

# COMPARISON OF CLASSICAL AND RATIONAL THERMODYNAMICS OF REACTING FLUID MIXTURES WITH LINEAR TRANSPORT PROPERTIES

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The results of the application of rational thermodynamics to a reacting fluid mixture from the preceding work are compared explicitly with the theories of irreversible thermodynamics and equilibrium thermodynamics of mixtures. The principle of local equilibrium can be in this way derived, provided that the thermodynamic pressure in a chemically reacting viscous mixture need not have the common physical meaning and a complete agreement with the classical thermochemistry of mixtures is achieved only after a certain form invariance of the starting postulate is made use of. Equations for the transport phenomena have (or can be transformed to) the common linear form, but the results are not restricted to the linear relations for chemical reaction rates and no interaction between them and the linear friction exists. The Onsager relations (between diffusion and heat fluxes) do not follow from the studied material model, however they can be obtained after introducing additional simple assumptions. In the case of equilibrium, we obtain the results of the classical thermodynamics of mixtures.

In the preceding communication<sup>1</sup> we applied the method of Truesdell's school<sup>2,3</sup> to reacting fluid mixtures with linear transport properties. This material represents a classical case treated by the older theories — irreversible thermodynamics and equilibrium thermodynamics of mixtures.

In the present work we shall compare explicitly the results of these older theories with those of rational thermodynamics from the preceding communication<sup>1</sup>. Such a comparison has been discussed in other rational-thermodynamical studies (refs<sup>1,5-9,11,12,16-18</sup> in ref.<sup>1</sup>) but these are all restricted (if we disregard nonlinearity) to a more special case than that studied in the present work.

By a suitable definition of the partial thermodynamic pressure (which in a chemically reacting viscous fluid mixture need not have the common physical meaning of a partial pressure) and other thermodynamic quantities we obtain a majority of classical thermodynamic relations (*e.g.*, the Gibbs equation), but the Gibbs–Duhem equation holds only for the chemical potential. The question about the validity of this equation in nonuniform systems (with space gradients of the properties) is namely not trivial<sup>5,6</sup> (ref.<sup>4</sup>, paragraph 260). To solve this problem here, we shall make use of a certain form invariance<sup>7,8</sup> of *a priori* introduced quantities in ref.<sup>1</sup> consisting in that some of them can be supplemented by two sets of arbitrary functions of temperature and

densities without changing the form of general postulates and constitutive equations and hence without changing the form of the relations derived from them.

By a suitable choice of these functions it can be achieved that the Gibbs–Duhem equations hold for all partial thermodynamic quantities, hence a complete accord with the structure of the classical thermochemistry of mixture can be achieved and the validity of the local equilibrium principle of irreversible thermodynamics for the studied material can be proved. By such a choice the partial quantities are in agreement with the classical definitions in an equilibrium uniform thermodynamic system.

The constitutive equations for chemical reactions derived in ref.<sup>1</sup> can be modified with the aid of the vector notation of chemical reactions<sup>9</sup> to an expression which is generally nonlinear with respect to affinities. The mentioned constitutive equations are independent of the deformation rate tensors, *i.e.*, no interaction between chemical reactions and linear friction (assumed in irreversible thermodynamics<sup>10</sup>) exists.

The concept of an equilibrium must be introduced in rational thermodynamics by a suitable definition<sup>2,3</sup>. The definition chosen here involves the results of the classical theory – equilibria in centrifugal and external force fields and equilibrium in a uniform system.

The results of irreversible thermodynamics (based on equal conservation laws)<sup>11,12</sup> agree with those obtained here if we take into consideration the known concept of the thermodynamic pressure and partial quantities. The Onsager reciprocal relations (which must be postulated in phenomenological irreversible thermodynamics<sup>12</sup>) between the diffusion and heat fluxes follow only after additional simple assumptions are introduced.

We shall write vectors and tensors in the physical space in the component form in cartesian coordinates (subscripts *i, j, k, ...*) and assume the validity of the summation convention for them. The mixture constituents will be denoted by Greek superscripts. Deviations from these rules are mentioned in the section about chemical reactions.

Symbols such as (I–10) refer to equations (here Eq. (10)) in the preceding communication<sup>1</sup>, from which the mathematical symbols are used also in the present work.

### *Thermodynamic Structure and Form Invariance*

We shall discuss only the “thermodynamic” relations obtained previously<sup>1</sup>, *viz.*, (I–24), (I–41)–(I–43), (I–45)–(I–52), and supplement them with the following definitions (it follows from the results<sup>1</sup> that all these quantities are functions only of temperature *T* and densities of the constituents  $\varrho^1, \varrho^2, \dots, \varrho^n$ ):

Partial thermodynamic pressure  $P^\alpha$  of the constituent  $\alpha$  in an *n*-component mixture

$$P^\alpha = \pi^\alpha + p^\alpha, \quad \alpha = 1, 2, \dots, n, \quad (1)$$

where  $\pi^\alpha$  denotes partial pressure in the constitutive equation for the partial stress tensor (1-22) and  $p^\alpha$  is defined by Eq. (1-38).

