eq. (55) are

$$f = \hat{f}(\boldsymbol{F}_n, \varrho_\delta, T, \beta_q) , \quad s = \hat{s}(\boldsymbol{F}_n, \varrho_\delta, T, \beta_q) . \tag{75}$$

Equilibrium

Keeping in mind the zero production of entropy, we define the equilibrium as a state for which

$$\boldsymbol{u}_\beta = \boldsymbol{o} \equiv \boldsymbol{u}_\beta^\circ \quad \beta = 1, \ldots, n-1 , \quad \boldsymbol{g} = \boldsymbol{o} \equiv \boldsymbol{g}^\circ , \tag{76}, \tag{77}$$

$$r_\varphi^o = 0 \quad \varphi = 1, \ldots, n - 2, \quad \beta_q^o = 0 \quad q = 1, \ldots, s, \qquad (78), (79)$$

(where the superscript 0 refers to equilibrium). Hence, in equilibrium we have $\sigma = 0$ according to Eq. (70). Other independent variables attain their equilibrium values $\mathbf{F}_n^o$, $\mathbf{G}_n^o$, ϱ_δ^o, h_δ^o, T^o, and β_q^o for $\delta = 1, \ldots, n - 1$, $q = 1, \ldots, s$. Hence, for example, according to Eqs (36) and (37)

$$r_\varphi^o = \hat{r}_\varphi(\mathbf{F}_n^o, \mathbf{G}_n^o, \varrho_\delta^o, h_\delta^o, \mathbf{o}, T^o, \mathbf{o}, \beta_q^o) = 0, \qquad (80)$$

$$\beta_q^o = l_q(\mathbf{F}_n^o, \mathbf{G}_n^o, \varrho_\delta^o, h_\delta^o, \mathbf{o}, T^o, \mathbf{o}, \beta_q^o) = 0. \qquad (81)$$

Hence, according to Eqs (20), (22), and (78) $r_\alpha^o = 0$ for $\alpha = 1, \ldots, n$ and in the equilibrium we have according to Eq. (34)

$$J^{\alpha o} = 0 \quad \alpha = 1, \ldots, n, \quad J_p^o = 0 \quad p = 1, \ldots, n - h, \qquad (82), (83)$$

where the latter equation follows from (35) and (82) and from the rank $n - h$ of the matrix of stoichiometric coefficients $P^{p\alpha}$.

It follows from the definitions (76)–(79) that the quantity $T\sigma \equiv \Pi = \hat{\Pi}(\mathbf{F}_n, \mathbf{G}_n, \varrho_\delta, h_\delta, \mathbf{u}_\delta, T, \mathbf{g}, \beta_q)$ has in the equilibrium the value of zero, which is at the same time the minimum (compare Eq. (67)). Hence,

$$\frac{\mathrm{d}}{\mathrm{d}\lambda} \hat{\Pi}(\mathbf{F}_n^o + \lambda\mathbf{C}, \mathbf{G}_n^o + \lambda\mathbf{B}, \varrho_\delta^o + \lambda\alpha_\delta, h_\delta^o + \lambda\gamma_\delta, \lambda\mathbf{u}_\delta, T^o + \lambda\tau, \lambda\mathbf{g}, \beta_q^o + \lambda\xi_q)\big|_{\lambda=0} = 0$$

$$\delta = 1, \ldots, n - 1, \quad q = 1, \ldots, s, \qquad (84)$$

where λ is a real parameter and the quantities $\mathbf{C}$ (tensor of the second order), $\mathbf{B}$ (tensor of the third order), γ_δ, $\mathbf{u}_\delta$, $\mathbf{g}$ (vectors), α_δ, τ, and ξ_q (scalars) are arbitrary (whatever values they have, Π is defined if λ is sufficiently small). For the same reason,

$$\frac{\mathrm{d}^2 \hat{\Pi}}{\mathrm{d}\lambda^2}\bigg|_{\lambda=0} \geqq 0, \qquad (85)$$

however the implications of this inequality will not be dealt with here.

