

## GENERAL VALIDITY OF PRIGOGINE THEOREM IN IRREVERSIBLE THERMODYNAMICS

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The validity of the Prigogine theorem under any conditions (hence not only at mechanical equilibrium) was achieved by a suitable definition of driving forces of diffusion, which are always interrelated. Such driving forces can be obtained by supplementing the driving forces of diffusion following from the expression for production of entropy (derived on the basis of more exact balances of momentum and energy) with barycentric acceleration. This generalization does not change the production of entropy and at the same time it ensures the validity of mechanical equilibrium at thermodynamic equilibrium. In the approximate classical expression for driving forces of diffusion, such generalization weakens considerably the assumptions necessary for the validity of the Prigogine theorem.

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The classical method of deriving diffusion equations based on irreversible thermodynamics gives independent driving forces of diffusion<sup>1-5</sup>. Only at conditions of a so-called mechanical equilibrium<sup>1-4,8,12</sup>, usually fulfilled in diffusion experiments, the driving forces of diffusion begin to be mutually dependent. Based on this dependence, the Prigogine theorem can be derived, which states that the production of entropy caused by diffusion is invariant with respect to the definition of the diffusion flux, *i.e.* with respect to the choice of reference velocity of diffusion<sup>1-4</sup>. As shown by Fitts<sup>3</sup> in appendix D, the driving forces of diffusion obtained from the statistical-mechanical theory of Bearman for nonreacting mixture<sup>6</sup> are generally linearly dependent. Since Bearman's result<sup>6</sup> was obtained earlier<sup>7</sup> in a general, purely phenomenological manner, it could be expected that the Prigogine theorem, which is a result of this dependence, is valid generally. That this conclusion is true, is shown in the present work. The basic idea is supplementing the driving force of diffusion (following from the expression for entropy production) by barycentric acceleration  $D\mathbf{v}/Dt$ . This does not change the expression for entropy production owing to the mutual dependence of barycentric diffusion fluxes. It will be shown in the final part that already in classical irreversible thermodynamics<sup>1-5</sup> such generalization leads to mutual dependence of diffusion driving forces under much less severe assumptions than a mechanical equilibrium. However, even such assumptions are abandoned if more accurate balances<sup>7,8</sup> are used.\*

### *Definition of Driving Forces and Fluxes*

It was shown<sup>7</sup> with the use of more accurate balances of momentum and energy following from the Truesdell theory of a multicomponent continuum<sup>8</sup> that for an

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\* The paper dealing with similar subject and leading to the same results in a special case was recently published<sup>9</sup>.

$n$ -component, chemically reacting system without polarization and magnetization, in a field of conservative forces, with symmetrical partial friction pressure tensors, the expression for production of entropy  $\sigma$  has the form (Eqs (55) and (58) in ref.<sup>7</sup>)

$$\begin{aligned}
 -T\sigma = & \sum_{i=1}^n \mu_i r_i + \sum_{i=1}^n \psi_i r_i + \mathbf{J} \cdot \nabla \ln T + \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \\
 & + \sum_{i=1}^n \mathbf{\Pi}_i : \nabla \otimes \omega_i + \sum_{i=1}^n \mathbf{J}_i \cdot [\nabla_{\tau} \mu_i - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot (\mathbf{\Pi}_i + \frac{1}{2} \varrho_i \omega_i \otimes \omega_i)] + \\
 & + \left( \sum_{i=1}^n \varrho_i \omega_i \otimes \omega_i \right) : \nabla \otimes \mathbf{v} + \sum_{i=1}^n \left( \frac{1}{2} \varrho_i \omega_i \otimes \omega_i \right) : \nabla \otimes \omega_i + \frac{1}{2} \varrho \frac{D}{Dt} \sum_{i=1}^n w_i \omega_i^2. \quad (1)
 \end{aligned}$$

This equation is not identical with Eq. (259.4) in ref.<sup>8</sup> obtained in an analogous way, since the entropy balance, Eq. (49) in ref.<sup>7</sup>, differs from that in ref.<sup>8</sup>, Eq. (259.3) (in contrast to the accord in other balances). In the latter, different definitions of chemical potential and partial volume are used (ref.<sup>8</sup>, § 255 and 260) as compared with the balance (49) in ref.<sup>7</sup> (used also in classical monographs<sup>1-5</sup>). Differences in these definitions will be discussed elsewhere<sup>10</sup>. Eq. (1) can be rearranged with the use of (48) (see Appendix) as follows:

$$\begin{aligned}
 -T\sigma = & \sum_{i=1}^n \mu_i r_i + \sum_{i=1}^n \psi_i r_i + \mathbf{J} \cdot \nabla \ln T + \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \sum_{i=1}^n \mathbf{\Pi}_i : \nabla \otimes \omega_i + \\
 & + \sum_{i=1}^n \left\{ \mathbf{J}_i \cdot [\nabla_{\tau} \mu_i - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot \mathbf{\Pi}_i + \varrho_i^{-1} \nabla \cdot (\varrho_i \omega_i \otimes \omega_i) - \frac{1}{2} \varrho_i^{-1} \nabla \cdot (\varrho_i \omega_i \otimes \omega_i)] + \right. \\
 & \left. + \varrho_i \omega_i \cdot [(\omega_i \cdot \nabla) \mathbf{v}] + \varrho_i \omega_i \cdot [\frac{1}{2} (\omega_i \cdot \nabla) \omega_i] + \frac{1}{2} \omega_i^2 \varrho \frac{D w_i}{Dt} + \varrho_i \omega_i \cdot \frac{D \omega_i}{Dt} \right\}. \quad (1a)
 \end{aligned}$$

On introducing Eqs (49), (50), (55) (equations of continuity for  $i$ -th species) and (60) and using the definition of substantial derivative (52) for  $\varphi = \omega_i$ , we obtain the equation (which for a nonreacting mixture is identical with (58a) in ref.<sup>7</sup>)

$$\begin{aligned}
 -T\sigma = & \sum_{i=1}^n \mu_i r_i + \sum_{i=1}^n \psi_i r_i + \mathbf{J} \cdot \nabla \ln T + \sum_{i=1}^n \mathbf{\Pi}_i : \nabla \otimes \mathbf{v}_i + \sum_{i=1}^n \mathbf{J}_i \cdot \left\{ \nabla_{\tau} \mu_i - \right. \\
 & - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot [\mathbf{\Pi}_i + (\varrho_i \omega_i \otimes \omega_i)] - \frac{1}{2} \varrho_i^{-1} \nabla \cdot (\varrho_i \omega_i \otimes \omega_i) + \omega_i \cdot (\nabla \otimes \mathbf{v}) + \\
 & \left. + \frac{1}{2} \omega_i \cdot (\nabla \otimes \omega_i) + \frac{1}{2} \varrho_i^{-1} \omega_i r_i - \frac{1}{2} \varrho_i^{-1} \omega_i (\nabla \cdot \mathbf{J}_i) + \frac{\partial \omega_i}{\partial t} + (\mathbf{v} \cdot \nabla) \omega_i \right\}. \quad (2)
 \end{aligned}$$

Now we add to the right side of this equation the identity

$$\sum_{i=1}^n \mathbf{J}_i \cdot (\mathbf{D}\mathbf{v}/\mathbf{D}t) = 0, \quad (3)$$

which follows from the property of barycentric fluxes (51), and further we add and subtract on the right side of Eq. (2) the expression

$$\sum_{i=1}^n \frac{1}{2} \omega_i^2 r_i = \sum_{i=1}^n \mathbf{J}_i \cdot (\frac{1}{2} \varrho_i^{-1} \omega_i r_i). \quad (4)$$

Thus, we obtain

$$\begin{aligned} -T\sigma = & \sum_{i=1}^n \mu_i r_i - \sum_{i=1}^n \frac{1}{2} \omega_i^2 r_i + \sum_{i=1}^n \psi_i r_i + \mathbf{J} \cdot \nabla \ln T + \\ & + \sum_{i=1}^n \Pi_i : \nabla \otimes \mathbf{v}_i + \sum_{i=1}^n \mathbf{J}_i \cdot X_i, \end{aligned} \quad (5)$$

where, regarding the arbitrariness in defining fluxes and forces in irreversible thermodynamics<sup>3,5,8</sup>, we define the driving forces of diffusion as

$$\begin{aligned} X_i \equiv & \nabla_T \mu_i - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot (\Pi_i + \varrho_i \omega_i \otimes \omega_i) - \frac{1}{2} \varrho_i^{-1} \nabla \cdot (\varrho_i \omega_i \otimes \omega_i) + \\ & + \omega_i \cdot (\nabla \otimes \mathbf{v}) + \frac{1}{2} \omega_i \cdot (\nabla \otimes \omega_i) - \frac{1}{2} \varrho_i^{-1} \omega_i (\nabla \cdot \mathbf{J}_i) + \partial \omega_i / \partial t + \\ & + \mathbf{D}\mathbf{v}/\mathbf{D}t + (\mathbf{v} \cdot \nabla) \omega_i + \varrho_i^{-1} \omega_i r_i. \end{aligned} \quad (6)$$