With the use of the quantity  $P^\alpha$ , further considerations are analogous as with nonreacting mixtures<sup>7,8</sup> (as already shown<sup>1</sup>, in this case Eq. (1-56) holds, hence both partial pressures become identical), therefore we shall mention them only briefly.

We define the thermodynamic pressure  $P$

$$P = \sum_{\alpha=1}^n P^\alpha \quad (2)$$

and further the partial volume  $v^\alpha$  and partial enthalpy  $h^\alpha$  of the constituent  $\alpha$

$$v^\alpha = P^\alpha / P \rho^\alpha, \quad h^\alpha = u^\alpha + P v^\alpha, \quad (3), (4)$$

where  $\alpha = 1, 2, \dots, n$  and  $u^\alpha$  denotes partial internal energy.

If we denote the partial quantities  $u^\alpha$ ,  $h^\alpha$ ,  $v^\alpha$ ,  $s^\alpha$  (partial entropy),  $f^\alpha$  (partial free energy),  $\mu^\alpha$  (specific chemical potential) as  $y^\alpha$ , we can the corresponding specific quantities of the mixture  $u$  (internal energy),  $h$  (enthalpy),  $v$  (volume),  $s$  (entropy),  $f$  (free energy) and  $g$  (free enthalpy), represented by the symbol  $y$ , define as

$$y = \sum_{\alpha=1}^n w^\alpha y^\alpha, \quad (5)$$

where  $w^\alpha$  means mass fraction (compare (1-46)–(1-48)). By means of these relations we can derive the classical ones, such as

$$\mu^\alpha = f^\alpha + P v^\alpha, \quad \alpha = 1, 2, \dots, n, \quad (6)$$

which is in substance Eq. (1-52),

$$v = 1/\rho, \quad g = u - Ts + Pv \quad (7), (8)$$

( $\rho$  means density of the mixture according to (1-45)), various forms of the Gibbs equation

$$d(\rho f) = -\rho s dT + \sum_{\alpha=1}^n \mu^\alpha d\rho^\alpha, \quad (9)$$

$$du = T ds - P dv + \sum_{s=1}^{n-1} (\mu^s - \mu^n) dw^s, \quad (10)$$

$$dg = -s dT + v dP + \sum_{s=1}^{n-1} (\mu^s - \mu^n) dw^s \quad (11)$$

and the Gibbs–Duhem equation for the chemical potential

$$-s dT + v dP - \sum_{\alpha=1}^n w^{\alpha} d\mu^{\alpha} = 0. \quad (12)$$

Further we can derive the expression

$$P^{\alpha} = \varrho^{\alpha} \sum_{\gamma=1}^n \varrho^{\gamma} \frac{\partial \hat{f}^{\gamma}}{\partial \varrho^{\alpha}}, \quad \alpha = 1, 2, \dots, n. \quad (13)$$

(The sign  $\hat{\phantom{x}}$  will mean that the quantity so denoted will be understood as a function of  $T, \varrho^1, \varrho^2, \dots, \varrho^n$  – compare (1–28)). With the aid of Eqs (13), (1–36), (1–49), (1–52) and (1) we obtain

$$\sum_{\gamma=1}^n \omega^{\beta\gamma} d\varrho^{\gamma} = dP^{\beta} - \varrho^{\beta} d\mu^{\beta} + \varrho^{\beta} \frac{\partial \hat{f}^{\beta}}{\partial T} dT, \quad (14)$$

$$\sum_{\beta=1}^{n-1} \sum_{\gamma=1}^n \omega^{\beta\gamma} d\varrho^{\gamma} = -dP^n + \varrho^n d\mu^n - \varrho^n \frac{\partial \hat{f}^n}{\partial T} dT, \quad (15)$$

where  $\beta = 1, 2, \dots, n-1$  and  $\omega^{\beta\gamma}$  are coefficients in the constitutive equations (1–21).

In all such relations it is possible to replace the differential operator by time, space or substantial derivatives since all quantities in them are functions<sup>1</sup> of the observer's coordinate  $x_i$  and time  $t$ .

With respect to Eq. (2),  $P$  is a function of  $T, \varrho^1, \varrho^2, \dots, \varrho^n$  and hence according to (1–46) and (7) it is also a function of  $T, v, w^1, w^2, \dots, w^{n-1}$ . If we assume that there exists an inversion of this function with respect to  $v$ , we can (with regard to the mentioned relations) express any function of  $T, \varrho^1, \varrho^2, \dots, \varrho^n$  as a function of  $T, P, w^1, w^2, \dots, w^{n-1}$ . Such a function will be denoted by the sign  $\sim$ , for example

$$y = \tilde{y}(T, P, w^1, w^2, \dots, w^{n-1}) = \tilde{y}(T, P, w^{\beta}); \\ y^{\alpha} = \tilde{y}^{\alpha}(T, P, w^{\beta}), \quad \alpha = 1, 2, \dots, n; \beta = 1, 2, \dots, n-1. \quad (16)$$

