

RATIONAL THERMODYNAMICS OF A REACTING MIXTURE WITH LINEAR TRANSPORT PROPERTIES

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The method of rational thermodynamics according to Truesdell was applied to a reacting fluid mixture. The conservation laws of mass, momentum and its moment, energy, and the second law of thermodynamics were postulated. The model of the material was defined by constitutive equations linear in the vector and tensor variables so as to enable a comparison with classical thermodynamic theories. The constitutive equations are reduced to the final form by the principles of the constitutive theory: objectivity (independence of the material on the observer) and admissibility (use of the second law of thermodynamics according to Coleman and Noll). Their finite form is linear in the transport properties; the transport coefficients in them and the constitutive equations for thermodynamic properties and chemical reaction rates are nonlinear functions only of temperatures and densities. The constitutive equations are not mutually independent — the free energy determines the entropy and one kind of transport coefficients but not generally the pressure.

Rational thermodynamics, based on a critical revision of the continuum thermo-mechanics by the school of Truesdell, Coleman and Noll¹⁻⁴, has been applied to chemically reacting mixtures⁵⁻⁹ under certain restrictions, *e.g.*, absence of diffusion⁶ or absence of viscosity effects⁷⁻⁹. In the present work we shall consider all such phenomena but we shall restrict ourselves to chemically reacting fluid mixtures that are linear in the transport properties (such as viscosity, heat conduction, diffusion, and cross effects), *i.e.*, the classical case of the thermodynamics of irreversible processes. This will make it possible to compare explicitly the results obtained from rational thermodynamics with those from the thermodynamics of irreversible processes and thermochemistry of mixtures¹⁰.

The rational thermodynamics is an axiomatic and phenomenological theory (*i.e.*, it does not make use of a molecular model). First the general laws are postulated: the conservation laws (of mass, momentum, moment of momentum, and energy) and the second law of thermodynamics. Further are postulated the constitutive equations defining the model of the material. Their formulation and further rearrangement is based on the principles of the theory of constitutive equations¹⁻⁴: determinism, local action, memory, equipresence, objectivity, and admissibility. The obtained constitutive equations in the definitive form and relations among them involve linear equations of transport phenomena and nonlinear relations for thermo-

dynamic quantities and rates of chemical conversions. Contrary to nonreacting mixtures, the pressure is generally not determined only by thermodynamic quantities.

The present study is a continuation of the preceding work about nonreacting fluid mixtures^{11,12}. Vector and tensor equations are written in the component form in a cartesian coordinate system, which is expressed by subscripts i, j, k, l , etc., and the validity of the summation convention is assumed for them. The mixture constituents are denoted by superscripts α, β, γ , etc.

General Postulates

The following quantities are *a priori* introduced in the case of a reacting mixture with n constituents:

t	time
x_i	radius vector of the observer's coordinates
v_i^α	velocity of constituent α ; $\alpha = 1, 2, \dots, n$
ρ^α	density of constituent α , $\rho^\alpha > 0$
r^α	mass source of constituent α (in unit volume per unit time) by chemical conversions
T	temperature, $T > 0$
u^α	partial free energy of constituent α
s^α	partial entropy of constituent α
J_i	heat flux
R	heat source (for example by radiation)
k_i^α	force by which (in unit volume) other constituents act upon the constituent α
T_{ij}^α	partial stress tensor of constituent α
F_i^α	volume force acting upon constituent α
σ	production of entropy

On the basis of the Truesdell's concept of mixture¹³⁻¹⁵ the general postulates can be formulated in the local form as follows: Conservation of mass of the mixture constituent α

$$\frac{\partial \rho^\alpha}{\partial t} + \frac{\partial \rho^\alpha v_i^\alpha}{\partial x_i} = r^\alpha, \quad \alpha = 1, 2, \dots, n, \quad (1)$$

conservation of mass of the mixture

$$\frac{\partial}{\partial t} \sum_{\alpha=1}^n \rho^\alpha + \frac{\partial}{\partial x_i} \sum_{\alpha=1}^n \rho^\alpha v_i^\alpha = 0, \quad (2)$$

conservation of momentum of the mixture constituent α

$$\frac{\partial \varrho^\alpha v_i^\alpha}{\partial t} + \frac{\partial \varrho^\alpha v_i^\alpha v_j^\alpha}{\partial x_j} = \frac{\partial T_{ij}^\alpha}{\partial x_j} + \varrho^\alpha F_i^\alpha + k_i^\alpha + r^\alpha v_i^\alpha, \quad (3)$$

