

## REDUCTION OF THERMODYNAMIC CONSTITUTIVE EQUATIONS FOR FLUID MIXTURES USING FORM INVARIANCE

Ivan SAMOHÝL

*Department of Physical Chemistry,  
Prague Institute of Chemical Technology, 166 28 Prague 6*

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Balances of mass, momentum and its moment, energy, and entropy in Truesdell's model of  $n$ -constituent mixtures have the property of form invariance: a certain change of primitive properties by means of  $2n - 1$  arbitrary quantities does not cause a change in their form. This arbitrariness can be used to make also the constitutive equations for partial thermodynamic quantities independent of the transport quantities (e.g. on temperature gradients or deformation rates). The classical method of Coleman and Noll used in rational thermodynamics of fluid mixtures namely permits to obtain such an independence with constitutive equations for thermodynamic quantities of mixtures only, and not for the partial quantities.

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In describing thermodynamic and transport phenomena in nonlinear continuum thermomechanics (rational thermodynamics), a mixture is often modelled by a superposition of its constituents (Truesdell<sup>1,2</sup>). Three principles are used<sup>1</sup> (p. 221; cf. refs<sup>3,4</sup>), from which it follows that the partial properties (i.e. those of the constituents) are considered in this theory as primitive notions. Such a concept permits to utilize so-called form invariance<sup>5,6</sup> (cf. refs<sup>3,4</sup>): the partial (mostly primitive) quantities can be changed in a certain way without changing the form of the balances (of mass, momentum and its moment, energy, and entropy). Then the other results also do not change in form (when the standard procedure involving the constitutive principles is used<sup>1,4,3,7</sup>), and it is thus possible to make sure that the partial quantities used at the start have preselected properties.

Thus, for example, the form invariance in a fluid mixture with linear transport properties was used to make the partial thermodynamic properties identical with partial molar quantities known from classical thermochemistry of mixtures<sup>3-6</sup>. Another example is given in the present paper. Using the standard procedure after Coleman and Noll<sup>7</sup> we obtain that, in contrast to partial thermodynamic quantities, the thermodynamic quantities for a mixture are independent of the transport variables (e.g. temperature gradients or deformation rates). We shall show here that this property can be attained with the aid of the form invariance also in the case of partial

thermodynamic quantities, whereby a considerable simplification of their constitutive equations is achieved.

### *Balances and Entropic Inequality*

We shall deal with the balances of mass, momentum and its moment, energy, and the entropic inequality, used in the theory of mixtures<sup>2-6,8</sup> based on the model of superimposed constituents of the mixture and the three above mentioned principles of Truesdell<sup>1</sup>. These relations are postulated for both the constituents and the mixture in the integral form and are given here in the local form for an  $n$ -constituent mixture. For simplicity, we restrict ourselves to mechanically nonpolar constituents (cf. Eq. (5)) and a single temperature for all constituents of the mixture (so that the balance of energy need be made only for the mixture<sup>1,3,4</sup>).

The momentum balance for constituent  $\alpha$  is

$$\frac{\partial \varrho_\alpha}{\partial t} + \operatorname{div} \varrho_\alpha \mathbf{v}_\alpha = r_\alpha, \quad (1)$$

where  $\varrho_\alpha$  denotes density of the constituent  $\alpha$  ("weight" concentration),  $\mathbf{v}_\alpha$  its velocity,  $r_\alpha$  its source due to chemical reactions (mass of constituent  $\alpha$  formed or consumed per unit time in a unit volume), and  $t$  is time;  $\operatorname{div}$  denotes, as usual, divergence in space coordinates. Subscripts  $\alpha$  and  $\gamma$  run through 1, 2, ...,  $n$  and  $\beta, \delta$  through 1, 2, ...,  $n - 1$ .

The mass balance for the mixture is

$$\sum_{\alpha=1}^n r_\alpha = 0. \quad (2)$$

The momentum balances for the constituents have the form

$$\frac{\partial \varrho_\alpha \mathbf{v}_\alpha}{\partial t} + \operatorname{div} (\varrho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \operatorname{div} \mathbf{T}_\alpha + \varrho_\alpha \mathbf{b}_\alpha + \mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha, \quad (3)$$

where  $\mathbf{T}_\alpha$  denotes partial stress tensor of constituent  $\alpha$ ,  $\mathbf{b}_\alpha$  is the external volume force (e.g. gravitation) acting upon constituent  $\alpha$ ,  $\mathbf{k}_\alpha$  is the interaction (volume) force acting upon it and originating from the other constituents, and the last term expresses the change of momentum due to chemical reactions.