All the formulas mentioned up to now are the same as in classical thermochemistry of mixtures (in specific quantities). However, there is the following inconsistency: The quantities  $y^{\alpha}$  do not fulfil the classical Gibbs–Duhem equation (except for  $\mu^{\alpha}$ ; Eq. (12))

$$\frac{\partial \tilde{y}}{\partial T} dT + \frac{\partial \tilde{y}}{\partial P} dP - \sum_{\alpha=1}^n w^{\alpha} dy^{\alpha} = 0 \quad (17)$$

and the classical relation

$$\frac{\partial \bar{y}}{\partial w^\beta} = y^\beta - y^n, \quad \beta = 1, 2, \dots, n-1 \quad (18)$$

as far as the following additional condition is not fulfilled:

$$\sum_{\alpha=1}^n w^\alpha \frac{\partial \bar{y}^\alpha}{\partial w^\beta} = 0, \quad \beta = 1, 2, \dots, n-1 \quad (19)$$

(as follows from Eqs (5) and (16)). Nevertheless, we shall show that this condition can be always fulfilled owing to the invariance of the form of the equations mentioned up to now with respect to two sets of  $n-1$  arbitrary functions of  $T, \varrho^1, \varrho^2, \dots, \varrho^n$  (which can be differentiated and have the dimensions of energy and entropy),

$$u^{(\beta)} = \hat{u}^{(\beta)}(T, \varrho^\alpha), \quad s^{(\beta)} = \hat{s}^{(\beta)}(T, \varrho^\alpha), \quad \alpha = 1, 2, \dots, n-1 \quad (20)$$

if instead of the original quantities listed in ref.<sup>1</sup> new, primed quantities are introduced:

$$u'^\alpha = u^\alpha + \sum_{\beta=1}^{n-1} (\delta^{\beta\alpha} - w^\beta) u^{(\beta)}, \quad (21)$$

$$s'^\alpha = s^\alpha + \sum_{\beta=1}^{n-1} (\delta^{\beta\alpha} - w^\beta) s^{(\beta)}, \quad (22)$$

$$J'_i = J_i - T \sum_{\beta=1}^{n-1} \varrho^\beta \sum_{\delta=1}^{n-1} (\delta^{\delta\beta} - w^\delta) s^{(\delta)} V_i^\beta, \quad (23)$$

$$k_i'^\alpha = k_i^\alpha - \frac{\partial}{\partial x_i} \left[ \varrho^\alpha \sum_{\beta=1}^{n-1} (\delta^{\beta\alpha} - w^\beta) f^{(\beta)} \right], \quad (24)$$

$$T'_{ij}{}^\alpha = T_{ij}{}^\alpha + \left[ \varrho^\alpha \sum_{\beta=1}^{n-1} (\delta^{\beta\alpha} - w^\beta) f^{(\beta)} \right] \delta_{ij}. \quad (25)$$

Here  $\alpha = 1, 2, \dots, n$  and we defined

$$f^{(\beta)} = u^{(\beta)} - T s^{(\beta)}, \quad \beta = 1, 2, \dots, n-1 \quad (26)$$

and used the definitions (1-45), (1-46) and the diffusion velocity  $V_i^\beta$  (1-14);  $J_i$  denotes heat flux,  $T_{ij}^\alpha$  partial stress tensor of constituent  $\alpha$ ,  $k_i^\alpha$  force by which other constituents act upon constituent  $\alpha$ ;  $\delta_{ij}$ ,  $\delta^{\delta\beta}$  and  $\delta^{\beta\alpha}$  are Kronecker delta symbols. Other quantities of those listed in ref.<sup>1</sup> remain without change.

Indeed, by this transformation the forms of the basic postulates (1-1), (1-3), (1-7)-(1-11) do not change, and also the considerations about constitutive

equations remain the same, *i.e.*, their resulting form and the form of all other relations (by using suitable definitions of the primed quantities) remains the same<sup>7,8</sup>.

Since the transformation (20)–(26) does not change the form of the general postulates, we can expect analogous invariant behaviour also in other material models.

The physical meaning of the form invariance consists in that the invariant quantities (*e.g.*,  $y$ ,  $P$ ,  $\mu^\alpha$ ) are directly measurable quantities of mixtures (or are derivable from them), whereas the noninvariant ones (*e.g.*,  $y^\alpha$ ,  $P^\alpha$ ) are without additional assumptions not experimentally accessible. Indeed (compare Eqs (3), (4), (20), (26), (1–45) and (1–49)) we obtain for such quantities

$$y'^\alpha = y^\alpha + \sum_{\beta=1}^{n-1} (\delta^{\beta\alpha} - w^\beta) y^{(\beta)}, \quad \alpha = 1, 2, \dots, n, \quad (27)$$

where  $y^{(\beta)}$  represents (according to the choice of  $y^\alpha$ )  $u^{(\beta)}$ ,  $s^{(\beta)}$ ,  $f^{(\beta)}$ ,  $v^{(\beta)} = -f^{(\beta)}/P$ ,  $h^{(\beta)} = Ts^{(\beta)}$ ,  $\mu^{(\beta)} = 0$  (the chemical potential is an invariant, *cf.* (1–49)), or (*cf.* (13))

$$P'^\alpha = P^\alpha - \varrho^\alpha \sum_{\beta=1}^{n-1} (\delta^{\alpha\beta} - w^\beta) f^{(\beta)}, \quad \alpha = 1, 2, \dots, n, \quad (28)$$

and so on<sup>7,8</sup>.