$$\alpha = 1, 2, \dots, n$$

conservation of momentum of the mixture

$$\frac{\partial}{\partial t} \sum_{\alpha=1}^n \varrho^\alpha v_i^\alpha + \frac{\partial}{\partial x_j} \sum_{\alpha=1}^n \varrho^\alpha v_i^\alpha v_j^\alpha = \frac{\partial}{\partial x_j} \sum_{\alpha=1}^n T_{ij}^\alpha + \sum_{\alpha=1}^n \varrho^\alpha F_i^\alpha \quad (4)$$

and conservation of moment of momentum of the constituent α

$$\frac{\partial \varepsilon_{lki} x_k v_i^\alpha \varrho^\alpha}{\partial t} + \frac{\partial \varepsilon_{lki} x_k v_i^\alpha \varrho^\alpha v_j^\alpha}{\partial x_j} = \frac{\partial \varepsilon_{lki} x_k T_{ij}^\alpha}{\partial x_j} + \varepsilon_{lki} x_k \varrho^\alpha F_i^\alpha + \varepsilon_{lki} x_k k_i^\alpha + \varepsilon_{lki} x_k v_i^\alpha r^\alpha, \quad (5)$$

$$\alpha = 1, 2, \dots, n$$

where ε_{lki} is a permutation symbol. In this way we restrict ourselves to such mixture constituents which do not exchange their moment of momentum among themselves (so-called nonpolar constituents).

Conservation of moment of momentum of the mixture is postulated as a sum of Eqs (5) over all constituents ($\alpha = 1, 2, \dots, n$).

Conservation of total energy of the mixture

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{\alpha=1}^n (\varrho^\alpha u^\alpha + \frac{1}{2} \varrho^\alpha v_i^\alpha v_i^\alpha) + \frac{\partial}{\partial x_j} \sum_{\alpha=1}^n (\varrho^\alpha u^\alpha + \frac{1}{2} \varrho^\alpha v_i^\alpha v_i^\alpha) v_j^\alpha = \\ = \frac{\partial}{\partial x_j} \sum_{\alpha=1}^n v_i^\alpha T_{ij}^\alpha - \frac{\partial J_i}{\partial x_i} + R + \sum_{\alpha=1}^n \varrho^\alpha F_i^\alpha v_i^\alpha \end{aligned} \quad (6)$$

and finally we postulate the second law of thermodynamics in the form of the Clausius–Duhem inequality

$$\sigma = \sum_{\alpha=1}^n \frac{\partial \varrho^\alpha s^\alpha}{\partial t} + \sum_{\alpha=1}^n \frac{\partial \varrho^\alpha s^\alpha v_i^\alpha}{\partial x_i} + \frac{\partial}{\partial x_i} \left(\frac{J_i}{T} \right) - \frac{R}{T} \geq 0. \quad (7)$$

Energy and entropy balances for the mixture constituents are not necessary since this study is restricted to mixtures with equal temperature of its constituents¹.

With the aid of Eqs (1) and (2) the mass conservation of the mixture can be ex-

pressed in the equivalent from

$$\sum_{\alpha=1}^n r^{\alpha} = 0 \quad (8)$$

and analogously from Eqs (3) and (4) follows the equivalent expression for the conservation of momentum of the mixture

$$\sum_{\alpha=1}^n (k_i^{\alpha} + r^{\alpha} v_i^{\alpha}) = 0. \quad (9)$$

Eq. (3) multiplied vectorially by x_k gives after comparing with (5) the equivalent expression for the conservation of moment of momentum of the constituent α ,

$$T_{ij}^{\alpha} = T_{ji}^{\alpha}. \quad \alpha = 1, 2, \dots, n \quad (10)$$

The analogous conservation of moment of momentum of the mixture is given as the sum of (10) over all constituents $\alpha = 1, 2, \dots, n$. Finally, by subtracting the kinetic energy balance (which is obtained by multiplying Eq. (3) by the velocities and summing over all mixture constituents) from the total energy balance (6) and using (1) we obtain the conservation of energy of the mixture as the internal energy balance:

$$\sum_{\alpha=1}^n \frac{\partial \rho^{\alpha} u^{\alpha}}{\partial t} + \sum_{\alpha=1}^n \frac{\partial \rho^{\alpha} u^{\alpha} v_j^{\alpha}}{\partial x_j} = \sum_{\alpha=1}^n T_{ij}^{\alpha} \frac{\partial v_i^{\alpha}}{\partial x_j} - \frac{\partial J_i}{\partial x_i} + R - \sum_{\alpha=1}^n v_i^{\alpha} k_i^{\alpha} - \sum_{\alpha=1}^n \frac{1}{2} r^{\alpha} v_i^{\alpha} v_i^{\alpha}. \quad (11)$$

We shall use further these postulates in the independent forms (1), (3), (7)–(11).