With the use of Eqs (49)–(53), (55) and (58) (see Appendix) and by an analogous rearrangement as in deriving Eq. (59) from (58a) in ref.<sup>7</sup> we obtain the driving forces of diffusion in the form

$$\begin{aligned} X_i = & \nabla_T \mu_i - \mathbf{F}_i + \varrho_i^{-1} \partial(\varrho_i \mathbf{v}_i) / \partial t + \varrho_i^{-1} \nabla \cdot [\Pi_i + \varrho_i \omega_i \otimes \omega_i + \\ & + \varrho_i (\mathbf{v}_i \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{v}_i - \mathbf{v} \otimes \mathbf{v})] - \varrho_i^{-1} \mathbf{v} r_i, \end{aligned} \quad (7)$$

which is for nonreacting mixtures ( $r_i = 0$ ) identical with that given by Fitts<sup>3</sup>, Eq. (D3) since our term  $-(\Pi_i + \varrho_i \omega_i \otimes \omega_i)$  corresponds to Bearman's "viscous contribution to the partial stress tensor"<sup>6</sup> (cf. discussion of Eq. (58) in ref.<sup>7</sup>).

Eq. (7) can be further rearranged with the use of (47), (48), (52) (for  $\varphi = \mathbf{v}$ ) and (54) into the form

$$\begin{aligned} X_i = & \nabla_T \mu_i - \mathbf{F}_i + \varrho_i^{-1} \partial \mathbf{J}_i / \partial t + \varrho_i^{-1} \nabla \cdot [\Pi_i + \varrho_i \omega_i \otimes \omega_i] + \\ & + \varrho_i^{-1} [\nabla \cdot (\mathbf{J}_i \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{J}_i) - (\mathbf{v} \otimes \nabla) \cdot \mathbf{J}_i] + \mathbf{D}\mathbf{v}/\mathbf{D}t. \end{aligned} \quad (8)$$

This driving force  $X_i$  has, except for the term  $\mathbf{D}\mathbf{v}/\mathbf{D}t$ , which is (Eq. (3)) meaningless in the entropy production, the same form as that defined by Bearman<sup>6</sup>, Eq. (16), for nonreacting mixtures.

The driving forces of diffusion defined by Eqs (6)–(8) for  $i = 1$  to  $n$  have an important property, namely they are linearly dependent:

$$\sum_{i=1}^n \varrho_i X_i = 0. \quad (9)$$

This can be derived from the definition (7) similarly as by Fitts for nonreacting mixtures (Eq. (D5) in ref.<sup>3</sup>):

$$\begin{aligned} \sum_{i=1}^n \varrho_i X_i &= \sum_{i=1}^n \varrho_i \nabla_T \mu_i - \sum_{i=1}^n \varrho_i F_i + \nabla \cdot \left( \sum_{i=1}^n \Pi_i + \sum_{i=1}^n \varrho_i \omega_i \otimes \omega_i \right) + \\ &+ \sum_{i=1}^n \partial \varrho_i \mathbf{v}_i / \partial t + \nabla \cdot \sum_{i=1}^n \varrho_i (\mathbf{v}_i \otimes \mathbf{v} + \mathbf{v} \otimes \mathbf{v}_i - \mathbf{v} \otimes \mathbf{v}) - \mathbf{v} \sum_{i=1}^n r_i. \end{aligned} \quad (10)$$

The Gibbs–Duhem equation can be with the use of the definition of isothermal gradient  $\nabla_T$  written in the form (Eq. (V-6) in ref.<sup>2</sup>)

$$\sum_{i=1}^n \varrho_i \nabla_T \mu_i = \nabla P. \quad (11)$$

In accord with most authors<sup>1–5,11,12</sup>, we shall assume that Eq. (11) holds. Truesdell<sup>8</sup> in § 261 (*cf.*<sup>13</sup>) doubts whether Eq. (11) is valid except for equilibrium; however, as will be shown in our work<sup>10</sup>, his doubts are the result of a more general concept of partial quantities, chemical potential and principle of local equilibrium in his work<sup>8,13</sup> (see also discussion of Eq. (1)). On introducing Eq. (11) into (10) and expressing the first three terms from the equations of continuity of momentum (59) and (60), it is seen that the last term cancels as a consequence of Eq. (56) and the rest can be rearranged with the use of Eqs (47), (49)–(51) into the form

$$\sum_{i=1}^n \varrho_i X_i = -\varrho D\mathbf{v}/Dt + \varrho \partial \mathbf{v} / \partial t + \mathbf{v} \partial \varrho / \partial t + (\nabla \cdot \varrho \mathbf{v}) \mathbf{v}.$$

This expression is equal to zero as is obvious when the last term is expressed from the definition (52) for  $\varphi = \mathbf{v}$  and from the equation of continuity of mass (57). Thus, the relation (9) is confirmed.