It should be noted that Eq. (23) for the heat flux involves all common formulations of this quantity in irreversible thermodynamics (*ref.*<sup>10</sup>, chapter III/3).

We shall now use this invariance to obtain the additional condition (19) for the primed quantities  $y'^\alpha$ . We choose the functions (20) as follows:

$$y^{(\beta)} = \sum_{\alpha=1}^n w^\alpha \partial \tilde{y}^\alpha / \partial w^\beta, \quad \beta = 1, 2, \dots, n-1. \quad (29)$$

Here  $y^{(\beta)}$  means  $u^{(\beta)}$  and  $s^{(\beta)}$ , but it can be shown<sup>7,8</sup> from the definitions of  $y'^\alpha$  that this expression holds also with other meanings of  $y^{(\beta)}$ . On introducing Eq. (29) into (27), the validity of (19) for the primed quantities  $y'^\alpha$  can be checked.

In further text we therefore assume that  $y'^\alpha$  was found and so the condition (19) is valid for the partial quantities  $y^\alpha$  used (such quantities will not be further denoted with a comma).

Now the validity of the general Gibbs–Duhem equation (17) and Eq. (18) can hence be assumed. From (1–46), (5), (11) and (18) we obtain the classical relations

$$\partial \tilde{\mu}^\alpha / \partial T = -s^\alpha, \quad \partial \tilde{\mu}^\alpha / \partial P = v^\alpha, \quad \alpha = 1, 2, \dots, n. \quad (30), (31)$$

It should be noted that owing to Eq. (30) an expression analogous to (1–50) in partial quantities is generally invalid.

## Chemical Reactions

In this section we shall discuss the results of the preceding work<sup>1</sup> related to chemical reactions, (1-40) and (1-55); by the Bowen's method<sup>2,9,13,15</sup>. Since we shall use rectilinear vector bases, vectors will be denoted by superscripts and subscripts.

We shall assume that a molecular mass  $M_\alpha$  can be *a priori* assigned to each constituent  $\alpha = 1, 2, \dots, n$  and that the constituents are composed of  $z$  chemical elements with atomic masses  $A^\omega$  ( $\omega = 1, 2, \dots, z$ ):

$$M_\alpha = \sum_{\omega=1}^z T_{\omega\alpha} A^\omega, \quad \alpha = 1, 2, \dots, n. \quad (32)$$

We now postulate the permanence of the chemical elements in chemical reactions:

$$\sum_{\alpha=1}^n \mathcal{J}^\alpha T_{\omega\alpha} = 0, \quad \omega = 1, 2, \dots, z, \quad (33)$$

where we define

$$\mathcal{J}^\alpha = r^\alpha / M_\alpha, \quad \alpha = 1, 2, \dots, n \quad (34)$$

( $r^\alpha$  is the mass of constituent  $\alpha$  produced in a time unit and a volume unit by chemical reactions). By combining Eqs (32)–(34) we naturally obtain the mass conservation law (1-8) (see also Eq. (40)).

In further text only such equations of (33) have significance which are linearly independent, or their linearly independent combinations. Their number is equal to the rank  $h$  of the matrix  $\|T_{\omega\alpha}\|$ , hence the permanence of the chemical elements can be expressed as

$$\sum_{\alpha=1}^n \mathcal{J}^\alpha S_{\omega\alpha} = 0, \quad \omega = 1, 2, \dots, h, \quad (35)$$

where the  $h \times n$  matrix  $\|S_{\omega\alpha}\|$  formed in the described manner from  $\|T_{\omega\alpha}\|$  has the rank  $h$ .

We now consider an abstract,  $n$ -dimensional linear vector space of constituents of the mixture,  $\mathcal{U}$ , with a base  $\mathbf{e}_\alpha$  and a reciprocal base  $\mathbf{e}^\alpha$  ( $\alpha = 1, 2, \dots, n$ ). We define in it: the molar mass vector  $\mathbf{M}$  and the reaction rate vector  $\mathcal{J}$

$$\mathbf{M} = \sum_{\alpha=1}^n M_\alpha \mathbf{e}^\alpha, \quad \mathcal{J} = \sum_{\alpha=1}^n \mathcal{J}^\alpha \mathbf{e}_\alpha \quad (36), (37)$$

and  $h$  vectors  $\mathbf{f}_\omega$  given by

$$\mathbf{f}_\omega = \sum_{\alpha=1}^n S_{\omega\alpha} \mathbf{e}^\alpha, \quad \omega = 1, 2, \dots, h. \quad (38)$$

Since the matrix  $\|S_{\omega\alpha}\|$  has the rank  $h$ , these vectors are linearly independent and therefore form a base of an  $h$ -dimensional subspace  $\mathcal{W}$  in the space of the constituents  $\mathcal{U}$ . This subspace  $\mathcal{W}$  determines in the space  $\mathcal{U}$  uniquely a complementary orthogonal  $(n-h)$ -dimensional subspace, which we shall call the reaction subspace  $\mathcal{V}$ .