The momentum balance for the mixture is

$$\sum_{\alpha=1}^n (\mathbf{k}_\alpha + r_\alpha \mathbf{v}_\alpha) = \mathbf{0}, \quad (4)$$

and the balances of the moment of momentum for mechanically nonpolar consti-

tuents  $\alpha = 1, \dots, n$  have the form

$$\mathbf{T}_\alpha = \mathbf{T}_\alpha^T, \quad (5)$$

where the superscript T denotes transposition. The balance of the moment of momentum is obtained by summing Eq. (5) over all constituents. The energy balance has the form

$$\sum_{\alpha=1}^n \frac{\partial \varrho_\alpha u_\alpha}{\partial t} + \sum_{\alpha=1}^n \operatorname{div} \varrho_\alpha u_\alpha \mathbf{v}_\alpha = \sum_{\alpha=1}^n \operatorname{tr} \mathbf{T}_\alpha \mathbf{D}_\alpha - \operatorname{div} \mathbf{q} + Q - \sum_{\beta=1}^{n-1} \mathbf{k}_\beta \cdot \mathbf{u}_\beta - \frac{1}{2} \sum_{\beta=1}^{n-1} r_\beta \mathbf{u}_\beta^2, \quad (6)$$

where  $u_\alpha$  denotes (specific) internal energy of constituent  $\alpha$ ,  $\mathbf{D}_\alpha$  partial stretching tensor (symmetrical part of the velocity gradient of constituent  $\alpha$ ),  $\mathbf{q}$  heat flux,  $Q$  heat source (by radiation), and  $\mathbf{u}_\beta$  diffusion velocity defined as

$$\mathbf{u}_\beta \equiv \mathbf{v}_\beta - \mathbf{v}_n \quad (7)$$

Equation (6) can be derived from the total (i.e. internal plus kinetic) energy balance

$$\begin{aligned} \frac{\partial}{\partial t} \sum_{\alpha=1}^n \varrho_\alpha (u_\alpha + \frac{1}{2} \mathbf{v}_\alpha^2) + \operatorname{div} \sum_{\alpha=1}^n \varrho_\alpha (u_\alpha + \frac{1}{2} \mathbf{v}_\alpha^2) \mathbf{v}_\alpha = \\ = \operatorname{div} \sum_{\alpha=1}^n \mathbf{v}_\alpha \mathbf{T}_\alpha + \sum_{\alpha=1}^n \varrho_\alpha \mathbf{b}_\alpha \cdot \mathbf{v}_\alpha - \operatorname{div} \mathbf{q} + Q \end{aligned} \quad (8)$$

by subtracting the balances (3) multiplied by constituent velocities. Finally, the entropic inequality has the form

$$\sigma \equiv \sum_{\alpha=1}^n \frac{\partial \varrho_\alpha s_\alpha}{\partial t} + \sum_{\alpha=1}^n \operatorname{div} \varrho_\alpha s_\alpha \mathbf{v}_\alpha + \operatorname{div} (\mathbf{q}/T) - \frac{Q}{T} \geq 0 \quad (9)$$

whose left-hand side represents the production of entropy  $\sigma$ ,  $s_\alpha$  is the (specific) entropy of constituent  $\alpha$  and  $T$  absolute temperature.

