

Equivalence of energy, entropy, and thermodynamic potentials in relation to the thermodynamic equilibrium of multitemperature gas mixtures

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The central theme of this study is the thermodynamic equilibrium of multitemperature gas mixtures. The presented material is meant to complement and, for certain aspects, to complete a previous contribution of the author on the subject matter. The analysis begins with a brief introductory survey of the main theoretical approaches pursued to characterize quantitatively multitemperature equilibria with the intent to emphasize the discordant findings of these approaches and the diverging opinions they have originated in the literature. The equilibrium problem is then confronted within the framework of axiomatic thermodynamics. The general equilibrium principle in its axiomatic form is recalled and the importance of the physical constraints imposed on the gas mixture in connection with the application of the principle is recognized. A rigorous proof is given of the equivalence between energy minimization and entropy maximization for the purpose of determining the equilibrium conditions in multitemperature circumstances and regardless of the active internal constraints. Moreover, the influence of the kind of internal constraints in establishing the mathematical form of the equilibrium equations is pointed out and the divergence among the findings of other approaches is thus explained. The equivalence feature is also considered in relation to the thermodynamic potentials. Evidence is given that not all thermodynamic potentials possess the equivalence property, i.e., attainment of an extremum, in conditions of thermodynamic equilibrium. Consistently, mathematical properties relevant to the search of the extrema of the Legendre transforms are recalled and elaborated upon. A selection rule is formulated that permits the identification of the thermodynamic potentials possessing the equivalence property. The essential role played by the internal constraints in the selection procedure is described and fully evidenced in the subsequent application of the method to two representative cases of equilibrium that occur often in the applications, namely, in the absence of internal constraints and when energetic freezing prevails.

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I. INTRODUCTION

Multitemperature gas mixtures are important in the study of hypersonic flows, nozzle flows, jets and plumes, combustion and flames, plasma flows, etc., and are therefore of primary interest in a variety of engineering applications such as planetary-entry spacecraft design, advanced high-temperature propulsion systems, high-enthalpy wind tunnels, advanced material processing and manufacturing, and so on. In general, the nature of the problems encountered in the mentioned applications requires a thermochemical nonequilibrium description of the gas mixture, but there can be circumstances under which it acquires importance to consider states of thermodynamic equilibrium that are compatible with the existence of distinct temperatures and to determine quantitatively the corresponding state parameters. Different theoretical approaches have been pursued (see, e.g., Refs. [1–10] and references therein) for this purpose, but there does not seem to be common agreement among their findings. There are attempts [6,9,10] to confront the problem within a kinetic framework but, expectedly, the preference of the researchers has been devoted to approaches of thermodynamic character. With regard to the latter, an attentive survey of the published (and unpublished) contributions on the subject reveals a manifest disagreement about which state function should be minimized or maximized to obtain the conditions of equilibrium. Historically, the minimization of the

Helmholtz and Gibbs potentials has been considered the correct procedure to apply [1,7]; the generalization to multitemperature situations was believed implied in the enforcement of the constancy of all temperatures together with that of volume or pressure, respectively. The widespread acceptance of this approach has been largely favored by the fact that it leads to the vanishing of the chemical affinities as prescript of chemical equilibrium even in the presence of different temperatures, a result in accordance with and seemingly obvious generalization of that relative to single-temperature gas mixtures. On the other hand, Morro and Romeo [2–4] have dealt with the multitemperature equilibrium problem in the context of irreversible thermodynamics. Their analysis, based on the minimization of the entropy production, does not lead to the vanishing of the chemical affinities but of similar linear combinations in which the chemical potentials appear divided by appropriate temperatures. The discrepancy between the results of the two approaches has raised a debate on the correct form of a “generalized law of mass action” and has promoted further investigations of thermodynamically more traditional nature aimed to reproduce the form of the law obtained by Morro and Romeo. Thus van de Sanden and co-workers [5,6], using arguments of classical thermodynamics, started from the second law appropriately rephrased for multitemperature circumstances and introduced a “generalized free energy” [11] whose minimization, keeping constant all temperatures and volume, yields the sought result. Martinez-Sanchez [8] followed a statistical thermody-

namics approach and reproduced Morro and Romeo's result via the maximization of the entropy for prescribed volume and energies of the molecular degrees of freedom of the gas mixture. An attempt to reconcile the two distinct forms of the generalized law of mass action was made by Chen and Eddy [12], who proposed some theoretical considerations related to openness or isolation of the thermodynamic (sub)system(s) to justify the applicability of, respectively, Helmholtz- and Gibbs-potential minimization or entropy maximization.