Now we shall continue rearranging Eq. (5). The potential energy in a chemical reaction is constant,

$$\sum_{i=1}^n r_i \psi_i = 0, \quad (12)$$

since mass and electric charge do not change during chemical reaction (*cf.*<sup>2</sup>, Eq. (II–27)). This probably does not apply for the kinetic energy of diffusion, *i.e.* the term  $\frac{1}{2} \sum r_i \omega_i^2$ , which expresses the change of (macroscopic) kinetic energy of diffusion during chemical reaction, is generally different from zero. With respect to the right side of Eq. (4), this term could be attributed also to diffusion, but if we want

the driving forces of diffusion to have the property (9) we must attribute the mentioned term to chemical reactions analogously as done by Truesdell<sup>8</sup>, § 259. This appears plausible since one can imagine that, *e.g.* one of the components is introduced into the reaction as a macroscopic flux. The macroscopic kinetic energy of diffusion is degraded by a chemical reaction to internal energy (bonding energy and kinetic energy of thermal motion) and so contributes to the increase of entropy during the reaction. The part of the expression for entropy production caused by chemical reactions (Eq. (5)) can be modified by introducing the rates of chemical reactions,  $\gamma_k$

$$r_i = \sum_{k=1}^r M_i v_{ik} \gamma_k, \quad i = 1 \text{ to } n, \quad (13)$$

and the affinity of  $k$ -th chemical reaction,

$$A_k = - \sum_{i=1}^n v_{ik} M_i \mu_i, \quad k = 1 \text{ to } r, \quad (14)$$

where  $v_{ik}$  are molar stoichiometric coefficients and  $M_i$  relative molar masses of components. In contrast to the definition used earlier<sup>2</sup> (Eq. (55) in ref.<sup>7</sup>), we used the original definition<sup>1,4,11,12,14</sup>.

Further, by analogous use of the standard method<sup>2-4,12</sup> we divide the partial friction tensors  $\Pi_i$  into partial friction pressures  $\pi_i$  and partial friction divergenceless tensors  $\overset{0}{\Pi}_i$  defined by

$$\pi_i \equiv \frac{1}{3} \text{Tr} \Pi_i, \quad (15)$$

$$\Pi_i \equiv \pi_i \mathbf{U} + \overset{0}{\Pi}_i, \quad (16)$$

where  $\mathbf{U}$  denotes unit tensor and  $i = 1$  to  $n$ . Since the tensors  $\Pi_i$  are assumed to be symmetrical, one can derive the following expression with the aid of Eqs (15) and (16):

$$\sum_{i=1}^n \Pi_i : \nabla \otimes \mathbf{v}_i = \sum_{i=1}^n \pi_i (\nabla \cdot \mathbf{v}_i) + \sum_{i=1}^n \overset{0}{\Pi}_i : (\overline{\nabla \otimes \mathbf{v}_i})^s, \quad (17)$$

where  $()^s$  denotes symmetry and  $\overset{0}{}$  means divergenceless tensor. With the use of the definitions

$$\pi \equiv \sum_{i=1}^n \pi_i, \quad \overset{0}{\Pi} \equiv \sum_{i=1}^n \overset{0}{\Pi}_i, \quad (18)$$

which are in accord with Eqs (16) and (60), and with Eq. (49) it is possible to rewrite Eq. (17) in the form

$$\sum_{i=1}^n \Pi_i : \nabla \otimes \mathbf{v}_i = \pi \nabla \cdot \mathbf{v} + \sum_{i=1}^n \pi_i \nabla \cdot \omega_i + \overset{0}{\Pi} : (\overline{\nabla \otimes \mathbf{v}})^s + \sum_{i=1}^n \overset{0}{\Pi}_i : (\overline{\nabla \otimes \omega_i})^s. \quad (19)$$

On introducing Eqs (12)–(14) and (17) into (5) we obtain finally the expression for entropy production

$$\begin{aligned}
 -T\sigma = & - \sum_{k=1}^r \gamma_k (A_k + \sum_{i=1}^n \frac{1}{2} \omega_i^2 M_i v_{ik}) + \sum_{i=1}^n \pi_i \nabla \cdot \mathbf{v}_i + \mathbf{J} \cdot \nabla \ln T + \\
 & + \sum_{i=1}^n \mathbf{J}_i \cdot X_i + \sum_{i=1}^n \mathbf{I}_i : \frac{0}{(\nabla \otimes \mathbf{v}_i)^s}. \quad (20)
 \end{aligned}$$

The driving forces of diffusion are defined by one of the Eqs (6)–(8) and are linearly dependent by Eq. (9). The fluxes are defined in the usual manner:  $\gamma_k$  rate of  $k$ -th chemical reaction,  $\mathbf{J}$  reduced heat flow,  $\mathbf{J}_i$  barycentric diffusion flow of  $i$ -th component (these fluxes are linearly interdependent), the friction pressures  $\pi_i$  and friction tensors  $\mathbf{I}_i$  are also analogous<sup>1-5,12</sup> with respect to Eq. (19).