### Form Invariance

The balances (1)–(6) and (9) have a property called form invariance<sup>3-6</sup>: when we choose  $n - 1$  arbitrary quantities  $u_{(\beta)}$  (of the dimension of specific energy) and  $n - 1$  arbitrary quantities  $s_{(\beta)}$  (of the dimension of specific entropy) and when we introduce new (primed) ones

$$u'_\alpha = u_\alpha + \sum_{\beta=1}^{n-1} (\delta_{\beta\alpha} - w_\beta) u_{(\beta)} \quad (10)$$

$$s'_\alpha = s_\alpha + \sum_{\beta=1}^{n-1} (\delta_{\beta\alpha} - w_\beta) s_{(\beta)} \quad (11)$$

$$\mathbf{q}' = \mathbf{q} - T \sum_{\beta=1}^{n-1} \sum_{\delta=1}^{n-1} \varrho_{\beta} (\delta_{\delta\beta} - w_{\delta}) s_{(\delta)} \mathbf{u}_{\beta} \quad (12)$$

$$\mathbf{k}'_{\alpha} = \mathbf{k}_{\alpha} - \text{grad} \left[ \varrho_{\alpha} \sum_{\beta=1}^{n-1} (\delta_{\alpha\beta} - w_{\beta}) f_{(\beta)} \right] \quad (13)$$

$$\mathbf{T}'_{\alpha} = \mathbf{T}_{\alpha} + \varrho_{\alpha} \sum_{\beta=1}^{n-1} (\delta_{\beta\alpha} - w_{\beta}) f_{(\beta)} \mathbf{1} \quad (14)$$

other quantities ( $t$ ,  $r_{\alpha}$ ,  $\varrho_{\alpha}$ ,  $\mathbf{v}_{\alpha}$ ,  $\mathbf{b}_{\alpha}$ ,  $Q$ ,  $\mathbf{D}_{\alpha}$ ) in these balances remaining without change, i.e.

$$r'_{\alpha} = r_{\alpha}, \quad \varrho'_{\alpha} = \varrho_{\alpha} \text{ etc.}, \quad (15)$$

then the form of the balances (1)–(6) and (9) remains the same in the primed as well as in the non-primed quantities. Here,  $w_{\alpha}$  are mass (“weight”) fractions

$$w_{\alpha} \equiv \varrho_{\alpha} / \varrho, \quad \sum_{\alpha=1}^n w_{\alpha} = 1, \quad (16), (17)$$

where  $\varrho$  denotes density of the mixture

$$\varrho \equiv \sum_{\alpha=1}^n \varrho_{\alpha}, \quad (18)$$

further (cf. Eq. (22))

$$f_{(\beta)} \equiv \mathbf{u}_{(\beta)} - T s_{(\beta)}, \quad (19)$$

$\delta_{\beta\alpha}$  is Kronecker’s delta (equal to zero for  $\alpha = n$ ),  $\alpha = 1, \dots, n$ ,  $\beta = 1, \dots, n-1$  as already mentioned, and  $\mathbf{1}$  is unit tensor.

This form invariance can be evidenced by direct substitution of Eqs. (10)–(15) into the balances (1)–(6) and (9) and by using the formula

$$\sum_{\alpha=1}^n \varrho_{\alpha} \sum_{\beta=1}^{n-1} (\delta_{\beta\alpha} - w_{\beta}) y_{(\beta)} = 0, \quad (20)$$

where  $y_{(\beta)}$  stands for  $\mathbf{u}_{(\beta)}$ ,  $s_{(\beta)}$ ,  $f_{(\beta)}$ .

That the primed quantities can be substituted for the non-primed ones is obvious from the fact that the quantities (10)–(14) are primitive, not defined in this theory, and not directly measurable; hence it is possible to start from whichever (primed or not primed) primitive quantities (only mixtures with non-negligible interactions between constituents are considered, since otherwise the form invariance would be of no use). This is in contrast to other “form-invariant” quantities of the type (15), which are measurable similarly to, e.g., thermodynamic quantities,  $y$ , of the mixture (such as specific entropy  $s$ , internal energy  $u$ , or free energy  $f$ ) defined as

$$y \equiv \sum_{\alpha=1}^n w_{\alpha} y_{\alpha}, \quad (21)$$

where  $y_\alpha$  stands for  $s_\alpha$ ,  $u_\alpha$ ,  $f_\alpha$ , etc. The partial free energy  $f_\alpha$  is defined as

$$f_\alpha \equiv u_\alpha - Ts_\alpha. \quad (22)$$

Similarly, the sums  $\sum_{\alpha=1}^n \mathbf{k}_\alpha$ ,  $\sum_{\alpha=1}^n \mathbf{T}_\alpha$  and other quantities (such as chemical potential in fluids<sup>3-6</sup>) are form-invariant. It is apparent from Eq. (12) that the heat flux  $\mathbf{q}$  is form-invariant in absence of diffusion (i.e. when  $\mathbf{u}_\beta = \mathbf{o}$ ). In the general case, Eq. (12) reflects difficulties in the definition of the heat flux in the presence of diffusion, and its form expresses (with a suitable choice of  $s_{(\beta)}$ ) all the usual formulations of the heat flux in the presence of diffusion used in irreversible thermodynamics<sup>9</sup>.