Bowen<sup>2,9</sup> showed that the permanence of chemical elements in chemical reactions (35) can be expressed in an equivalent form as follows. The molar mass vector  $\mathbf{M}$  lies in the subspace  $\mathcal{W}$  and the vector of reaction rates  $\mathcal{J}$  lies always in the reaction subspace  $\mathcal{V}$  of the constituent space  $\mathcal{U}$ , *i.e.*

$$\mathbf{M} \in \mathcal{W}, \quad \mathcal{J} \in \mathcal{V}, \quad (39)$$

where  $\mathcal{W} \perp \mathcal{V}$  and  $\mathcal{W} \oplus \mathcal{V} = \mathcal{U}$  ( $\oplus$  denotes direct sum). From this follows

$$\mathbf{M} \cdot \mathcal{J} = 0, \quad (40)$$

which is according to (36) and (37) equivalent to conservation of the total mass (1-8). The vector  $\mathbf{M}$  can be expressed as

$$\mathbf{M} = \sum_{\omega=1}^h E^{\omega} \mathbf{f}_{\omega}. \quad (41)$$

From this and Eqs (36) and (37) we obtain

$$M_{\alpha} = \sum_{\omega=1}^h S_{\omega\alpha} E^{\omega}, \quad \alpha = 1, 2, \dots, n, \quad (42)$$

which is an equivalent expression of the postulate (32).

Now we choose  $n-h$  linearly independent vectors  $\mathbf{g}^p$  in the reaction subspace  $\mathcal{V}$  as its base. These can be expressed as

$$\mathbf{g}^p = \sum_{\alpha=1}^n P^{p\alpha} \mathbf{e}_{\alpha}, \quad p = 1, 2, \dots, n-h, \quad (43)$$

where the  $(n-h) \times n$  matrix  $\|P^{p\alpha}\|$  is called the matrix of stoichiometrical coefficients, has the rank  $n-h$  and fulfils the relations

$$\sum_{\alpha=1}^n S_{\omega\alpha} P^{p\alpha} = 0, \quad \omega = 1, 2, \dots, h; \quad p = 1, 2, \dots, n-h, \quad (44)$$

which follow from the orthogonality of the vectors of the bases of the subspaces  $\mathcal{W}$  and  $\mathcal{V}$  (38), (39) and (43). On multiplying Eq. (44) with  $E^{\omega}$  and summing over  $\omega = 1, 2, \dots, h$  we obtain with the use of (42) the relations

$$\sum_{\alpha=1}^n P^{p\alpha} M_{\alpha} = 0, \quad p = 1, 2, \dots, n-h, \quad (45)$$



which express  $n-h$  independent chemical reactions chosen to describe the reacting mixture (if we substitute for  $M_\alpha$  the corresponding chemical symbols). We shall consider as reaction products such constituents in the  $p$ -th reaction for which the value of  $P^{p\alpha}$  is positive, and as starting substances those for which this value is negative. Eqs (39) allow us to write

$$\mathcal{J} = \sum_{p=1}^{n-h} \mathcal{J}_p \mathbf{g}^p, \quad (46)$$

where  $\mathcal{J}_p$  ( $p = 1, 2, \dots, n-h$ ) can be called the rate of the  $p$ -th chemical reaction. Indeed, according to (37) and (43)

$$\mathcal{J}^\alpha = \sum_{p=1}^{n-h} \mathcal{J}_p P^{p\alpha}, \quad \alpha = 1, 2, \dots, n. \quad (47)$$

Now we define in the constituent space the vector of the molar chemical potential

$$\boldsymbol{\mu} = \sum_{\alpha=1}^n \mu^\alpha M_\alpha \mathbf{e}^\alpha. \quad (48)$$

This vector can be uniquely decomposed into its projections  $\mathbf{A}$  and  $\mathbf{B}$  into the mutually orthogonal and complementary subspaces  $\mathcal{V}$  and  $\mathcal{W}$ :

$$\boldsymbol{\mu} = \mathbf{A} + \mathbf{B}, \quad (49)$$

where  $\boldsymbol{\mu} \in \mathcal{U}$ ,  $\mathbf{A} \in \mathcal{V}$ ,  $\mathbf{B} \in \mathcal{W}$ . The vector  $\mathbf{A}$  can be called the affinity vector, since according to (49)

$$\mathbf{A} = \sum_{p=1}^{n-h} A^p \mathbf{g}_p \quad (50)$$

and its components  $A^p$  represent the affinities of the individual independent chemical reactions chosen for the description (by the choice of the base (43)). Indeed, according to Eqs (43), (48)–(50)

$$A^p = \boldsymbol{\mu} \cdot \mathbf{g}^p = \sum_{\alpha=1}^n \mu^\alpha M_\alpha P^{p\alpha}, \quad p = 1, 2, \dots, n-h, \quad (51)$$

which is the definition of the affinity of the  $p$ -th chemical reaction<sup>10</sup> (differing from the classical one by the sign).