Constitutive Equations

Even if we assume that the values of R and F_i^{α} are given beforehand and if we determine the quantities r^{α} , k_i^{α} , σ and the three components T_{ij}^{α} from Eqs (7)–(10), the remaining differential equations (1), (3) and (11) are not sufficient to determine the quantities involved in them as functions of x_i and t . The reason is that the general postulates do not distinguish among individual materials; the differences between them are taken into account in constitutive equations^{1-4,13} by which we supplement the missing relations. By their postulation, we define the model of the material emphasizing such features of the real material which are important under the studied conditions. We propose the constitutive equations and modify them according to the principles of the theory of constitutive equations¹⁻⁴.

For our n -constituent, chemically reacting mixture of fluids we postulate the constitutive equations as follows^{1,5,9}: The quantities

$$r^{\beta}, u^{\alpha}, s^{\alpha}, J_i, k_i^{\beta}, T_{ij}^{\alpha} \quad (\text{symmetrical}) \quad (12)$$

are functions of the independent variables

$$T, \varrho^\alpha, \frac{\partial T}{\partial x_i}, \frac{\partial \varrho^\alpha}{\partial x_i}, v_i^\alpha, \frac{\partial v_i^\alpha}{\partial x_j} \quad (13)$$

with $\alpha = 1, 2, \dots, n$, $\beta = 1, 2, \dots, n-1$, and the dependence on the vectors and tensors in (13) is linear.

The condition of linearity is introduced for simplicity and for the possibility of a direct comparison with linear thermodynamics of irreversible processes; it is not usual, but on the other hand the published studies of chemically reacting mixtures omit in the group (13) the quantities $\partial \varrho^\alpha / \partial x_i$, v_i^α (materials without diffusion)^{5,6} or $\partial v_i^\alpha / \partial x_j$ (materials without viscosity)⁷⁻⁹.

The following principles of the constitutive theory were made use of in the above formulation of the constitutive equations¹⁻⁴:

Determinism — all independent variables (13) follow from a present or past motion and deformation of the material and temperature field. Fluids are characterized by the fact^{2,4} that the deformation gradient can be expressed as a function only of the densities ϱ^α . Strictly speaking, this applies exactly in chemically nonreacting mixtures; in chemically reacting mixtures of fluids still another quantity characterizing the deformation is introduced besides (ref.⁷, Eq. 8.8) to express the mentioned dependence. For simplicity of our material model we assume that this quantity is not involved among the independent variables (13).

Local action — only the immediate surroundings has an influence on the dependent variables (12), which is manifested by the presence of space gradients in (13).

Memory — only the immediate past has an influence on the dependent variables (12); therefore the quantities v_i^α and $\partial v_i^\alpha / \partial x_j$ are present in (13).

Equipresence — in all constitutive equations for the quantities (12) the same independent variables (13) are involved, hence no constitutive equation is preferred against others in their postulation.

We shall modify the constitutive equations between the quantities (12) and (13) by using further principles of the constitutive theory — principles of objectivity and admissibility.

Objectivity (material frame indifference)¹⁻⁴ requires that the constitutive equations (*i.e.*, the properties of the material) be independent of the motion of the coordinate system and origin of the time scale. As a result of this principle, the last two variables in (13) can occur in the constitutive equations for the quantities (12) only in the following combinations¹⁶ (otherwise the objectivity would not be fulfilled for two observers moving with respect to the material with different velocities of translation or rotation):

The diffusion rate of constituent β

$$V_i^\beta = v_i^\beta - v_i^n, \quad \beta = 1, 2, \dots, n-1, \quad (14)$$

the partial deformation rate tensor for constituent α

$$d_{ij}^\alpha = \frac{1}{2} \left(\frac{\partial v_i^\alpha}{\partial x_j} + \frac{\partial v_j^\alpha}{\partial x_i} \right), \quad \alpha = 1, 2, \dots, n \quad (15)$$

and the partial relative spin tensor of constituent β

$$\Omega_{ij}^\beta = \frac{1}{2} \left[\left(\frac{\partial v_i^\beta}{\partial x_j} - \frac{\partial v_j^\beta}{\partial x_i} \right) - \left(\frac{\partial v_i^n}{\partial x_j} - \frac{\partial v_j^n}{\partial x_i} \right) \right], \quad \beta = 1, 2, \dots, n-1. \quad (16)$$