Reduction of Eq. (20) to usual balances<sup>1-5</sup> will be discussed in the final paragraph (*cf.* discussion in ref.<sup>7</sup>).

#### *Prigogine Theorem and its Consequences*

The result of the linear dependence (9) of driving forces of diffusion defined by Eqs (6)–(8) is the general validity of the Prigogine theorem: The entropy production is invariant with respect to the definition of the diffusion flux. The general diffusion flux with respect to an arbitrary reference velocity  $\mathbf{v}^a$  can be defined as

$$\mathbf{J}_i^a \equiv \varrho_i (\mathbf{v}_i - \mathbf{v}^a), \quad i = 1 \text{ to } n. \quad (21)$$

This equation in combination with (9) and (50) gives the Prigogine theorem:

$$\sum_{i=1}^n \mathbf{J}_i \cdot X_i = \sum_{i=1}^n \varrho_i (\mathbf{v}_i - \mathbf{v}^a) \cdot X_i + (\mathbf{v}^a - \mathbf{v}) \cdot \sum_{i=1}^n \varrho_i X_i = \sum_{i=1}^n \mathbf{J}_i^a \cdot X_i, \quad (22)$$

which is hence valid under all conditions and not only at a so-called mechanical equilibrium<sup>1-4</sup>. The reference velocity  $\mathbf{v}^a$  is in practice defined as

$$\mathbf{v}^a \equiv \sum_{i=1}^n a_i \mathbf{v}_i, \quad \sum_{i=1}^n a_i = 1, \quad (23), (24)$$

(ref.<sup>2</sup>, chapter XI, § 2), where  $a_i$  are weight coefficients depending on the definition of  $\mathbf{v}^a$  (for barycentric velocity  $\mathbf{v}$  is  $a_i = w_i$ ). The diffusion fluxes  $\mathbf{J}_i^a$  in Eq. (21) are linearly dependent:

$$\sum_{i=1}^n a_i \mathbf{J}_i^a / w_i = 0. \quad (25)$$

For a barycentric flux  $\mathbf{J}_i$ , Eq. (25) is reduced to (51). The condition (9) can be

written with the use of (48) as

$$\sum_{i=1}^n w_i X_i = 0. \quad (26)$$

In view of the general validity of the Prigogine theorem (22), a part of the entropy production due to vector phenomena,  $\sigma_v$ , can be rearranged analogously as in ref.<sup>2</sup>, chapter XI, § 2 (the Curie theorem can be applied in the usual manner):

$$\begin{aligned} -T\sigma_v &\equiv \sum_{i=1}^n \mathbf{J}_i \cdot X_i + \mathbf{J} \cdot \nabla \ln T = \sum_{i=1}^n \mathbf{J}_i^a \cdot X_i + \mathbf{J} \cdot \nabla \ln T = \\ &= \sum_{i=1}^{n-1} \mathbf{J}_i^a \cdot \left( X_i - \frac{w_n}{a_n} \frac{a_i}{w_i} X_n \right) + \mathbf{J} \cdot \nabla \ln T = \sum_{i=1}^{n-1} \mathbf{J}_i^a \cdot X_i^a + \mathbf{J} \cdot \nabla \ln T. \end{aligned} \quad (27)$$

Here we used Eq. (25) and define the driving force of diffusion from Eq. (26) as

$$X_i^a \equiv \sum_{i=1}^{n-1} \left( \delta_{ii} + \frac{a_i w_i}{a_n w_i} \right) X_i, \quad i = 1 \text{ to } n. \quad (28)$$

Eq. (27) can be written concisely in the matrix form

$$-T\sigma_v = \tilde{\mathbf{J}}^a \mathbf{X}^a, \quad (29)$$

where  $\mathbf{J}^a$  and  $\mathbf{X}^a$  are matrices  $n \times 1$  composed of elements  $\mathbf{J}_\alpha^a$  and  $X_\alpha^a$ , respectively,  $\alpha = 1, 2, \dots, n-1, q$ , the symbol  $\sim$  denotes transposition, and

$$\mathbf{J}_q^a \equiv \mathbf{J}, \quad X_q^a \equiv \nabla \ln T. \quad (30)$$

Eqs (29) and (30) are valid for any index  $a$ . If we choose another reference velocity  $\mathbf{v}^b$  defined by Eq. (23) with weight coefficients  $b_i$  instead of  $a_i$  (index  $b$  is used instead of  $a$ ), we must use the transformation (ref.<sup>2</sup>, chapter XI)

$$\mathbf{J}^b = \mathbf{B}^{ba} \mathbf{J}^a, \quad (31)$$

where the  $n \times n$  matrix  $\mathbf{B}^{ba}$  has the elements

$$B_{\beta\alpha}^{ba} = \left[ \delta_{\beta\alpha} + \left( b_n \frac{a_\alpha}{a_n} - b_\alpha \right) \frac{w_\beta}{w_\alpha} \right] (1 - \delta_{q\alpha}) (1 - \delta_{\beta q}) + \delta_{q\alpha} \delta_{\beta q}. \quad (32)$$