By introducing Eqs (70)–(75) into (84) we obtain for $\lambda = 0$ (with the aid of Eqs (77)–(79) and (83) and constitutive equations (36) and (37)) after rearrangement an expression, which is linear with respect to the arbitrary quantities occurring in Eq. (84), so that the corresponding multiplicative terms, which are given below, must be equal to zero (the term occurring with B_n^{iJK} must be symmetrized with respect to the last two superscripts, since the tensor B_n^{iJK} has the same symmetry — see Eq. (87))

$$\sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial F_n^{iJ})^\circ A^{po} + \sum_{q=1}^{s} \varrho^\circ a_q^\circ (\partial l_q / \partial F_n^{iJ})^\circ = 0 , \tag{86}$$

$$\sum_{p=1}^{n-h} [(\partial \hat{J}_p / \partial G_n^{iJK})^\circ + (\partial \hat{J}_p / \partial G_n^{iKJ})^\circ] A^{po} +$$

$$+ \sum_{q=1}^{s} [(\partial l_q / \partial G_n^{iJK})^\circ + (\partial l_q / \partial G_n^{iKJ})^\circ] \varrho^\circ a_q^\circ = 0 , \tag{87}$$

$$\sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial \varrho_\delta)^\circ A^{po} + \sum_{q=1}^{s} (\partial l_q / \partial \varrho_\delta)^\circ \varrho^\circ a_q^\circ = 0 \quad \delta = 1, ..., n-1 , \tag{88}$$

$$\sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial \mathbf{h}_\delta)^\circ A^{po} + \sum_{q=1}^{s} (\partial l_q / \partial \mathbf{h}_\delta)^\circ \varrho^\circ a_q^\circ = \mathbf{o} \quad \delta = 1, ..., n-1 , \tag{89}$$

$$\sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial T)^\circ A^{po} + \sum_{q=1}^{s} (\partial l_q / \partial T)^\circ \varrho^\circ a_q^\circ = 0 , \tag{90}$$

$$\sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial \beta_r)^\circ A^{po} + \sum_{q=1}^{s} (\partial l_q / \partial \beta_r)^\circ \varrho^\circ a_q^\circ = 0 \quad r = 1, ..., s , \tag{91}$$

$$\sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial u_\beta^j)^\circ A^{po} + \sum_{q=1}^{s} (\partial l_q / \partial u_\beta^j)^\circ \varrho^\circ a_q^\circ + k_\beta^{jo} - g_\beta^\circ h_\beta^{jo} + \tag{92}$$

$$+ \sum_{\delta=1}^{n-1} (\partial \varrho_\beta \hat{J}_\beta / \partial \varrho_\delta)^\circ h_\delta^{jo} + (\partial \varrho_\beta \hat{J}_\beta / \partial F_n^{iJ})^\circ G_n^{iJKo} F_n^{-1 KJo} = 0 ,$$

$$\beta = 1, ..., n-1 ,$$

$$(1/T^\circ) \mathbf{q}^\circ + \sum_{p=1}^{n-h} (\partial \hat{J}_p / \partial \mathbf{g})^\circ A^{po} + \sum_{q=1}^{s} (\partial l_q / \partial \mathbf{g})^\circ \varrho^\circ a_q^\circ = \mathbf{o} . \tag{93}$$

Let us now consider a system of linear homogeneous equations consisting of $n - 1 + s$ equations (88) and (91) for $n - h + s$ unknowns A^{po}, a_q° ($p = 1, ..., n - h$; $q = 1, ..., s$). Since $h \geq 1$, we have $n - 1 + s \geq n - h + s$, hence if we assume that the matrix of this system has the rank $n - h + s$, then in the equilibrium

$$A^{po} = 0 \quad p = 1, ..., n - h , \quad a_q^\circ = 0 \quad q = 1, ..., s . \tag{94}, (95)$$

The mentioned assumption seems plausible, since in the opposite case (if, for the conditions (78) and (79), the conditions (94) and (95) were invalid) we would have to deal with "frozen" chemical reactions or internal parameters.

Conversely, it would be possible to use the conditions (94) and (95) to define the so-called strong equilibrium[2] in place of the conditions (78) and (79), which can then be derived under a similar plausible assumption as a consequence.

The resulting conditions (94) and (95) imply trivial validity of the other relations

$(86)-(91)$ and reduce Eqs (92) and (93) to the form

$$k_\beta^{jo} = g_\beta^o h_\beta^{jo} - \sum_{\delta=1}^{n-1} (\partial \varrho_\beta \hat{f}_\beta / \partial \varrho_\delta)^o h_\delta^{jo} - (\partial \varrho_\beta \hat{f}_\beta / \partial F_n^{iJ})^o G_n^{iJKo} F_n^{-1 Kjo}$$

$$\beta = 1, \dots, n-1, \tag{96}$$

$$q^o = o ; \tag{97}$$

the latter equation means that the heat flux in the equilibrium is equal to zero Hence, according to Eqs (73), (74), and (76)

$$p_\beta^o = o \quad \beta = 1, \dots, n-1, \quad m^o = o \tag{98}, (99)$$

in accord with zero production of entropy in the equilibrium.

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