# RATIONAL THERMODYNAMICS OF A NONREACTING
# BINARY LINEAR FLUID*

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The methods of nonlinear thermomechanics of continuous media are used for an analysis of transfer phenomena in binary fluid mixtures. From the derived relations, as a special case, are then deduced fundamental relations for the thermodynamics of irreversible processes to describe transfer phenomena in binary mixtures.

An attempt is made in this article to demonstrate how the classical problem of irreversible thermodynamics can be solved by the method of so-called rational thermodynamics. This method is based on a critical review of continuum physics according to Prof. Truesdell's school of thought [1-5]. The scope of this method is very broad: in principle, it can render an interpretation of irreversible processes in any material.

Using the example of a nonreacting binary fluid mixture with a certain linearity characteristic, we will show that this method yields all the results known from the theory of irreversible thermodynamics (see also [8-14] and, especially, [15-19]).

Characteristic of rational thermodynamics is an a priori definition of fundamental concepts (including the thermodynamic concepts [2-7]);

$t$ is time; $x$ is the radius vector of space coordinates; $v_\alpha$ is the velocity of component $\alpha$ ($\alpha = 1$, 2) of the mixture; $\rho_\alpha$ is the density (weight concentration) of component $\alpha$, $\rho_\alpha > 0$; T is the temperature, T > 0; $\mu_\alpha$ is the partial internal energy of component $\alpha$; $s_\alpha$ is the partial entropy of component $\alpha$; $\mathbf{J}$ is the thermal flux; $\mathbf{k}_\alpha$ is the momentum source in component $\alpha$ originating in the other component; $\underline{T}_\alpha$ is a partial tensor of stresses in component $\alpha$; $\mathbf{F}_\alpha$ is the external force per unit mass of component $\alpha$; and $\sigma$ is the increase in entropy. (1)

On the basis of the concept of a mixture as a superposition of one-component substances [1], we impose on these quantities the following restrictions expressed in terms of conservation postulates (with respect to a volume V with a surface $\Omega$ defined in space coordinates [1, 3, 20, 21]:

a.  conservation of mass, referred to component $\alpha$ (of a nonreacting mixture)

$$\frac{d}{dt} \int_V \rho_\alpha dV = - \int_\Omega \rho_\alpha v_\alpha \cdot \vec{d\Omega}, \qquad (2)$$

b.  conservation of momentum, referred to component $\alpha$

$$\frac{d}{dt} \int_V \rho_\alpha v_\alpha dV = - \int_\Omega \rho_\alpha v_\alpha (v_\alpha \cdot \vec{d\Omega}) + \int_\Omega \underset{\rightarrow}{T_\alpha} \cdot \vec{d\Omega} + \int_V \rho_\alpha F_\alpha dV + \int_V k_\alpha dV, \qquad (3)$$

*Rational thermodynamics, in the author's view, is part of the linear thermomechanics of continuous media. This new trend in the theory of transfer phenomen is a very progressive one and represents a further development in the thermodynamics of irreversible processes. In featuring this article here, the editors wish to acquaint the readers with some interesting specific results which the author has obtained in his work on the theory of transfer in a binary mixture using the methods of continuum thermomechanics (see A. B. Lykov [32-35], Russian editor's note).

with

$$\sum_\alpha \mathbf{k}_\alpha = 0 \tag{4}$$

(for brevity, $\sum_\alpha$ means $\sum_{\alpha=1}^{2}$).

    c.  conservation of the moment of momentum, referred to a mixture component (this restricts us to nonpolar materials [5])

$$\frac{d}{dt} \int_V (\mathbf{x} \times \rho_\alpha \mathbf{v}_\alpha)\, dV = -\int_\Omega \mathbf{x} \times \rho_\alpha \mathbf{v}_\alpha (\mathbf{v}_\alpha \cdot d\vec{\Omega}) + \int_\Omega \mathbf{x} \times (T_\alpha \cdot d\vec{\Omega}) + \int_V (\mathbf{x} \times \rho_\alpha \mathbf{F}_\alpha)\, dV + \int_V (\mathbf{x} \times \mathbf{k}_\alpha)\, dV \tag{5}$$

(conservation of these quantities referred to an entire mixture involves a summation with respect to all components, with (4) taken into account).

    d.  conservation of energy in the mixture (no energy transfer by radiation is assumed to occur)

$$\frac{d}{dt} \int_V \sum_\alpha \left( \rho_\alpha u_\alpha + \frac{1}{2}\, \rho_\alpha v_\alpha^2 \right) dV = -\int_\Omega \sum_\alpha \left( \rho_\alpha u_\alpha \right.$$

$$\left. + \frac{1}{2}\, \rho_\alpha v_\alpha^2 \right) \mathbf{v}_\alpha \cdot d\vec{\Omega} + \int_\Omega \sum_\alpha \mathbf{v}_\alpha \cdot (T_\alpha \cdot d\vec{\Omega}) + \int_V \sum_\alpha \rho_\alpha \mathbf{F}_\alpha \cdot \mathbf{v}_\alpha dV - \int_\Omega \mathbf{J} \cdot d\vec{\Omega}; \tag{6}$$

    e.  Second Law of Thermodynamics

$$\frac{d}{dt} \int_V \sum_\alpha \rho_\alpha s_\alpha dV = -\int_\Omega \sum_\alpha \rho_\alpha s_\alpha \mathbf{v}_\alpha \cdot d\vec{\Omega} - \int_\Omega \frac{\mathbf{J}}{T} \cdot d\vec{\Omega} + \int_V \sigma dV, \tag{7}$$

with

$$\sigma \geqslant 0. \tag{8}$$

These equations of balance differ from those used in [15-19].