Here  $\alpha, \beta = 1, 2, \dots, n-1, q$  and  $a_q, b_q, w_q$  are constants different from zero. By a change of symbols and indexes  $b$  for  $a$  in Eqs (31) and (32) we obtain

$$\mathbf{J}^a = \mathbf{B}^{ab} \mathbf{J}^b, \quad (33)$$

which can be obtained also by inversion of (31), hence

$$\mathbf{B}^{ab} = (\mathbf{B}^{ba})^{-1}. \quad (34)$$

By introducing Eq. (33) into (29) we obtain, considering the invariance of  $T\sigma_v$ ,

$$-T\sigma_v = \mathbf{J}^b \tilde{\mathbf{B}}^{ab} \mathbf{X}^a = \mathbf{J}^b \mathbf{X}^b, \quad (35)$$

where

$$\mathbf{X}^b = \tilde{\mathbf{B}}^{ab} \mathbf{X}^a. \quad (36)$$

The fluxes  $\mathbf{J}^b$  can be expressed as linear functions of thermodynamic forces  $\mathbf{X}^b$ :

$$\mathbf{J}^b = -\mathbf{L}^b \mathbf{X}^b, \quad (37)$$

where  $\mathbf{L}^b$  denotes  $n \times n$  matrix of phenomenological coefficients; we assume that they fulfil the Onsager reciprocal relations

$$\mathbf{L}^b = \tilde{\mathbf{L}}^b. \quad (38)$$

It is known that these relations must be postulated in phenomenological thermodynamics<sup>12,13,15</sup>, usually for fluxes (defined with respect to barycentric velocity in the case of diffusion) and forces, which are mutually independent. These conditions are fulfilled in Eq. (37) except that our definition of the driving force contains the flux (as is apparent from Eq. (8) when the divergences are performed). As will be shown below, the terms involving the diffusion flux are negligible in practical cases. Let Eq. (38) be a postulate valid for a barycentric velocity  $\mathbf{v}^b = \mathbf{v}$ ; we shall prove that it retains its validity if another, arbitrary reference velocity  $\mathbf{v}^a$  is chosen. Indeed, on introducing Eq. (36) into (37) and the result into (33), we obtain the linear relationship

$$\mathbf{J}^a = -\mathbf{B}^{ab} \mathbf{L}^b \tilde{\mathbf{B}}^{ab} \mathbf{X}^a, \quad (39)$$

where the new phenomenological coefficients are

$$\mathbf{L}^a = \mathbf{B}^{ab} \mathbf{L}^b \tilde{\mathbf{B}}^{ab}. \quad (40)$$

It is seen after transposition of this relation that these new coefficients, as a consequence of Eq. (38), fulfil also the Onsager reciprocal relations:

$$\tilde{\mathbf{L}}^a = \tilde{\tilde{\mathbf{B}}}^{ab} \tilde{\mathbf{L}}^b \tilde{\mathbf{B}}^{ab} = \mathbf{B}^{ab} \mathbf{L}^b \tilde{\mathbf{B}}^{ab} = \mathbf{L}^a. \quad (41)$$

As discussed in detail in ref.<sup>7</sup>, it is possible under usual conditions to neglect those



terms in the entropy production which contain squares of diffusion velocity components (compare conditions (45) and (46) in ref.<sup>7</sup>), so that Eq. (1) gives

$$-T\sigma \approx \sum_{i=1}^n \mu_i r_i + \sum_{i=1}^n \psi_i r_i + \mathbf{J} \cdot \nabla \ln T + \mathbf{\Pi} : \nabla \otimes \mathbf{v} + \sum_{i=1}^n \mathbf{\Pi}_i : \nabla \otimes \boldsymbol{\omega}_i + \sum_{i=1}^n \mathbf{J}_i \cdot (\nabla_T \mu_i - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot \mathbf{\Pi}_i). \quad (42)$$

From this we obtain with the use of Eqs (3), (12)–(16) an approximate expression corresponding to Eq. (20):

$$-T\sigma \approx -\sum_{k=1}^r \gamma_k A_k + \sum_{i=1}^n \pi_i \nabla \cdot \mathbf{v}_i + \sum_{i=1}^n \mathbf{\Pi}_i : \overline{(\nabla \otimes \mathbf{v}_i)^2} + \mathbf{J} \cdot \nabla \ln T + \sum_{i=1}^n \mathbf{J}_i \cdot (\nabla_T \mu_i - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot \mathbf{\Pi}_i + D\mathbf{v}/Dt). \quad (43)$$