Further it follows from the objectivity principle that the constitutive equations must be isotropic functions with respect to a full orthogonal group of coordinate transformation since the material properties must not depend on rotation or inversion of the coordinate axes of the observer. The form of such functions is for our constitutive equations (12)–(16) given by the results of Smith¹⁷ and is considerably reduced by the assumed linearity as follows^{5,16,18}:

$$r^\beta = r_{(0)}^\beta + \sum_{\gamma=1}^n r_{(\gamma)}^\beta d_{ij}^\gamma, \quad (17)$$

$$u^\alpha = u_{(0)}^\alpha + \sum_{\gamma=1}^n u_{(\gamma)}^\alpha d_{ij}^\gamma, \quad (18)$$

$$s^\alpha = s_{(0)}^\alpha + \sum_{\gamma=1}^n s_{(\gamma)}^\alpha d_{ij}^\gamma, \quad (19)$$

$$J_i = -\kappa \frac{\partial T}{\partial x_i} - \sum_{\beta=1}^{n-1} \lambda^\beta V_i^\beta + \sum_{\alpha=1}^n \chi^\alpha \frac{\partial \varrho^\alpha}{\partial x_i}, \quad (20)$$

$$k_i^\beta = -\xi^\beta \frac{\partial T}{\partial x_i} - \sum_{\delta=1}^{n-1} \nu^{\beta\delta} V_i^\delta + \sum_{\gamma=1}^n \omega^{\beta\gamma} \frac{\partial \varrho^\gamma}{\partial x_i}, \quad (21)$$

$$T_{ij}^\alpha = -\pi^\alpha \delta_{ij} + \sum_{\gamma=1}^n \zeta^{\alpha\gamma} d_{kk}^\gamma \delta_{ij} + \sum_{\gamma=1}^n 2\eta^{\alpha\gamma} d_{ij}^{0\gamma}. \quad (22)$$

We assume throughout that $\alpha, \gamma = 1, 2, \dots, n$ and $\beta, \delta = 1, 2, \dots, n-1$. All the coefficients $r_{(0)}^\beta, r_{(\gamma)}^\beta, u_{(0)}^\alpha, u_{(\gamma)}^\alpha, s_{(0)}^\alpha, s_{(\gamma)}^\alpha, \kappa, \lambda^\beta, \chi^\alpha, \xi^\beta, \nu^{\beta\delta}, \omega^{\beta\gamma}, \pi^\alpha, \zeta^{\alpha\gamma}$, and $\eta^{\alpha\gamma}$ are functions only of $T, \varrho^1, \varrho^2, \dots, \varrho^n$; δ_{ij} denotes unit tensor, d_{kk}^γ trace of the tensor d_{ij}^γ , and $d_{ij}^{0\gamma}$

its divergenceless part defined as

$$d_{ij}^{0\gamma} = d_{ij}^{\gamma} - \frac{1}{3} d_{kk}^{\gamma} \delta_{ij}, \quad \gamma = 1, 2, \dots, n. \quad (23)$$

In the case of nonpolar constituents, where Eq. (10) holds, the quantities (12) are not linearly dependent upon Ω_{ij}^{β} (Eq. (16)) (cf. ^{16,18}).

Further it is advantageous to define the partial free energy of the constituent α

$$f^{\alpha} = u^{\alpha} - Ts^{\alpha}, \quad \alpha = 1, 2, \dots, n. \quad (24)$$

The corresponding constitutive equation can be obtained by combining Eqs (18) and (19):

$$f^{\alpha} = f_{(0)}^{\alpha} + \sum_{\gamma=1}^n f_{(\gamma)}^{\alpha} d_{ij}^{\gamma}, \quad \delta = 1, 2, \dots, n, \quad (25)$$

where we define the following quantities:

$$f_{(0)}^{\alpha} = u_{(0)}^{\alpha} - Ts_{(0)}^{\alpha}, f_{(\gamma)}^{\alpha} = u_{(\gamma)}^{\alpha} - Ts_{(\gamma)}^{\alpha}, \quad \alpha, \gamma = 1, 2, \dots, n, \quad (26), (27)$$

which are obviously functions only of $T, \varrho^1, \varrho^2, \dots, \varrho^n$. In further text we shall denote such functions by the sign \wedge over the corresponding symbol, for example

$$f_{(0)}^{\alpha} = \hat{f}_{(0)}^{\alpha}(T, \varrho^1, \varrho^2, \dots, \varrho^n) = \hat{f}_{(0)}^{\alpha}(T, \varrho^{\gamma}), \quad \alpha, \gamma = 1, 2, \dots, n. \quad (28)$$