By well known operations, these postulates are transformed to the following local terms:

from (2) we obtain the equation of mass continuity for component $\alpha$

$$\frac{\partial \rho_\alpha}{\partial t} + \vec{\nabla} \cdot (\rho_\alpha \mathbf{v}_\alpha) = 0; \tag{9}$$

from (5) and (3) we obtain the symmetry of partial stress tensors

$$T_\alpha = \tilde{T}_\alpha \tag{10}$$

and, with the aid of this equation, we obtain from (3)

$$\frac{\partial}{\partial t} (\rho_\alpha \mathbf{v}_\alpha) + \vec{\nabla} \cdot (\rho_\alpha \mathbf{v}_\alpha \otimes \mathbf{v}_\alpha) = \vec{\nabla} \cdot T_\alpha + \rho_\alpha \mathbf{F}_\alpha + \mathbf{k}_\alpha \tag{11}$$

(the symbol $\otimes$ denotes a diad).

    Transforming (6) to local terms and eliminating the kinetic energy with the aid of (11), we obtain the First Law of Thermodynamics

$$\sum_\alpha \frac{\partial}{\partial t} (\rho_\alpha u_\alpha) + \sum_\alpha \vec{\nabla} \cdot (\rho_\alpha u_\alpha \mathbf{v}_\alpha) = \sum_\alpha T_\alpha : \vec{\nabla} \otimes \mathbf{v}_\alpha - \vec{\nabla} \cdot \mathbf{J} - \sum_\alpha \mathbf{k}_\alpha \cdot \mathbf{v}_\alpha \tag{12}$$

(the symbol : denotes summation over both tensor indices). Finally, (7) and (8) yield the Clausius—Duhem inequality

$$\sigma = \sum_\alpha \frac{\partial}{\partial t} (\rho_\alpha s_\alpha) + \sum_\alpha \vec{\nabla} \cdot (\rho_\alpha s_\alpha \mathbf{v}_\alpha) + \vec{\nabla} \cdot \left( \frac{\mathbf{J}}{T} \right) \geqslant 0. \tag{13}$$

With $\mathbf{F}_\alpha$ assumed known and $\alpha$ defined according to Eq. (13) (from now on we will use only the inequality in (13)), while $\mathbf{k}_2$ and three components of tensors $T_\alpha$ are defined according to Eqs. (9) and (10), the nine remaining equations (9), (11), (12) are not sufficient for defining the 31 unknowns:

$$T, \; \rho_\alpha, \; u_\alpha, \; s_\alpha, \; \mathbf{J}, \; \mathbf{v}_\alpha, \; k_1, \; \underset{\rightarrow}{T}_\alpha \quad \text{(symmetrical)} \tag{14}$$

as functions of x and t. This is understandable, inasmuch as the general equations considered so far do not express the specific properties of the material.

These properties appear in the defining equations for an ideal material, i.e., a model which simulates the given real material with emphasis on the properties that are important under conditions of concern here [1-7]. For a formulation of the defining equations, it would be very appropriate to use the general and lucid axioms of continuum thermomechanics [1, 2, 7].

For our linear binary fluid mixture we will postulate the 22 necessary defining equations in the following way [15, 18, 19]: the quantities

$$u_\alpha, \; s_\alpha, \; \mathbf{J}, \; k_1, \; \underset{\rightarrow}{T}_\alpha \tag{15}$$

are functions of the following independent variables:

$$T, \; \rho_1, \; \rho_2, \; \vec{\nabla}T, \; \vec{\nabla}\rho_1, \; \vec{\nabla}\rho_2, \; \mathbf{v}_1, \; \mathbf{v}_2, \; \vec{\nabla}\otimes\mathbf{v}_1, \; \vec{\nabla}\otimes\mathbf{v}_2 \tag{16}$$

and linearity of vector and tensor quantities is postulated in the sense that the defining equations for (15) are polynomials of not higher than first degree with respect to components of vectors and tensors (16) (they may be arbitrary functions of scalars in (16)).

In this formulation we have already used some axioms of continuum thermomechanics. According to the axioms of causality and determinism, the variables in the defining equations should reflect past and present motion (deformation) of the material as well as past and present temperature fields, and the variables (16) meet this qualification (it is characteristic of a fluid, in fact, that its deformation can be expressed only in terms of the density $\rho_\alpha$ [3, 7, 11, 13, 16, 18]). The history is reflected here only in the velocities and their time derivatives (memory axiom [7]), and the influence of only the immediate vicinity is reflected in the spatial gradients (locality axiom). All structural equations for (15) contain the same variables (16) (simultaneity axiom).

These defining equations for (15)-(16) can be substantially simplified as a consequence of the objectivity axiom [1, 2, 3, 7], which states that a property of a material does not depend on the motion of the observer, i.e., that the defining equations must be invariant with respect to any translation of the origin, to any rotation and reflection of space coordinates (during any even nonuniform motion of the observer), and also with respect to the beginning of the time count. Without going into detail, we will only present the results. The objectivity axiom must be applicable (i.e., objective must be) especially the independent variables in the defining equations. This matches with the absence of the nonobjective quantities x and t among those in (16) (their inclusion here would be expected as a consequence of the causality axion), while the quantities in (15) depend on those variables only through the quantities in (16). The nonobjective quantities in (16) $\mathbf{v}_\alpha$ and $\vec{\nabla}\otimes\mathbf{v}_\alpha$ must appear in the following objective combinations [15]: in the diffusion rate of component 1 relative to the velocity of component 2

$$\mathbf{V}_{12} = \mathbf{v}_1 - \mathbf{v}_2, \tag{17}$$

in the partial tensor of strain rates

$$\underset{\rightarrow}{d}_\alpha = \frac{1}{2}\,[\vec{\nabla}\otimes\mathbf{v}_\alpha + \overparen{\vec{\nabla}\otimes\mathbf{v}_\alpha}] \tag{18}$$

and in

$$\underset{\rightarrow}{\Omega}_{12} = \frac{1}{2}\,[(\vec{\nabla}\otimes\mathbf{v}_1 - \overparen{\vec{\nabla}\otimes\mathbf{v}_1}) - (\vec{\nabla}\otimes\mathbf{v}_2 - \overparen{\vec{\nabla}\otimes\mathbf{v}_2})]. \tag{19}$$