We now apply this vector formalism to the inequality (1–55), which can be with the use of (1–8), (33), (37), (47)–(50) written as

$$-\sum_{\beta=1}^{n-1} (\mu^\beta - \mu^n) r^\beta = -\sum_{\alpha=1}^n \mu^\alpha r^\alpha = -\boldsymbol{\mu} \cdot \mathcal{J} = -\mathbf{A} \cdot \mathcal{J} = -\sum_{p=1}^{n-h} A^p \mathcal{J}_p \geq 0. \quad (52)$$

With the assumption that the functions  $\mu^\alpha = \mu^\alpha(T, \varrho^\gamma)$  ( $\alpha, \gamma = 1, 2, \dots, n$ ) are invertible with respect to the densities  $\varrho^\gamma$ , these inversions can be introduced into the constitutive equation (1-40), which can be with the use of (34), (37), (48) and (49) written in the form

$$\mathcal{J} = \mathcal{J}(T, \boldsymbol{\mu}) = \mathcal{J}(T, \mathbf{A} + \mathbf{B}). \quad (53)$$

If this function is continuous with respect to  $\boldsymbol{\mu}$  then it is necessary for the inequality (52) to hold that

$$\mathcal{J} = \mathcal{J}(T, \mathbf{0} + \mathbf{B}) = \mathbf{0} \quad \text{for } \mathbf{A} = \mathbf{0}. \quad (54)$$

Indeed, if we fix  $\mathbf{B}$ , choose  $A^1$  arbitrarily and set  $A^p = 0$  for  $p = 2, 3, \dots, n-h$ , we obtain from the continuity of the function (53) and from (52)  $\mathcal{J}_1 = 0$  for  $\mathbf{A} = \mathbf{0}$ ; then we choose  $A^2$  arbitrarily and so on, until we arrive at (54).

It can hence be concluded that for chemical reactions the constitutive equation can be expressed by Eq. (53), which is generally nonlinear in  $\mathbf{A}$  with the property (54), i.e. by constitutive equations for  $n-h$  rates of chemical reactions  $\mathcal{J}_p$  nonlinearly dependent on the affinities of all reactions  $A^r$  ( $p, r = 1, 2, \dots, n-h$ ) in such a way that the reaction rates are equal to zero if all the affinities are equal to zero. The reaction rates depend only on the affinities, temperature  $T$  and densities  $\varrho^\alpha$  through certain combinations of chemical potentials following from  $\mathbf{B}$ . The deduction of the mass action law of chemical kinetics will be shown in the subsequent paper<sup>16</sup>.

### Equilibrium

In rational thermodynamics, the equilibrium is defined as a special case of the choice of independent variables in constitutive equations<sup>2,3</sup>. We shall make this choice so that we might arrive at the classical concept of the equilibrium (as a special case). In our material we define the equilibrium by

$$\begin{aligned} d_{ij}^\alpha &= 0, \quad V_i^\beta = 0, \quad \partial T / \partial x_i = 0, \quad A^p = 0, \\ \alpha &= 1, 2, \dots, n, \quad \beta = 1, 2, \dots, n-1, \quad p = 1, 2, \dots, n-h \end{aligned} \quad (55)$$

( $d_{ij}^\alpha$  is the partial deformation rate tensor (1-15)). Then it follows from (1-23), (1-53) and (1-54) that the entropy production is zero

$$\sigma = 0 \quad (56)$$

and no chemical reactions proceed in the mixture (with the use of (34) and (54)):

$$r^\alpha = 0, \quad \alpha = 1, 2, \dots, n. \quad (57)$$

In the equilibrium, the partial pressure  $\pi^\alpha$  and thermodynamic pressure  $P^\alpha$  for all constituents are identical since, owing to Eqs (55) and (57), Eq. (1-56) holds.

We shall briefly mention other results since with respect to Eq. (57) the procedure is analogous as for nonreacting mixtures<sup>7,8</sup>. The constitutive equations (1-21), (1-22) and (1-44) are in the equilibrium reduced to the form

$$T_{ij}^\alpha = -P^\alpha \delta_{ij}, \quad \alpha = 1, 2, \dots, n \quad (58)$$

(i.e., the total stress in the equilibrium is also reduced to the thermodynamic pressure  $P$ , Eq. (2)),

$$k_i^\beta = \sum_{\gamma=1}^n \omega^{\beta\gamma} \partial q^\gamma / \partial x_i, \quad J_i = 0, \quad \beta = 1, 2, \dots, n-1 \quad (59), (60)$$

(the heat flux in the equilibrium is equal to zero). The other constitutive equations (1-41)–(1-43) remain in the equilibrium without change (the constitutive equation (1-40) is according to (57) identically zero).

Now we can introduce all these relations into the general postulates (conservation laws) in the preceding work<sup>1</sup>. We note that from Eqs (14), (15), (55), (57), (59), (1-8) and (1-9) follows in the equilibrium that the velocities of all constituents are the same

$$v_i^\alpha = v_i, \quad \alpha = 1, 2, \dots, n \quad (61)$$

and we have

$$-\partial P^\alpha / \partial x_i + k_i^\alpha = -q^\alpha \partial \mu^\alpha / \partial x_i, \quad \alpha = 1, 2, \dots, n. \quad (62)$$

The resulting relations are the same as in refs<sup>7,8</sup> and therefore we concentrate ourselves on their notation in the special case of the traditional equilibrium concept expressed by the additional conditions for  $\alpha = 1, 2, \dots, n$

$$R = 0, \quad \partial T / \partial t = 0, \quad \partial v_i / \partial t = 0, \quad \partial q^\alpha / \partial t = 0 \quad (63)$$