The driving forces of diffusion following from this equation as an approximation of Eqs (6)–(8) are again interdependent:

$$\sum_{i=1}^n \varrho_i (\nabla_T \mu_i - \mathbf{F}_i + \varrho_i^{-1} \nabla \cdot \mathbf{\Pi}_i + D\mathbf{v}/Dt) = 0. \quad (44)$$

This relation corresponding to (9) was derived with the aid of Eqs (11), (47), (60) and the equation of continuity of momentum (59) which in the given approximation takes the form

$$\varrho D\mathbf{v}/Dt \approx -\nabla P - \nabla \cdot \mathbf{\Pi} + \sum_{i=1}^n \varrho_i \mathbf{F}_i. \quad (45)$$

Hence, in the mentioned approximation the Prigogine theorem (22) and its consequences also apply while the driving forces and fluxes following from Eqs (27) and (28) are now independent (cf. discussion of Eq. (38)). If we, moreover, assume that

$$\nabla \cdot \mathbf{\Pi}_i \approx 0, \quad i = 1 \text{ to } n \quad (46)$$

(or in addition,  $\nabla \otimes \boldsymbol{\omega}_i \approx 0$ ), Eqs (42) and (43) are reduced (with regard to (3)) to the classical expression of entropy production<sup>1-5</sup>. The driving forces of diffusion are now interdependent by Eq. (9) since the equation of continuity of momentum (45) is simplified by (46). It is seen that the general validity of Eq. (9) and hence of the Prigogine theorem is secured by adding the term  $D\mathbf{v}/Dt$  to the driving force of diffusion. This term does not affect the results known as yet: the entropy production does not change (with regard to Eq. (3)), and most authors<sup>1-5</sup> either start from the expression of the driving force of diffusion following from Eq. (27) for barycentric velocity so that the term  $D\mathbf{v}/Dt$  cancels, or they assume a mechanical equilibrium,

$D\mathbf{v}/Dt = 0$ . The assumption of  $\Pi = 0$  is unnecessarily severe; Eq. (46) is sufficient. In favour of the presence of the term  $D\mathbf{v}/Dt$  in the driving force of diffusion is also the fact that in thermodynamic equilibrium, when  $\sigma = 0$  and all fluxes as well as all driving forces are zero, a mechanical equilibrium must exist. This indeed follows from Eqs (20) and (43) (e.g.,  $D\mathbf{v}/Dt$  must be equal to zero,  $\nabla \cdot \Pi_i = 0$ , and so on).

## APPENDIX

We shall give here some equations used in the text without derivation. The densities (weight concentrations) of components,  $\varrho_i$ , and the density of the mixture,  $\varrho$ , fulfil the relationships<sup>2-4,7</sup>

$$\sum_{i=1}^n \varrho_i = \varrho, \quad \varrho_i = w_i \varrho, \quad (47), (48)$$

where  $w_i$  denotes weight fraction of  $i$ -th component of the mixture. The diffusion velocity  $\omega_i$  and diffusion flux  $J_i$  relative to barycentric velocity  $\mathbf{v}$  (defined by Eq. (23) for  $a_i = w_i$ ) are given by

$$\omega_i = \mathbf{v}_i - \mathbf{v}, \quad J_i = \varrho_i(\mathbf{v}_i - \mathbf{v}), \quad (49), (50)$$

where  $\mathbf{v}_i$  denotes macroscopic velocity of  $i$ -th component<sup>2-4,7</sup>. The barycentric diffusion fluxes have the property

$$\sum_{i=1}^n J_i = 0. \quad (51)$$

The substantial derivatives are operators acting upon some function of time and position,  $\varphi$ , which can be a vector. The substantial derivatives with respect to a mixture<sup>2,3,7,8,12</sup> and to the velocity of  $i$ -th component<sup>7,8,12</sup> are, respectively,

$$D\varphi/Dt = \partial\varphi/\partial t + (\mathbf{v} \cdot \nabla) \varphi, \quad (52)$$

$$D_i\varphi/Dt = \partial\varphi/\partial t + (\mathbf{v}_i \cdot \nabla) \varphi. \quad (53)$$

The equation of continuity of mass of  $i$ -th component<sup>2-4,7,12</sup> has two equivalent forms:

$$\partial\varrho_i/\partial t + \nabla \cdot (\varrho_i \mathbf{v}_i) = r_i, \quad (54)$$

$$\varrho D w_i / Dt + \nabla \cdot J_i = r_i, \quad (55)$$

where  $r_i$  denotes amount of  $i$ -th component formed during a time unit in a unit volume by chemical reactions. For the whole mixture the mass conservation and the equation of continuity of the total mass apply:

$$\sum_{i=1}^n r_i = 0, \quad \partial\varrho/\partial t + \nabla \cdot (\varrho \mathbf{v}) = 0. \quad (56), (57)$$