Thus, the defining equations for (15) are expressed as functions of the variables

$$T, \; \rho_1, \; \rho_2, \; \vec{\nabla}\rho_1, \; \vec{\nabla}\rho_2, \; \vec{\nabla}T, \; \mathbf{V}_{12}, \; \underset{\rightarrow}{d}_1, \; \underset{\rightarrow}{d}_2, \; \underset{\rightarrow}{\Omega}_{12}, \tag{20}$$

linear with respect to the components of four vectors, two symmetric tensors, and one antisymmetric tensor (by virtue of (17), (18), and (19), the linearity with respect to vectors and tensors in (16) is maintained).

The objectivity axiom has most influence on the form of the defining equations [2, 7]. The invariance with respect to rotation and reflection of coordinates requires that all scalar, vector, and also

(symmetric) tensor functions in (16) be isotropic. Such functions of variables (20), linear with respect to vector and tensor components, have the form [22, 23]:

$$u_\alpha = {}^{(0)}u_\alpha + {}^{(1)}u_\alpha tr\vec{d_1} + {}^{(2)}u_\alpha tr\vec{d_2}, \tag{21}$$

$$s_\alpha = {}^{(0)}s_\alpha + {}^{(1)}s_\alpha tr\vec{d_1} + {}^{(2)}s_\alpha tr\vec{d_2}, \tag{22}$$

$$\mathbf{J} = -\varkappa\vec{\nabla}T - \gamma\mathbf{V}_{12} + \xi_1\vec{\nabla}\rho_1 + \xi_2\vec{\nabla}\rho_2, \tag{23}$$

$$\mathbf{k}_1 = -\alpha_1\vec{\nabla}T - \beta_1\mathbf{V}_{12} + \varepsilon_{11}\vec{\nabla}\rho_1 + \varepsilon_{12}\vec{\nabla}\rho_2, \tag{24}$$

$$\vec{T}_\alpha = -P_\alpha\underset{\rightarrow}{U} + \sum_\beta \zeta_{\alpha\beta}(tr\vec{d_\beta})\underset{\rightarrow}{U} + \sum_\beta 2\eta_{\alpha\beta}\vec{d}_\beta^0, \tag{25}$$

where $\alpha$, $\beta = 1$, 2, all the coefficients ${}^{(0)}u_\alpha$, ${}^{(1)}u_\alpha$, ${}^{(2)}u_\alpha$, ${}^{(0)}s_\alpha$, ${}^{(1)}s_\alpha$, ${}^{(2)}s_\alpha$, $\varkappa$, $\gamma$, $\xi_1$, $\xi_2$, $\alpha_1$, $\beta_1$, $\varepsilon_{11}$, $\varepsilon_{12}$, $\eta_{\alpha\beta}$, $\zeta_{\alpha\beta}$, $P_\alpha$ are (arbitrary) functions of T, $\rho_1$, and $\rho_2$, where $\underset{\rightarrow}{U}$ is the unit tensor and $\vec{d}_\beta^0$ is the non-divertive tensor of strain rates in component $\beta$ of the mixture.

The admissibility axiom states that the defining equations must correspond to the conservation postulates (9), (11), (12), and the Clausius—Duhem inequality (13) under all possible deformations of the material and distortions of the temperature field. This is the gist of the powerful Coleman—Hall method [4], which leads up to rational thermodynamics [2, 3, 6]. We insert (12) into inequality (13) and obtain

$$\underset{\rightarrow}{\sigma}T = -\frac{\partial}{\partial t}\left(\sum_\alpha \rho_\alpha f_\alpha\right) - \sum_\alpha \vec{\nabla}\cdot(\rho_\alpha f_\alpha v_\alpha) - \mathbf{k}_1\cdot\mathbf{V}_{12} - \frac{\mathbf{J}}{T}\cdot\vec{\nabla}T$$
$$- \sum_\alpha (\rho_\alpha s_\alpha v_\alpha)\cdot\vec{\nabla}T - \left(\sum_\alpha \rho_\alpha s_\alpha\right)\frac{\partial T}{\partial t} + \sum_\alpha \vec{T}_\alpha:\vec{\nabla}\otimes v_\alpha \geqslant 0, \tag{26}$$

where the following definition of partial free energy in a component $\alpha$

$$f_\alpha \equiv u_\alpha - Ts_\alpha. \tag{27}$$

has been used. In inequality (26) we replace the corresponding quantities by their defining expressions (21)-(22) and, after lengthy transformations, we obtain an unwieldy inequality of the following form:

$$\sum_i c_iZ_i + \sum_j b_jY_j + \sum_{k,l} b_{kl}X_lY_k + \sum_m a_mX_m + \sum_{n,p} a_{np}X_nX_p + \sum_{r,s,t} a_{rst}X_rX_sX_t + \sum_{u,v,w} b_{uvw}X_uX_vY_w > 0, \tag{28}$$

where $Z_i$, $Y_j$, and $X_l$ denote $\partial T/\partial t$, $\partial tr\underset{\rightarrow}{d}_\alpha/\partial t$, and components of the following vectors and tensors $\vec{\nabla}(tr\underset{\rightarrow}{d}_\alpha)$. $\vec{\nabla}\rho_\alpha$, $\vec{\nabla}T$, $\underset{\rightarrow}{d}_\alpha$, $\mathbf{v}_\alpha$ respectively. Coefficients $c_i$, $b_j$, $b_{kl}$, $b_{uvw}$, $a_m$, $a_{np}$, and $a_{rst}$ are functions of T, $\rho_1$, and $\rho_2$ only.