(no time changes proceed and we neglect the source of heat  $R$ , for example by radiation). In this case, the general postulates expressing the preservation of mass (1-1), (1-2), momentum (1-3), (1-4), energy (1-11), and the second law of thermodynamics (1-7) take the form for  $\alpha = 1, 2, \dots, n$

$$v_i \partial q^\alpha / \partial x_i = 0, \quad v_i \partial q / \partial x_i = 0, \quad (64), (65)$$

$$\frac{1}{2} v_j (\partial v_i / \partial x_j - \partial v_j / \partial x_i) = -\partial \mu^\alpha / \partial x_i + F_i^\alpha, \quad (66)$$

$$\frac{1}{2} \rho v_j (\partial v_i / \partial x_j - \partial v_j / \partial x_i) = -\partial P / \partial x_i + \sum_{\alpha=1}^n \rho^\alpha F_i^\alpha, \quad (67)$$

$$v_i \partial u / \partial x_i = 0, \quad v_i \partial s / \partial x_i = 0 \quad (68), (69)$$

( $F^\alpha$  in (66) and (67) means the volume force acting upon the constituent  $\alpha$ ). The preservation of the moment of momentum (1-10) is trivially fulfilled by Eq. (58). From these equations follow the traditional cases of the equilibrium:

Equilibrium in the centrifugal force field (for all  $F_i^\alpha = 0$ ; the expressions on the left side of Eqs (66) and (67) contain the spin tensor),

equilibrium in the external force field (for  $v_i = 0$ ; Eqs (66) and (67) represent "barometric formulas"),

equilibrium in a uniform (called traditionally "homogeneous") system. It takes place if all volume forces  $F_i^\alpha$  and the spin tensor (*i.e.* the left sides of Eqs (66) and (67)) are equal to zero;  $v_i$  is independent of coordinates and time owing to (55) and (63). According to the Galilei's relativity principle,  $v_i$  can be an arbitrary constant and thus from Eqs (5), (16), (64)–(69) follows the uniformity of the properties of such an equilibrium system for  $\alpha = 1, 2, \dots, n$ :

$$\partial \varrho^\alpha / \partial x_i = \partial T / \partial x_i = \partial P / \partial x_i = \partial y^\alpha / \partial x_i = \partial y / \partial x_i = 0. \quad (70)$$

In a volume  $V$  of a uniform equilibrium system it is possible to introduce extensive quantities – the mass,  $m^\alpha$ , of constituent  $\alpha$ , the mass,  $m$ , of the mixture, and the quantities  $Y$  (comprising internal energy, entropy, enthalpy, free energy, free enthalpy, and volume) as

$$m = \varrho V, \quad m^\alpha = \varrho^\alpha V, \quad Y = m y, \quad \alpha = 1, 2, \dots, n. \quad (71)$$

By their use we can derive the classical thermodynamic relations if we define the function  $\bar{Y}$  (by using (1-46) and (16)):

$$Y = m \bar{y}(T, P, w^1, w^2, \dots, w^{n-1}) = \bar{Y}(T, P, m^1, m^2, \dots, m^n). \quad (72)$$

For example, the classical relation used (in molar quantities) as a definition of partial quantities in classical thermodynamics of uniform systems

$$\partial \bar{Y} / \partial m^\alpha = y^\alpha, \quad \alpha = 1, 2, \dots, n \quad (73)$$

follows by using Eq. (18). However, we emphasize that this is true only if the additional condition (19) holds.

Other classical relations for a uniform equilibrium system (Gibbs equation, Gibbs–Duhem equation, *etc.*) follow easily from the relations mentioned in the section about thermodynamic structure<sup>7,8</sup>.

### Comparison with Irreversible Thermodynamics

It is obvious from the results mentioned so far that the local equilibrium principle of irreversible thermodynamics<sup>10</sup> applies for the material model studied in the present work. However, it should be mentioned that if chemical reactions take place, the thermodynamic pressure  $P^\alpha$  need not be identical with the pressure  $\pi^\alpha$  in the constitutive equation for the partial stress tensor (1-22) and that a complete agreement with the classical thermodynamics of solutions is obtained only after considering the form invariance discussed above.

The chemical reaction rates depend on the affinities generally nonlinearly and owing to the admissibility principle<sup>1</sup> they do not depend on the deformation rate tensors  $d_{ij}^\alpha$  (compare Eqs (1-33), (1-40) and (53)), i.e., in this material no interaction between chemical reactions and linear friction, assumed in irreversible thermodynamics<sup>10</sup>, exists.