With the aid of these formulas we can prove that (Eq. (22) in ref.<sup>7</sup>)

$$\partial(\varrho_i \mathbf{v}_i) / \partial t + \nabla \cdot (\varrho_i \mathbf{v}_i \otimes \mathbf{v}_i) = \varrho_i D_i \mathbf{v}_i / Dt + \mathbf{v}_i r_i. \quad (58)$$

The equation of continuity of momentum is<sup>7,8,12</sup>

$$\rho D\mathbf{v}/Dt = -\nabla P - \nabla \cdot (\boldsymbol{\Pi} + \sum_{i=1}^n \rho_i \omega_i \otimes \omega_i) + \sum_{i=1}^n \rho_i F_i, \quad (59)$$

where  $P$  denotes thermodynamic pressure,  $F_i$  volume force acting upon unit mass of  $i$ -th component and  $\boldsymbol{\Pi}$  friction pressure tensor equal to the sum of partial friction pressure tensors  $\boldsymbol{\Pi}_i$ :

$$\boldsymbol{\Pi} = \sum_{i=1}^n \boldsymbol{\Pi}_i. \quad (60)$$

#### LIST OF SYMBOLS

$a_i, a_\alpha, b_\alpha$	weights in definition of reference velocities
$\mathbf{B}^{\mathbf{a}\mathbf{b}}, \mathbf{B}^{\mathbf{b}\mathbf{a}}$	transformation matrices of fluxes and forces
$B_{\alpha\beta}^{\mathbf{a}\mathbf{b}}$	elements of transformation matrices
$F_i$	volume force of unit mass of $i$ -th component
$J$	reduced heat flow
$J_i$	barycentric diffusion flux of $i$ -th component
$J_i^{\mathbf{a}}$	diffusion flux of $i$ -th component referred to $\mathbf{v}^{\mathbf{a}}$
$J_q^{\mathbf{a}}$	reduced heat flow (see Eq. 30)
$J_\alpha^{\mathbf{a}}$	vector flux (heat conduction and diffusion)
$\mathbf{J}^{\mathbf{a}}, \mathbf{J}^{\mathbf{b}}$	matrices of vector fluxes
$\mathbf{L}^{\mathbf{a}}, \mathbf{L}^{\mathbf{b}}$	matrices of phenomenological coefficients
$M_i$	relative molecular mass of $i$ -th component
$P$	thermodynamic pressure
$r_i$	rate of formation of $i$ -th component by chemical reactions
$T$	absolute temperature
$\mathbf{U}$	unit tensor
$\mathbf{v}$	barycentric velocity
$\mathbf{v}_i$	velocity of $i$ -th component
$\mathbf{v}^{\mathbf{a}}, \mathbf{v}^{\mathbf{b}}$	reference velocities
$w_i$	weight fraction
$X_i$	driving force of diffusion
$X_i^{\mathbf{a}}$	independent driving force of diffusion
$X_q^{\mathbf{a}}$	driving force of heat conduction
$\mathbf{X}^{\mathbf{a}}, \mathbf{X}^{\mathbf{b}}$	matrices of driving forces of vector phenomena
$\gamma_k$	rate of $k$ -th chemical reaction
$\delta_{ij}$	Kronecker delta
$\mu_i$	specific chemical potential
$\nu_{ik}$	molar stoichiometric coefficient
$\pi$	friction pressure
$\pi_i$	partial friction pressure
$\boldsymbol{\Pi}$	friction pressure tensor
$\boldsymbol{\Pi}_i$	partial friction pressure tensor
$\rho$	density
$\rho_i$	density of $i$ -th component (weight concentration)
$\sigma$	entropy production
$\sigma_v$	production of entropy by vector phenomena

$\varphi$	function of coordinates and time (scalar or vector)
$\psi_i$	specific potential energy of $i$ -th component
$\omega_i$	diffusion velocity of $i$ -th component
$D/Dt$	substantial derivative
$D_i/Dt$	substantial derivative of $i$ -th component
Tr	trace of tensor
$\nabla_T$	isothermal gradient
$\otimes$	diadic product
:	double-dot scalar product of tensors
$^0, \underline{\quad}$	(above symbol of tensor) divergenceless tensor
$(\quad)^s$	denotation of symmetrical tensor
$\sim$	denotation of transposition of matrix
$a, b$	indexes of reference velocities
$i, j, l, n$	denotation of components
$k, r$	denotation of chemical reactions
$q$	index denoting heat conduction
$\alpha, \beta$	indexes of elements of transformation matrices

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