Finally we shall use the admissibility principle (after Coleman and Noll¹⁹) to obtain the resulting form of the constitutive equations: These must be consistent with the general postulates, especially with the Clausius-Duhem inequality (7) for arbitrary motion and deformations of the material and temperature field. To this purpose, we introduce the internal energy balance (11) into the Clausius-Duhem inequality (7) to eliminate the term $\partial J_i / \partial x_i - R$. (In the derivation of Eq. (11) we used already (1) and (3)). We modify the obtained expression by using the definitions (24) (we eliminate the partial internal energy u^{α}) and (23). Further we use all remaining relations (8)–(10) expressing the conservation laws and introduce the constitutive equations (17), (19)–(22) and (25) into the obtained inequality. After a longer rearrangement we obtain

$$\begin{aligned} T\sigma = & - \left[\sum_{\beta=1}^{n-1} \sum_{\alpha=1}^n \left(\frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial \varrho^{\beta}} - \frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial \varrho^{\alpha}} \right) r_{(0)}^{\beta} \right] - \left\{ \sum_{\alpha=1}^n \left(\frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial T} + \varrho^{\alpha} s_{(0)}^{\alpha} \right) \right\} \frac{\partial T}{\partial t} + \\ & + \sum_{\gamma=1}^n \left[\varrho^{\gamma} \sum_{\alpha=1}^n \frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial \varrho^{\gamma}} - \varrho^{\gamma} f_{(0)}^{\gamma} - \pi^{\gamma} - \sum_{\beta=1}^{n-1} \sum_{\alpha=1}^n \left(\frac{\partial \varrho^{\alpha} \hat{f}_{(\gamma)}^{\alpha}}{\partial \varrho^{\beta}} - \frac{\partial \varrho^{\alpha} \hat{f}_{(\gamma)}^{\alpha}}{\partial \varrho^{\alpha}} \right) r_{(0)}^{\beta} - \right. \end{aligned}$$

$$\begin{aligned}
& - \sum_{\beta=1}^{n-1} \sum_{\alpha=1}^n \left(\frac{\partial Q^\alpha \hat{f}_{(0)}^\alpha}{\partial Q^\beta} - \frac{\partial Q^\alpha \hat{f}_{(0)}^\alpha}{\partial Q^n} \right) r_{(\gamma)}^\beta \Big] d_{ii}^\gamma - \sum_{\gamma=1}^n \left\{ \sum_{\alpha=1}^n Q^\alpha f_{(\gamma)}^\alpha \right\} \frac{\partial d_{ii}^\gamma}{\partial t} + \\
& + \sum_{\gamma=1}^n \sum_{\beta=1}^{n-1} \left\{ \sum_{\alpha=1}^n \frac{\partial Q^\alpha \hat{f}_{(0)}^\alpha}{\partial Q^\gamma} \delta^{\beta\gamma} - \frac{\partial Q^\beta \hat{f}_{(0)}^\beta}{\partial Q^\gamma} - \omega^{\beta\gamma} \right\} V_i^\beta \frac{\partial Q^\gamma}{\partial x_i} - \\
& - \sum_{\alpha=1}^n \left\{ \frac{\chi^\alpha}{T} \right\} \frac{\partial Q^\alpha}{\partial x_i} \frac{\partial T}{\partial x_i} - \left\{ \sum_{\alpha=1}^n \left(\frac{\partial Q^\alpha \hat{f}_{(0)}^\alpha}{\partial T} + Q^\alpha s_{(0)}^\alpha \right) \right\} v_i^n \frac{\partial T}{\partial x_i} - \\
& - \sum_{\gamma=1}^n \left\{ \sum_{\alpha=1}^n \left(\frac{\partial Q^\alpha \hat{f}_{(\gamma)}^\alpha}{\partial T} + Q^\alpha s_{(\gamma)}^\alpha \right) \right\} d_{ii}^\gamma \frac{\partial T}{\partial t} - \sum_{\gamma=1}^n \sum_{\beta=1}^{n-1} \left\{ Q^\beta f_{(\gamma)}^\beta \right\} V_i^\beta \frac{\partial d_{jj}^\gamma}{\partial x_i} - \\
& - \sum_{\gamma=1}^n \left\{ \sum_{\alpha=1}^n Q^\alpha f_{(\gamma)}^\alpha \right\} v_i^n \frac{\partial d_{jj}^\gamma}{\partial x_i} + \left[\frac{\chi}{T} \right] \frac{\partial T}{\partial x_i} \frac{\partial T}{\partial x_i} + \sum_{\beta=1}^{n-1} \sum_{\delta=1}^{n-1} \left[v^{\beta\delta} - \frac{1}{2} r_{(0)}^\beta \delta^{\beta\delta} \right] V_i^\beta V_i^\delta + \\
& + \sum_{\beta=1}^{n-1} \left[\frac{\lambda^\beta}{T} + \zeta^\beta - \frac{\partial Q^\beta \hat{f}_{(0)}^\beta}{\partial T} - Q^\beta s_{(0)}^\beta \right] V_i^\beta \frac{\partial T}{\partial x_i} + \sum_{\epsilon=1}^n \sum_{\gamma=1}^n \left[Q^\epsilon \sum_{\alpha=1}^n \frac{\partial Q^\alpha \hat{f}_{(\gamma)}^\alpha}{\partial Q^\epsilon} - \right. \\
& \left. - \sum_{\beta=1}^{n-1} \sum_{\alpha=1}^n \left(\frac{\partial Q^\alpha \hat{f}_{(\gamma)}^\alpha}{\partial Q^\beta} - \frac{\partial Q^\alpha \hat{f}_{(\gamma)}^\alpha}{\partial Q^n} \right) r_{(\epsilon)}^\beta - Q^\epsilon f_{(\gamma)}^\epsilon + \zeta^{\epsilon\gamma} \right] d_{ii}^\epsilon d_{jj}^\gamma + \\
& + \sum_{\alpha=1}^n \sum_{\gamma=1}^n \left[2n^{\alpha\gamma} \right] d_{ij}^{0\gamma} d_{ij}^{0\alpha} + \sum_{\epsilon=1}^n \sum_{\gamma=1}^n \sum_{\beta=1}^{n-1} \left\{ \sum_{\alpha=1}^n \frac{\partial Q^\alpha \hat{f}_{(\gamma)}^\alpha}{\partial Q^\beta} \delta^{\beta\epsilon} - \frac{\partial Q^\beta \hat{f}_{(\gamma)}^\beta}{\partial Q^\epsilon} \right\} \frac{\partial Q^\epsilon}{\partial x_i} d_{jj}^\gamma V_i^\beta - \\
& - \sum_{\beta=1}^{n-1} \sum_{\gamma=1}^n \left\{ \frac{\partial Q^\beta \hat{f}_{(\gamma)}^\beta}{\partial T} + Q^\beta s_{(\gamma)}^\beta \right\} d_{jj}^\gamma V_i^\beta \frac{\partial T}{\partial x_i} - \sum_{\gamma=1}^n \sum_{\beta=1}^{n-1} \left\{ \frac{1}{2} r_{(\gamma)}^\beta \right\} V_i^\beta V_i^\beta d_{jj}^\gamma - \\
& - \sum_{\gamma=1}^n \left\{ \sum_{\alpha=1}^n \left(\frac{\partial Q^\alpha \hat{f}_{(\gamma)}^\alpha}{\partial T} + Q^\alpha s_{(\gamma)}^\alpha \right) \right\} d_{jj}^\gamma v_i^n \frac{\partial T}{\partial x_i} \geq 0 \tag{29}
\end{aligned}$$