The Coleman—Hall method [4] is based on the following theorem: in order that inequality (28) be satisfied under all possible deformations of the material and distortions of the temperature field, i.e., at all possible values of the independent variables $Z_i$, $Y_j$, $X_l$ (any real values) and $\rho_1$, $\rho_2$, T (only positive values), it is necessary and sufficient that all coefficients

$$c_i = b_j = b_{hl} = a_m = a_{rst} = b_{uvw} = 0 \tag{29}$$

be equal to zero and the remaining quadratic form be positive-semidefinite.

The sufficiency part of this theorem is obvious (a semidefinite form retains its sign for any real $X_n$), while the necessity part of it is demonstrated by the existence of such real $Z_i$, $Y_j$, $X_l$ for which the sense of inequality (28) changes when any coefficient in (29) is not zero.

The final results of applying this theorem are as follows:

$$^{(1)}u_\alpha = {}^{(2)}u_\alpha = 0, \tag{30}$$

$$^{(1)}s_\alpha = {}^{(2)}s_\alpha = 0,$$

$$\xi_1 = \xi_2 = 0, \tag{31}$$

$$\varepsilon_{11} = \rho_2\frac{\partial\hat{f}_2}{\partial\rho_1}, \qquad \varepsilon_{12} = -\rho_1\frac{\partial\hat{f}_1}{\partial\rho_2}, \tag{32}$$

$$\frac{\partial\hat{f}}{\partial T} = -s, \tag{33}$$

$$\mu_\alpha = f_\alpha + \frac{P_\alpha}{\rho_\alpha} \tag{34}$$

and the remaining quadratic form

$$T\sigma = \beta_1 V_{12}^2 + \vartheta V_{12} \cdot \vec{\nabla}T + \frac{\varkappa}{T}(\vec{\nabla}T)^2 + \sum_\alpha \sum_\beta \zeta_{\alpha\beta}(tr d_\alpha)(tr d_\beta) + \sum_\alpha \sum_\beta 2\eta_{\alpha\beta} d_\alpha^0 : d_\beta^0 \geqslant 0 \qquad (35)$$

is positive-semidefinite so that for the coefficients (functions of T, $\rho_1$, $\rho_2$) we have

$$\beta_1 \geqslant 0, \qquad \varkappa \geqslant 0, \qquad (36)$$

$$[\beta_1 \frac{\varkappa}{T} - \frac{1}{4}\vartheta^2 \geqslant 0, \qquad (37)$$

$$\eta_{11} \geqslant 0, \quad \eta_{22} \geqslant 0, \qquad \eta_{11}\eta_{22} - \frac{1}{4}(\eta_{12} + \eta_{21})^2 \geqslant 0, \qquad (38)$$

$$\zeta_{11} \geqslant 0, \quad \zeta_{22} \geqslant 0, \qquad \zeta_{11}\zeta_{22} - \frac{1}{4}(\zeta_{12} + \zeta_{21})^2 \geqslant 0. \qquad (39)$$

In (30)–(39) we have used the following definitions: free energy of the mixture

$$f \equiv \sum_\alpha w_\alpha f_\alpha, \qquad (40)$$

entropy of the mixture

$$s \equiv \sum_\alpha w_\alpha s_\alpha, \qquad (41)$$

density of the mixture $\rho$ and weight fraction $w_\alpha$ of component $\alpha$

$$\rho \equiv \sum_\alpha \rho_\alpha, \quad w_\alpha \equiv \frac{\rho_\alpha}{\rho}, \quad \sum_\alpha w_\alpha = 1,$$

chemical potential of component $\alpha$

$$\mu_\alpha \equiv \frac{\partial \rho \hat{f}}{\partial \rho_\alpha} \qquad (42)$$

and

$$\vartheta \equiv \alpha_1 + \frac{\gamma}{T} - \rho_1 \frac{\partial \hat{f}_1}{\partial T} - \rho_1 s_1. \qquad (43)$$

The sign $\frown$ above a symbol indicates that the respective quantity is a function of T, $\rho_1$, and $\rho_2$. Indeed, by virtue of (30), (21), and (22), all quantities (27), (40), (41), (43), and (32) are functions of these three variables only.

Thus, in the final form, the defining equations become

$$u_\alpha = \hat{u}_\alpha(T, \rho_1, \rho_2), \qquad (44)$$

$$s_\alpha = \hat{s}_\alpha(T, \rho_1, \rho_2) \qquad (45)$$

with the property (33), (34)

$$J = -\varkappa \vec{\nabla}T - \gamma V_{12}, \qquad (46)$$

$$k_1 = -\alpha_1 \vec{\nabla}T - \beta_1 V_{12} + \rho_2 \frac{\partial \hat{f}_2}{\partial \rho_1} \vec{\nabla}\rho_1 - \rho_1 \frac{\partial \hat{f}_1}{\partial \rho_2} \vec{\nabla}\rho_2. \qquad (47)$$

Coefficients $\varkappa$, $\gamma$, $\alpha_1$, $\beta_1$ are functions of T, $\rho_1$, $\rho_2$ and satisfy (36), (37).