It follows further from the form invariance that, regardless of whether we start from the primed or non-primed quantities (10)–(14), we obtain the same form of the balances (1)–(6) and (9), and also the same form of further results, e.g. the same form of constitutive equations constructed as usual on the basis of constitutive principles of rational thermodynamics. It can be seen that the form invariance can be generalized, e.g., for the case of mechanically non-polar constituents of the mixture, where Eq. (5) is invalid.

#### *Simplification of Constitutive Equations for Partial Thermodynamic Quantities with the Aid of Form Invariance*

The form invariance can be used suitably to modify the constitutive equations. Thus, it was shown<sup>3-6</sup> for a fluid mixture with linear transport properties that a suitable choice of  $u_{(\beta)}$  and  $s_{(\beta)}$  as functions of  $T$ ,  $\varrho_1$ , ...,  $\varrho_n$  makes the partial thermodynamic quantities  $y_\alpha$  identical with partial thermodynamic quantities of classical thermochemistry of mixtures (i.e. with partial molar quantities in specific units). Without using the form invariance, namely, the partial thermodynamic quantities  $y_\alpha$  are not form-invariant and do not satisfy the Gibbs–Duhem equations, except for the partial Gibbs energy (chemical potential in fluids).

Further, we shall deal with some nonlinear models of mixtures, where the typically partial thermodynamic quantities  $u_\alpha$ ,  $s_\alpha$ , and  $f_\alpha$  depend on all variables, whereas the thermodynamic quantities for the mixture,  $u$ ,  $s$ , and  $f$  (21) depend only on some of them: they do not depend on non-equilibrium variables (which attain zero values in equilibrium). Using the form invariance, we shall show that it is possible to choose the partial thermodynamic quantities so as to be independent of the non-equilibrium variables, too. This is the case of a mixture of materials with memory of a differential type with any symmetry<sup>3</sup> and a similar case described by Bowen<sup>10</sup>, among others in a special case of such fluid mixture<sup>3,10</sup>. We shall show this on the last example, i.e. on a mixture of non-linear, (mechanically) non-polar liquids studied in detail in ref.<sup>3</sup>, paragraph 40, and governed by the balances and other equations given above. Here, the partial specific thermodynamic quantities  $y_\alpha = u_\alpha$ ,  $s_\alpha$ , and  $f_\alpha$  are functions of all

variables

$$y_\alpha = \hat{y}_\alpha(\varrho_\gamma, \mathbf{h}_\gamma, \mathbf{D}_\gamma, \boldsymbol{\Omega}_\delta, \mathbf{u}_\delta, T, \mathbf{g}) \quad (23)$$

(this follows for  $f_\alpha$  from the definition (22)), where  $\mathbf{h}_\gamma \equiv \text{grad } \varrho_\gamma$ ,  $\boldsymbol{\Omega}_\delta$  denotes relative spin (difference between the spins of constituents  $\delta$  and  $n$ ; spin is the antisymmetrical part of the velocity gradient), and  $\mathbf{g} \equiv \text{grad } T$ . (For other quantities see Eqs (1), (6), (7), and (9);  $\varrho_\gamma$  in Eq. (23) denotes dependence on  $\varrho_1, \dots, \varrho_n$ ,  $\mathbf{u}_\delta$  dependence on  $\mathbf{u}_1, \dots, \mathbf{u}_{n-1}$  and so on.) In contrast to them, the specific thermodynamic quantities,  $y$ , defined for a mixture by Eq. (21), are simpler functions of the form

$$y = \hat{y}(\varrho_\gamma, \mathbf{h}_\gamma, T) \quad (24)$$

(for non-reacting mixtures, even  $\mathbf{h}_\gamma$  is cancelled; cf. ref.<sup>3</sup>).