($\delta^{\beta\gamma}$ denotes the Kronecker delta; we define $\delta^{\beta n} = 0$ for $\beta = 1, 2, \dots, n-1$).

According to the admissibility principle the inequality (29) must apply for all motions and deformations of the material and temperature fields, *i.e.*, for all real values of the following independent quantities:

$$\frac{\partial T}{\partial t}, \frac{\partial T}{\partial x_i}, \frac{\partial Q^\alpha}{\partial x_i}, V_i^\beta, v_i^n, d_{ii}^\alpha, d_{ij}^{0\alpha}, \frac{\partial d_{ii}^\alpha}{\partial t}, \frac{\partial d_{jj}^\alpha}{\partial x_i} \tag{30}$$

at any values $T > 0$, $Q^\alpha > 0$ ($\alpha = 1, 2, \dots, n$, $\beta = 1, 2, \dots, n-1$), on which the terms in parentheses in (29) are solely dependent. Then it is sufficient and necessary that the terms in composite parentheses be equal to zero. The sufficiency is obvious and the necessity follows by contradiction: If these expressions were not equal to

zero, it would be possible to find such real values of the quantities (30) (*i.e.*, such motion or deformation of the material and temperature fields) at which the inequality (29) would be invalid.

The nullity of the terms in composite parentheses in (29) implies the following equations:

$$f_{(\gamma)}^{\alpha} = 0, s_{(\gamma)}^{\alpha} = 0, r_{(\gamma)}^{\beta} = 0, \chi^{\alpha} = 0, \quad (31)-(34)$$

$$\sum_{\alpha=1}^n \frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial T} + \sum_{\alpha=1}^n \varrho^{\alpha} s_{(0)}^{\alpha} = 0 \quad (35)$$

$$\delta^{\beta\gamma} \frac{\partial}{\partial \varrho^{\gamma}} \left(\sum_{\alpha=1}^n \varrho^{\alpha} \hat{f}_{(0)}^{\alpha} \right) - \frac{\partial \varrho^{\beta} \hat{f}_{(0)}^{\beta}}{\partial \varrho^{\gamma}} = \omega^{\beta\gamma}, \quad (36)$$

where again $\alpha, \gamma = 1, 2, \dots, n$, $\beta = 1, 2, \dots, n-1$, and the inequality (29) takes the form