The defining equations (25) remain unchanged, where $\zeta_{\alpha\beta}$ and $\eta_{\alpha\beta}$ satisfy (38), (39) and are functions of T, $\rho_1$, $\rho_2$. This is true also for $P_\alpha$, which may be called the partial pressure of component $\alpha$ and is related to the thermodynamic quantities through Eq. (34).

Let us focus our attention on the thermodynamic relations (33), (34), (27), (40), (41), (42), (44), (45) only and supplement them with the following definitions:

pressure of the mixture

$$P \equiv \sum_\alpha P_\alpha, \qquad (48)$$

specific volume of the mixture

$$v \equiv \frac{1}{\rho}, \tag{49}$$

specific free enthalpy

$$g \equiv f + Pv, \tag{50}$$

partial specific volume of component $\alpha$

$$v_\alpha \equiv \frac{1}{\rho_\alpha} \frac{P_\alpha}{P}, \tag{51}$$

specific internal energy of the mixture

$$u \equiv \sum_\alpha w_\alpha u_\alpha, \tag{52}$$

partial specific enthalpy of component $\alpha$

$$h_\alpha \equiv u_\alpha + Pv_\alpha, \tag{53}$$

specific enthalpy of the mixture

$$h \equiv \sum_\alpha w_\alpha h_\alpha. \tag{54}$$

Obviously, all these and the subsequent quantities are functions of T, $\rho_1$, and $\rho_2$ only.

Next, by various transformations of these formulas, we obtain the well known thermodynamic structure. We note the relations

$$g = \sum_\alpha w_\alpha \mu_\alpha, \tag{55}$$

and (34), which becomes

$$\mu_\alpha = f_\alpha + Pv_\alpha, \tag{56}$$

$$v = \sum_\alpha w_\alpha v_\alpha \quad \text{or} \quad \sum_\alpha \rho_\alpha v_\alpha = 1. \tag{57}$$

Less known is the formula

$$P_\alpha = \sum_\beta \rho_\alpha \rho_\beta \frac{\partial \tilde{f}_\beta}{\partial \rho_\alpha}. \tag{58}$$

From (33) and (34) we obtain

$$d(\rho f) = -\rho s dT + \sum_\alpha \mu_\alpha d\rho_\alpha, \tag{59}$$

where the differential operator d may stand for $\partial/\partial t$, $\vec{\nabla}$, or the substantial derivative

$$\frac{D \cdot}{Dt} \equiv \frac{\partial \cdot}{\partial t} + (\mathbf{v} \cdot \vec{\nabla}). \tag{60}$$

Expression (59) can be easily transformed into the well known Gibbs equations

$$d(\rho u) = Td(\rho s) + \sum_\alpha \mu_\alpha d\rho_\alpha, \tag{61}$$

$$du = Tds - Pdv + (\mu_1 - \mu_2) dw_1. \tag{62}$$

The last equation and relation (55) yield the Gibbs—Duhem equation for the chemical potential:

$$-sdT + vdP - \sum_\alpha w_\alpha d\mu_\alpha = 0. \tag{63}$$

If quantities $u_\alpha$, $h_\alpha$, $v_\alpha$, $s_\alpha$, $f_\alpha$, $\mu_\alpha$ are denoted by the symbol $y_\alpha$ and the corresponding quantities u, h, v, s, f, g are denoted by y, then obviously

$$y = \sum_\alpha w_\alpha y_\alpha, \tag{64}$$

$$y_\alpha = \hat{y}_\alpha(T, \rho_1, \rho_2), \qquad y = \hat{y}(T, \rho_1, \rho_2). \tag{65}$$

Assuming the existence of the inversion $P = \hat{P}(T, \rho_1, \rho_2) = \hat{P}(T, w_1/v, (1-w_1)/v)$, we can use the conventional variables $T$, $P$, $w_1$ (functions of these variables are denoted by the sign $\hat{\hat{}}$). Thus, (65) yields

$$y_\alpha = \hat{\hat{y}}_\alpha(T, P, w_1), \qquad y = \hat{\hat{y}}(T, P, w_1). \tag{66}$$

Despite the complete identicity between this structure and that of classical thermochemistry, there is the following discrepancy between them: the quantities $y_\alpha$ (except $u_\alpha$) do not satisfy the Gibbs—Duhem equation, unless the following additional constraint is imposed on the quantities $y_\alpha$:

$$\sum_\alpha w_\alpha \frac{\partial \hat{\hat{y}}_\alpha}{\partial w_1} = 0. \tag{67}$$