The quantities  $\mathbf{D}_\gamma$ ,  $\boldsymbol{\Omega}_\delta$ ,  $\mathbf{u}_\delta$ , and  $\mathbf{g}$  can acquire zero values (e.g. in equilibrium), therefore we define

$$y_\alpha^0 \equiv \hat{y}_\alpha(\varrho_\gamma, \mathbf{h}_\gamma, \mathbf{O}, \mathbf{O}, \mathbf{o}, T, \mathbf{o}) \equiv \hat{y}_\alpha^0(\varrho_\gamma, \mathbf{h}_\gamma, T) \quad (25)$$

(there, of course,  $\mathbf{O}$  means that, e.g.,  $\mathbf{D}_\gamma = \mathbf{O}$  for any  $\gamma$  value). Hence,

$$y_\alpha^N \equiv y_\alpha - y_\alpha^0 \equiv \hat{y}_\alpha^N(\varrho_\gamma, \mathbf{h}_\gamma, \mathbf{D}_\gamma, \boldsymbol{\Omega}_\delta, \mathbf{u}_\delta, T, \mathbf{g}). \quad (26)$$

From this it follows that

$$\hat{y}_\alpha^N(\varrho_\gamma, \mathbf{h}_\gamma, \mathbf{O}, \mathbf{O}, \mathbf{o}, T, \mathbf{o}) = 0. \quad (27)$$

According to Eqs (21) and (26)

$$y = \sum_{\alpha=1}^n w_\alpha y_\alpha^0 + \sum_{\alpha=1}^n w_\alpha y_\alpha^N \quad (28)$$

and hence according to Eqs (24), (25), (16), and (18) the quantity

$$y^N \equiv \sum_{\alpha=1}^n w_\alpha y_\alpha^N = \hat{y}^N(\varrho_\gamma, \mathbf{h}_\gamma, T) \quad (29)$$

is a function of  $\varrho_\gamma$ ,  $\mathbf{h}_\gamma$ , and  $T$  only.

We now choose  $2(n-1)$  functions  $u_{(\beta)}, s_{(\beta)}$  as follows (we denote them  $y_{(\beta)}$ ):

$$y_{(\beta)} = - \left( y_\beta^N - y^N + \frac{1}{w_n} \sum_{\delta=1}^{n-1} y_\delta^N w_\delta \right) \quad (30)$$

for  $\beta = 1, \dots, n-1$ . By substitution into Eqs (10) and (11) we obtain after rearrange-

ment the corresponding primed quantities

$$y'_\alpha = y_\alpha^0 + y^N[w_n + \delta_{n\alpha}((1/w_n) - 1)] \quad (31)$$

for  $\alpha = 1, \dots, n$ . Hence, according to Eqs (25), (29), and (16) these quantities are only functions of  $T$ ,  $\varrho_y$ , and  $\mathbf{h}_y$

$$y'_\alpha = \hat{y}'_\alpha(\varrho_y, \mathbf{h}_y, T). \quad (32)$$

Further

$$y' \equiv \sum_{\alpha=1}^n w_\alpha y'_\alpha = \sum_{\alpha=1}^n w_\alpha y_\alpha = y, \quad (33)$$

i.e. the specific quantity of the mixture is form-invariant.

We have thus shown that the constitutive equations for  $u_\alpha$  and  $s_\alpha$  can be chosen so that they depend only on  $\varrho_y$ ,  $\mathbf{h}_y$  and  $T$ . In this way also the other partial thermodynamic quantities defined on the basis of  $u_\alpha$  and  $s_\alpha$ , such as  $f_\alpha$  (Eq. (22)) depend also on  $\varrho_y$ ,  $\mathbf{h}_y$  and  $T$  only; and according to Eq. (32) the corresponding quantities of the mixture, Eq. (21), are always invariant. Thus, the use of the form invariance ensures that the constitutive equations for partial thermodynamic quantities are considerably simplified, which results in simplification of further results given in references<sup>3,10</sup> (e.g. (40·21)–(40·25) in ref.<sup>3</sup>). Additional rearrangement by using the form invariance of a similar type as at the beginning of this paragraph is, of course, possible.

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