For an explicit comparison with irreversible thermodynamics (with results which are based on similar balances<sup>11,12</sup> as ref.<sup>1</sup>) we express the diffusion flux  $\varrho^\delta V_i^\delta$  from the constitutive equation (1-21) using the balance (1-3) and the following definitions of the traditional concepts: Isothermal gradient of the chemical potential

$$(\partial\mu^\alpha/\partial x_i)_T = \partial\mu^\alpha/\partial x_i + s^\alpha \partial T/\partial x_i, \quad \alpha = 1, 2, \dots, n, \quad (74)$$

partial friction tensor

$$\mathcal{P}_{ij}^\alpha = -(p^\alpha + \sum_{\gamma=1}^n \zeta^{\alpha\gamma} d_{kk}^{\gamma}) \delta_{ij} - \sum_{\gamma=1}^n 2\eta^{\alpha\gamma} d_{ij}^{0\gamma}, \quad \alpha = 1, 2, \dots, n \quad (75)$$

( $d_{kk}^\gamma$  and  $d_{ij}^{0\gamma}$  are the trace and the divergenceless part of  $d_{ij}^\gamma$ ) and the driving force of diffusion

$$x_i^\beta = \left( \frac{\partial\mu^\beta}{\partial x_i} \right)_T - F_i^\beta + \frac{1}{\varrho^\beta} \frac{\partial \mathcal{P}_{ij}^\beta}{\partial x_j} + \frac{1}{\varrho^\beta} \frac{\partial \varrho^\beta v_i^\beta}{\partial t} + \frac{1}{\varrho^\beta} \frac{\partial \varrho^\beta v_i^\beta v_j^\beta}{\partial x_j} - \frac{r^\beta}{\varrho^\beta} v_i^\beta \quad (76)$$

with  $\beta = 1, 2, \dots, n-1$ . So the equation for the diffusion flux takes the classical form

$$-\varrho^\delta V_i^\delta = \sum_{\beta=1}^{n-1} \left[ \varrho^\delta \varrho^\beta \frac{\bar{v}^{\beta\delta}}{v} \right] x_i^\beta + \left[ \sum_{\beta=1}^{n-1} \varrho^\delta T \frac{\bar{v}^{\beta\delta}}{v} \left( \varrho^\beta - \frac{\lambda^\beta}{T} \right) \right] \frac{\partial \ln T}{\partial x_i} \quad (77)$$

with  $\delta = 1, 2, \dots, n-1$ ;  $v$  is the determinant (assumed nonzero) and  $\bar{v}^{\beta\delta}$  the algebraic complement of the element  $v^{\beta\delta}$  of the coefficient matrix  $\|v^{\beta\delta}\|$  in the constitutive equation (1-21). On introducing Eq. (77) into the constitutive equation (1-44)

we obtain the classical expression for the heat flux

$$-J_i = \sum_{\delta=1}^{n-1} \left[ -\varrho^\delta \sum_{\beta=1}^{n-1} \lambda^\beta \frac{\bar{v}^{\delta\beta}}{\nu} \right] \mathcal{X}_i^\delta + \left[ \kappa T - \sum_{\beta=1}^{n-1} T \lambda^\beta \sum_{\delta=1}^{n-1} \frac{\bar{v}^{\delta\beta}}{\nu} \left( \mathcal{G}^\delta - \frac{\lambda^\delta}{T} \right) \right] \frac{\partial \ln T}{\partial x_i}. \quad (78)$$

The expressions in brackets in Eqs (77) and (78) are the phenomenological coefficients of irreversible thermodynamics expressed in terms of the constitutive equations (1-21) and (1-44), and therefore they are functions only of  $T$  and  $\varrho^1, \varrho^2, \dots, \varrho^n$ . Relation of the  $\nu^{\beta\delta}$  to diffusion coefficients follows from (76) and (77) when the isothermal gradients (74) are expressed by concentration gradients.

The driving force (76) can be obtained also by irreversible thermodynamics by rewriting the second and the last terms on the right side of Eq. (5) in ref.<sup>12</sup> in the form (with the use of the usual definitions of the barycentric diffusion flux and diffusion flux referred to the  $n$ -th constituent):

$$\frac{1}{2} \sum_{\beta=1}^{n-1} r^\beta V_i^\beta V_i^\beta + \sum_{\beta=1}^{n-1} \varrho^\beta V_i^\beta \mathcal{X}_i^\beta, \quad (79)$$

whence it follows by traditional arguments<sup>12</sup> that Eq. (76) is justified. In contrast to nonreacting mixtures<sup>7,8</sup>, however, the driving force (76) does not obey the Prigogine theorem<sup>10,12</sup>.

The Onsager reciprocal relations are in the envisaged material generally invalid as can be seen from Eqs (77) and (78). Their validity, however, can be simply achieved by the following additional assumptions:

$$\nu^{\beta\delta} = \nu^{\delta\beta}, \quad \mathcal{G}^\beta = 0, \quad \beta, \delta = 1, 2, \dots, n-1. \quad (80)$$

We note that if these assumptions apply, then in a special material (in which a relation analogous to (1-50) in partial quantities applies – compare the end of the section about thermodynamic structure and the definition (1-39)) we obtain the classical Onsagerian symmetry between the coefficients of the constitutive equations (1-21) and (1-44).

It can be concluded that by the method of rational thermodynamics it is possible to obtain most of the results of the classical equilibrium and nonequilibrium thermodynamics, and this in a manner excluding the problematicity of some postulates of these theories<sup>2</sup>. Moreover, the classical results represent only a minority of the possibilities of rational thermodynamics<sup>2,3</sup>.

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