It appears, however, that such an additional constraint (67) can always be introduced without any modification of the preceding expressions, if to the variables $t$, $\mathbf{x}$, $\mathbf{v}_\alpha$, $\rho_\alpha$, $T$, $\mathbf{F}_\alpha$, $\sigma$ from (1) are added the new variables $u'_\alpha$, $s'_\alpha$, $\mathbf{J}'$, $\mathbf{k}'_\alpha$, $\underset{\rightarrow}{\mathbf{T}}'_\alpha$, which differ from the remaining ones in (1) by arbitrary functions

$$u_0 = \hat{u}_0(T, \rho_1, \rho_2), \qquad s_0 = \hat{s}_0(T, \rho_1, \rho_2) \tag{68}$$

as follows:

$$u'_1 \equiv u_1 + w_2 u_0, \qquad u'_2 \equiv u_2 - w_1 u_0, \tag{69}$$

$$s'_1 \equiv s_1 + w_2 s_0, \qquad s'_2 \equiv s_2 - w_1 s_0, \tag{70}$$

$$\mathbf{J}' \equiv \mathbf{J} - T w_1 w_2 \rho s_0 \mathbf{V}_{12}, \tag{71}$$

$$\mathbf{k}'_1 \equiv \mathbf{k}_1 - \vec{\nabla}(w_1 w_2 \rho f_0), \qquad \mathbf{k}'_2 \equiv \mathbf{k}_2 + \vec{\nabla}(w_1 w_2 \rho f_0), \tag{72}$$

$$\underset{\rightarrow}{T}'_1 \equiv \underset{\rightarrow}{T}_1 + (w_1 w_2 \rho f_0) \underset{\rightarrow}{U}, \qquad \underset{\rightarrow}{T}'_2 \equiv \underset{\rightarrow}{T}_2 - (w_1 w_2 \rho f_0) \underset{\rightarrow}{U}, \tag{73}$$

where

$$f_0 \equiv u_0 - T s_0. \tag{74}$$

Indeed, if these definitions are used in the original equations (4), (11), (12), and (13) (Eq. (9) is not changed), then the form of these equations will remain the same also and the concepts on which the defining equations have been based will remain in force so that all results remain the same, if the corresponding quantities are replaced by dashed quantities (69)-(73). Some quantities will change accordingly, namely

$$P'_1 = P_1 - w_1 w_2 \rho f_0, \qquad P'_2 = P_2 + w_1 w_2 \rho f_0, \tag{75}$$

$$y'_1 = y_1 + w_2 y_0, \qquad y'_2 = y_2 - w_1 y_0, \tag{76}$$

where $y_0$ in (68) and (74), $v_0 = -f_0/P$, and $h_0 = u_0 + P v_0$, $\mu_0 = 0$.

On the other hand, most quantities remain unchanged: $P$, $\mu_\alpha$, $\vartheta$, and all $y$'s.

The arbitrariness in the choice of functions (69)-(73) is physically obvious, as these quantities cannot be read directly (this would involve difficulties, for example, in determining the thermal flux).

We will not take advantage of this arbitrariness, in order to reach full agreement with classical thermochemistry. Namely, we select functions $u_0$, $s_0$ (we denote them by $y_0$) so that

$$y_0 = w_1 \frac{\partial \hat{\hat{y}}_1}{\partial w_1} + w_2 \frac{\partial \hat{\hat{y}}_2}{\partial w_1} \tag{77}$$

($y_\alpha$ is $u_\alpha$ and $s_\alpha$). With the aid of such functions (77), quantities $y_\alpha$ (defined in (69), (70)) acquire the necessary property (67) and the same can be said about the remaining quantities $f_0$, $v_0$, $h_0$.

Thus, our $y_\alpha$ quantities may be considered to have the property (67) (here and later on we omit the dash in our notation) and it can be easily shown that

$$\frac{\partial \hat{\hat{y}}}{\partial w_1} = y_1 - y_2 \tag{78}$$

and the Gibbs—Duhem equations

$$\frac{\partial \hat{\bar{y}}}{\partial T} dT + \frac{\partial \hat{\bar{y}}}{\partial P} dP - \sum_\alpha w_\alpha dy_\alpha = 0 \tag{79}$$

are then satisfied for all $y_\alpha$'s, including $\mu_\alpha$ (see (63)).

A consequence of property (67) are also the formulas

$$\frac{\partial \hat{\bar{\mu}}_\alpha}{\partial T} = - s_\alpha, \tag{80}$$

$$\frac{\partial \hat{\bar{\mu}}_\alpha}{\partial P} = v_\alpha. \tag{81}$$

We thus have a full agreement with the structure recently developed in the theory of irreversible thermodynamics [24, 25] and, as will be shown in the subsequent equilibrium analysis, in complete agreement with the structure of classical thermochemistry, since the quantities $y_\alpha$ with the property (67) represent partial specific quantities (analogs of partial molar quantities). Definition (51) may be regarded as a generalization of Dalton's Law (in an ideal gas $\rho_\alpha v_\alpha$ represents a molar fraction [25]).

Equilibrium in rational thermodynamics must be defined as a special kind of state, since it does not follow from the postulates introduced here. Herein lies the gist of the main difference between this and other theories where the concept of equilibrium is always valid, at least implicitly. In the subsequent definition of equilibrium we strive toward an agreement with properties usually expected under equilibrium conditions. It is required, first of all, that during equilibrium the change in entropy be zero:

$$\sigma = 0 \tag{82}$$

at all positive values of $T$, $\rho_1$, and $\rho_2$.

This corresponds to the minimum of the function $\sigma = \bar{\sigma}(X_1, \ldots, X_{18})$ (see the left-hand sides of (35) and (28), (29)), while the necessary conditions of a minimum are·

$$\frac{\partial \bar{\sigma}}{\partial X_n} = 0 \tag{83}$$

and the matrix

$$\left\| \frac{\partial^2 \bar{\sigma}}{\partial X_n \partial X_p} \right\|, \tag{84}$$

is positive-semidefinite. This matrix is identical to the square matrix in (35), except for the coefficient $2/T$. If only the positive-definite matrix (84) is considered, then (83) yields the following conditions for equilibrium:

$$V_{12} = 0, \tag{85}$$

$$\vec{\nabla} T = 0, \tag{86}$$

$$\vec{d_1} = \vec{d_2} = \vec{0}, \tag{87}$$

which represent the expected equilibrium property (no diffusion, zero temperature gradient, and zero strain rate tensors). The restriction to a positive-definite matrix (87) represents an additional constraint on the definition of equilibrium (in addition to the inherent constraint (82)), since otherwise the determinant of matrix (84) would be equal to zero and the required results (85)-(87) would not be obtained.