$$\begin{aligned} T\sigma = & - \sum_{\beta=1}^{n-1} \sum_{\alpha=1}^n \left(\frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial \varrho^{\beta}} - \frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial \varrho^n} \right) r_{(0)}^{\beta} + \sum_{\gamma=1}^n p^{\gamma} d_{ii}^{\gamma} + \\ & + \sum_{\epsilon=1}^n \sum_{\gamma=1}^n \zeta^{\epsilon\gamma} d_{ii}^{\epsilon} d_{jj}^{\gamma} + \sum_{\alpha=1}^n \sum_{\gamma=1}^n 2\eta^{\alpha\gamma} d_{ij}^{0\alpha} d_{ij}^{0\gamma} + \\ & + \sum_{\beta=1}^{n-1} \sum_{\delta=1}^{n-1} \left[\nu^{\beta\delta} - \frac{1}{2} r_{(0)}^{\beta} \delta^{\beta\delta} \right] V_1^{\beta} V_1^{\delta} + \sum_{\beta=1}^{n-1} g^{\beta} V_1^{\beta} \frac{\partial T}{\partial x_i} + \frac{\kappa}{T} \left(\frac{\partial T}{\partial x_i} \right)^2 \geq 0. \quad (37) \end{aligned}$$

Here we use the definitions

$$p^{\gamma} = \varrho^{\gamma} \sum_{\alpha=1}^n \frac{\partial \varrho^{\alpha} \hat{f}_{(0)}^{\alpha}}{\partial \varrho^{\gamma}} - \varrho^{\gamma} f^{\gamma} - \pi^{\gamma}, \quad \gamma = 1, 2, \dots, n \quad (38)$$

$$g^{\beta} = \frac{\lambda^{\beta}}{T} + \xi^{\beta} - \frac{\partial \varrho^{\beta} \hat{f}_{(0)}^{\beta}}{\partial T} - \varrho^{\beta} s_{(0)}^{\beta}, \quad \beta = 1, 2, \dots, n-1 \quad (39)$$

(these quantities are again functions only of $T, \varrho^1, \varrho^2, \dots, \varrho^n$). With the use of Eqs. (31)–(34) and with regard to (27) the constitutive equations take the final form

$$r^{\beta} = \hat{r}^{\beta}(T, \varrho^1, \varrho^2, \dots, \varrho^n), \quad s^{\alpha} = \hat{s}^{\alpha}(T, \varrho^1, \varrho^2, \dots, \varrho^n), \quad (40), (41)$$

$$f^{\alpha} = \hat{f}^{\alpha}(T, \varrho^1, \varrho^2, \dots, \varrho^n), \quad u^{\alpha} = \hat{u}^{\alpha}(T, \varrho^1, \varrho^2, \dots, \varrho^n), \quad (42), (43)$$

where $\alpha = 1, 2, \dots, n$, $\beta = 1, 2, \dots, n-1$ (here and in further text we omit the

subscript (0)),

$$J_i = -\kappa \frac{\partial T}{\partial x_i} - \sum_{\beta=1}^{n-1} \lambda^\beta V_i^\beta \quad (44)$$

and the constitutive equations (21) and (22) do not change. The coefficients κ (heat conductivity), λ^β , ξ^β , $v^{\beta\delta}$, $\omega^{\beta\gamma}$, π^α (partial pressure), $\zeta^{\alpha\gamma}$ (volume viscosity), and $\eta^{\alpha\gamma}$ (viscosity) depend only on T and $\varrho^1, \varrho^2, \dots, \varrho^n$.

As a result of Eqs (35) and (36), the mentioned constitutive equations are not independent. Indeed, if we introduce the density of the mixture

$$\varrho = \sum_{\alpha=1}^n \varrho^\alpha, \quad (45)$$

the mass fraction

$$w^\alpha = \varrho^\alpha / \varrho, \quad \alpha = 1, 2, \dots, n; \quad \sum_{\alpha=1}^n w^\alpha = 1, \quad (46)$$

the specific free energy of the mixture

$$f = \sum_{\alpha=1}^n w^\alpha f^\alpha, \quad (47)$$

the specific entropy of the mixture

$$s = \sum_{\alpha=1}^n w^\alpha s^\alpha, \quad (48)$$

and the specific chemical potential of the constituent α

$$\mu^\alpha = \partial \hat{f} / \partial \varrho^\alpha, \quad \alpha = 1, 2, \dots, n, \quad (49)$$

we can rewrite Eqs (35) and (36) in the form

$$\partial \hat{f} / \partial T = -s, \quad \omega^{\beta\gamma} = \mu^\gamma \delta^{\beta\gamma} - \partial \varrho^\beta \hat{f}^\beta / \partial \varrho^\gamma \quad (50), (51)$$

with $\beta = 1, 2, \dots, n-1$, $\gamma = 1, 2, \dots, n$, and the definition (38) as

$$\mu^\gamma = f^\gamma + (\pi^\gamma + p^\gamma) / \varrho^\gamma, \quad \gamma = 1, 2, \dots, n. \quad (52)$$