Let us insert conditions (85)-(87) into the defining equations. The thermodynamic defining equations (44) and (45) do not change and, therefore, the entire thermodynamic structure remains unchanged. This factually proves the postulate of local equilibrium for our linear mixture of fluids. From the defining equation (46) we find that

$$J = 0, \tag{88}$$

i.e., at equilibrium the thermal flux is zero, from Eq. (47) we find that

$$k_1 = \rho_2 \frac{\partial \hat{f}_2}{\partial \rho_1} \vec{\nabla} \rho_1 - \rho_1 \frac{\partial \hat{f}_1}{\partial \rho_2} \vec{\nabla} \rho_2 \tag{89}$$

at equilibrium, and from the defining equation (25) we find that

$$\underset{\rightarrow}{T}_\alpha = -P_\alpha \underset{\rightarrow}{U}, \tag{90}$$

i.e., at equilibrium stress becomes pressure.

For equilibrium, the fundamental conservation equations (9), (11), (12), and (13) reduce respectively to

$$\frac{D\rho_\alpha}{Dt} = 0, \tag{91}$$

$$\rho_\alpha \frac{D\mathbf{v}}{Dt} = -\vec{\nabla}P_\alpha + \rho_\alpha \mathbf{F}_\alpha + \mathbf{k}_\alpha, \tag{92}$$

$$\frac{Du}{Dt} = 0, \tag{93}$$

$$\frac{Ds}{Dt} = 0. \tag{94}$$

(expression (60) as well as kinematic relations between (9) and derivatives with respect to time, as in [1, 21], have been used in these transformations). Summation over all components yields

$$\frac{D\rho}{Dt} = 0, \tag{95}$$

and (92) can be transformed (with the aid of (89), (4), (58), and (34)) into

$$\rho_\alpha \frac{D\mathbf{v}}{Dt} = \rho_\alpha \mathbf{F}_\alpha - \rho_\alpha \vec{\nabla}\mu_\alpha, \tag{96}$$

from where, with a summation and the aid of (49), (86), and (63), we obtain

$$\rho \frac{D\mathbf{v}}{Dt} = -\vec{\nabla}P + \sum_\alpha \rho_\alpha \mathbf{F}_\alpha. \tag{97}$$

As the results (91), (93)-(97) seem still not precise enough, we introduce an additional constraint on the definition of equilibrium, namely one stating that at equilibrium in a given location there occurs no variation with time:

$$\frac{\partial \rho_\alpha}{\partial t} = \frac{\partial s_\alpha}{\partial t} = \frac{\partial u_\alpha}{\partial t} = \frac{\partial T}{\partial t} = 0, \qquad \frac{\partial \mathbf{v}}{\partial t} = 0. \tag{98}$$

We have thus defined equilibrium by the constraint (82) with the additional constraints (98) and of a positive-definite matrix (84). A consequence of this definition are conditions (85)-(90) and the following relations (derived from (91), (93)-(97) after appropriate transformations):

$$\mathbf{v} \cdot \vec{\nabla}\rho_\alpha = 0, \tag{99}$$

$$\mathbf{v} \cdot \vec{\nabla}s_\alpha = 0, \tag{100}$$

$$\mathbf{v} \cdot \vec{\nabla}u_\alpha = 0, \tag{101}$$

$$\mathbf{v} \cdot (\vec{\nabla} \otimes \mathbf{v})^a = \mathbf{F}_\alpha - \vec{\nabla}\mu_\alpha, \tag{102}$$

$$\rho \mathbf{v} \cdot (\vec{\nabla} \otimes \mathbf{v})^a = \sum_\alpha \rho_\alpha \mathbf{F}_\alpha - \vec{\nabla}P, \tag{103}$$

where $(\nabla \otimes \mathbf{v})^a \equiv (1/2)[\vec{\nabla} \otimes \mathbf{v} - \overset{\frown}{\vec{\nabla} \otimes \mathbf{v}}]$ is the spin tensor.

From this equation we obtain well known cases of equilibrium, such as equilibrium in a field of centrifugal forces when $\mathbf{F}_\alpha = 0$, equilibrium in a field of external forces when $\mathbf{v} = 0$, and, most important, a homogeneous equilibrium system when $\mathbf{F}_\alpha = 0$ and the velocity gradients are zero.

Thus, in the last case we have (in addition to (85)-(88) and (90), from (89) and (99)-(103)):

$$\vec{\nabla}\rho_\alpha = \vec{\nabla}s_\alpha = \vec{\nabla}u_\alpha = \vec{\nabla}\mu_\alpha = \vec{\nabla}P_\alpha = 0 \tag{104}$$

and $\mathbf{k} = 0$, i.e., a homogeneity of properties in this system, inasmuch as the homogeneity property is logically invariant with respect to changes in velocity $\mathbf{v}$.

In a volume V of a homogeneous system at equilibrium we may let

the mass of component $\alpha$ be

$$m_\alpha \equiv \rho_\alpha V, \tag{105}$$

the mass of the mixture be

$$m \equiv \rho V \tag{106}$$

and the quantity Y

$$Y \equiv my, \tag{107}$$

representing the internal energy U, the entropy S, the enthalpy H, the free energy F, the free enthalpy G, and the volume V which correspond to the specific quantities of the mixture $y$ (u, s, h, f, g, v).

Using (66) and

$$w_\alpha = \frac{m_\alpha}{m}, \qquad m = \sum_\alpha m_\alpha, \tag{108}$$

we obtain

$$Y = m\hat{y}(T, P, w_1) \equiv \bar{Y}(T, P, m_1, m_2). \tag{109}$$

Differentiating functions $\bar{Y}$ and using (108), (64), (78) (we emphasize that Eq. (78) is satisfied under the additional constraint (67)) yields

$$\frac{\partial \bar{Y}}{\partial m_1} = y_1, \qquad \frac{\partial \bar{Y}}{\partial m_2} = y_2, \tag{110}$$

and it has thus been proved that in a homogeneous system at equilibrium $y_1$, $y_2$ coincide with the partial specific quantities which in a classical thermochemistry are defined (in molar units) as the left-hand sides of Eqs. (110).

It follows from (109) (see, for instance, (80), (81)) that

$$\frac{\partial \bar{Y}}{\partial T} = m \frac{\partial \hat{y}}{\partial T}, \qquad \frac{\partial \bar{Y}}{\partial P} = m \frac{\partial \hat{y}}{\partial P}. \tag{111}$$

It is now clear that we have obtained here the entire structure of classical thermochemistry for a homogeneous system at equilibrium (Gibbs equation, Gibbs—Duhem equation, etc.).

It seems that the definition of equilibrium needs to be further elaborated, since the additional constraints (98) and of a positive-definite matrix (84) are not sufficiently justified. On the other hand, we have not used here the typical property of equilibrium stability (see M. E. Gurtin [26, 3]).

Finally, we compare these results (see also [15-19]) with those of irreversible thermodynamics [27-30]. Within the scope of this presentation, we have proved the postulate of local equilibrium. It is to be noted that this postulate does not apply in the general case (nonlinearity [15]), but rational thermodynamics can be used successfully for analyzing all these cases.

The defining equations (46), (47), and (25) here are linear in form, with coefficients which are functions of T, $\rho_1$, $\rho_2$ only and satisfy the Curie postulate. In order to explain this better, we take the diffusion current $\rho_1 V_{12}$ of component 1 (referred to the velocity of component 2) from the defining equation (47), express $k_1$ in terms of the balance equation (11) with (4), (58), (34), and (25) as

$$\underset{\rightarrow}{T}_\alpha = -[P_\alpha \underset{\rightarrow}{U} + \underset{\rightarrow}{\Pi}_\alpha] \tag{112}$$

($\underset{\rightarrow}{\Pi}_\alpha$ denotes the tensor of partial friction), the isothermal gradient of chemical potential

$$\vec{\nabla}_T \mu_1 \equiv \vec{\nabla}\mu_1 - \frac{\partial \hat{\mu}_1}{\partial T} \vec{\nabla}T \tag{113}$$

and relation (80) (assuming, of course, that $\beta_1 \neq 0$), so that

$$-\rho_1 V_{12} = \frac{\rho_1^2}{\beta_1} X_1 + \frac{T\rho_1}{\beta_1}\left(\vartheta - \frac{\gamma}{T}\right)\vec{\nabla}\ln T, \tag{114}$$

where the diffusion motive force is defined as

$$\vec{X}_1 \equiv \vec{\nabla}_T \mu_1 - \vec{F}_1 + \frac{1}{\rho_1}\vec{\nabla}\cdot\vec{\Pi}_1 + \frac{1}{\rho_1}\frac{\partial(\rho_1 v_1)}{\partial t} + \frac{1}{\rho_1}\vec{\nabla}\cdot(\rho_1 v_1 \otimes v_1). \tag{115}$$

Inserting (114) into (46) yields

$$-\vec{J} = -\frac{\gamma\rho_1}{\beta_1}\vec{X}_1 + \left[\varkappa T + \frac{\gamma T}{\beta_1}\left(\frac{\gamma}{T} - \vartheta\right)\right]\vec{\nabla}\ln T. \tag{116}$$

Relations (114), (115), and (116) coincide exactly with the expressions derived by the conventional method of irreversible thermodynamics [31], when starting out from the same equations of balance [21]. In expressions (114) and (116) the motive forces $\vec{X}_1$ and $\vec{\nabla}\ln T$ have phenomenological coefficients which are functions of T, $\rho_1$, and $\rho_2$ only.

It is interesting to note in (114) and (116) that the **Onsager relations**, which so far not yet been derived by the method of rational thermodynamics, are valid in our case under the simple assumption that

$$\vartheta = 0. \tag{117}$$

This is not precluded by (37) and, furthermore, one of the additional constraints on equilibrium namely that of a positive-definite matrix (84), will be justified (see (36), (37)), if friction is disregarded ($\underline{d}_\alpha = 0$) with the logical assumption that $\beta_1 > 0$ and $\varkappa_1 > 0$. This again confirms the possibility of a relation between the Osnager relations and the equilibrium properties (see the note on page 114 in [3]).

In conclusion, we would like to repeat Truesdell's statement [3] that the term "rational thermodynamics" denotes only a new approach to the description of thermodynamic phenomena (it does not imply that some other approach is irrational). In fact, this is true thermodynamics and what we usually call thermodynamics is really thermostatics. In irreversible thermodynamics one uses the results of thermostatics and this is what, in principle, restricts the scope.

We endeavored to demonstrate that (rational) thermodynamics in the extreme case contains the results of reversible thermodynamics, but in addition to that very special case it can, in principle at least, describe the behavior of any material under any conditions.

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