Finally for the principle of admissibility (the quantities (30) acquire independently all real values) the following inequalities and properties follow from the inequality (37):

$$\sum_{\alpha=1}^n \sum_{\gamma=1}^n 2\eta^{\alpha\gamma} d_{ij}^{0\alpha} d_{ij}^{0\gamma} + \sum_{\beta=1}^{n-1} \sum_{\delta=1}^{n-1} [v^{\beta\delta} - \frac{1}{2}r^{\beta}\delta^{\beta\delta}] V_i^{\beta} V_i^{\delta} + \sum_{\beta=1}^{n-1} \vartheta^{\beta} V_i^{\beta} \frac{\partial T}{\partial x_i} + \frac{\kappa}{T} \left(\frac{\partial T}{\partial x_i} \right)^2 \geq 0. \quad (53)$$

This is a positively semidefinite quadratic form (hence follow inequalities for its coefficients according to the Sylvester theorem). Further we have

$$-\sum_{\beta=1}^{n-1} (\mu^{\beta} - \mu^n) r^{\beta} + \sum_{\gamma=1}^n p^{\gamma} d_{ii}^{\gamma} + \sum_{\alpha=1}^n \sum_{\gamma=1}^n \zeta^{\alpha\gamma} d_{ii}^{\alpha} d_{jj}^{\gamma} \geq 0, \quad (54)$$

where the quadratic form is also positively semidefinite, and finally

$$-\sum_{\beta=1}^{n-1} (\mu^{\beta} - \mu^n) r^{\beta} \geq 0. \quad (55)$$

An important special case occurs for a nonreacting mixture ($r^{\alpha} = 0$; $\alpha = 1, 2, \dots, n$) where it follows from (54) according to the principle of admissibility

$$p^{\gamma} = 0, \quad \gamma = 1, 2, \dots, n \quad (56)$$

(this case occurs also with a chemically reacting mixture for which $\zeta^{\alpha\alpha} = 0$, $\alpha = 1, 2, \dots, n$, for example, a nonviscous mixture). In this way the definition (52) is reduced, to another relation joining the constitutive equations^{11,12}. This relation represents similarly as (50), the classical thermodynamic relations¹⁰.

DISCUSSION

The mixture of chemically reacting fluids (defined by constitutive equations (12) and (13)) studied from the point of view of rational thermodynamics yields equations for transport properties (partial stress tensor, heat flow and forces caused by the constituents of the mixture) in the form of Eqs (21), (22) and (44), which are linear as a result of the assumed linearity in (12) and (13). The relations (22) have the classical form corresponding to Newtonian fluids, Eqs (21) and (44) contain the diffusion velocities and therefore it is possible to obtain from them the classical linear relations for the diffusion and heat fluxes¹⁰ (the coefficients $v^{\beta\delta}$ are related to the diffusion coefficients¹⁰; the inequalities $v^{\beta\beta} - \frac{1}{2}r^{\beta} \geq 0$ following from the quadratic form (53) represent a diffusion limit of the reaction rate and do not exclude the negative values of diffusion coefficients in reacting mixture).

The right-hand sides of the constitutive equations for the thermodynamic quantities

(41)–(43) are (nonlinear) functions of temperature, T , and densities, ρ^α ($\alpha = 1, 2, \dots, n$), and are joined by the classical thermodynamic relation (50). Similarly the coefficients in the transport relations (21), (22) and (44) are (nonlinear) functions only of T and ρ^α , but only $\omega^{\beta\gamma}$ (which play a role in the equilibria in external force fields¹⁰) are, according to (51), determined by the thermodynamic constitutive equations (42). These (as mentioned in the discussion of a special case (56)) do not determine the partial pressure π^γ and hence they do not determine the total pressure $\sum_{\gamma=1}^n \pi^\gamma$ either.

It will be shown in a subsequent work¹⁰ that it is possible to obtain the classical thermodynamic equations from the mentioned ones by suitable definitions and by the use of a certain form invariance of the starting postulates.

The constitutive equations for the rate of chemical conversions (40) are generally nonlinear functions only of temperature, T , and densities, ρ^α ; they do not depend any more on the trace of the partial tensors of the deformation rate (since Eqs (33) hold). We shall show¹⁰ that this fact leads to a generally nonlinear dependence of the chemical reaction rates on the affinities and to the nonexistence of the cross effect between chemical reactions and linear friction.

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