A contribution to the discussion on the subject was also given by the present author in Ref. [13]. The multitemperature equilibrium problem was dealt with within the framework of the axiomatic thermodynamics developed by Tisza [14] and Callen [15] on the foundations laid down by Gibbs [16] and applied to multitemperature gas mixtures by Napolitano [17]. Evidence was given that the presumed divergence of the findings of the various approaches is only apparent because the two forms found for the law of mass action correspond to differently constrained equilibria. Both forms are recoverable from the correct application of the general principle of energy minimization and entropy maximization if the important role played by the physical constraints imposed on the gas mixture is recognized and appropriately brought into account. In particular, it was shown that in multitemperature situations (a) energy minimization and entropy maximization are still equivalent for the purpose of determining the conditions of equilibrium and (b) there is no generalized law of mass action, but the applicable form of the law depends on what kind of internal constraints are active in the mixture. The former conclusion, however, was reached in a rather applicative manner by showing that the same equilibrium equations are obtained via the application of either energy minimization or entropy maximization to the particular case when energy redistribution is impeded among some molecular degrees of freedom. Furthermore, the use and features of the thermodynamic potentials for the purpose of determining the conditions of equilibrium were not elaborated upon, but only briefly mentioned.

The present work is meant to complement and, for certain aspects, to complete Ref. [13]. Its purpose is to consolidate with a more general proof the equivalence between energy minimization and entropy maximization in the presence of multiple temperatures and to address in a more detailed manner aspects concerning the use of the thermodynamic potentials in such a situation.

The thermodynamic system of interest is a gas mixture with n chemical components ($\epsilon = 1, \dots, n$) in a volume V . The ϵ th component is present with a mass m_ϵ and possesses l_ϵ independent molecular degrees of freedom ($\delta = 1, \dots, l_\epsilon$). The degrees of freedom represent the thermodynamic subsystems and are considered in disequilibrium with respect to mass and energy exchanges [17]. Each degree of freedom has associated an energy $U_{\epsilon\delta}$ and an entropy $S_{\epsilon\delta}$ that depend on each other via the fundamental relation $U_{\epsilon\delta}(S_{\epsilon\delta}, V, m_\epsilon)$ or $S_{\epsilon\delta}(U_{\epsilon\delta}, V, m_\epsilon)$. The independence of the degrees of freedom implies the additivity of the energies $U_{\epsilon\delta}$ and the entropies $S_{\epsilon\delta}$. The energetic and entropic fundamental relations of the gas mixture in thermochemical nonequilibrium read formally

$$U = \sum_{\epsilon, \delta} U_{\epsilon\delta}(S_{\epsilon\delta}, V, m_\epsilon) = U(\mathbf{S}, V, \mathbf{m}), \quad (1)$$

$$S = \sum_{\epsilon, \delta} S_{\epsilon\delta}(U_{\epsilon\delta}, V, m_\epsilon) = S(\mathbf{U}, V, \mathbf{m}). \quad (2)$$

In Eqs. (1) and (2), \mathbf{S} , \mathbf{U} , and \mathbf{m} represent the arrays of, respectively, the $\sum_{\epsilon} l_\epsilon$ entropies $\{S_{11}, S_{12}, \dots, S_{21}, \dots\}$, the $\sum_{\epsilon} l_\epsilon$ energies $\{U_{11}, U_{12}, \dots, U_{21}, \dots\}$, and the n masses $\{m_1, m_2, \dots\}$. The reader is referred to Ref. [13] for details relative to definitions and notation adopted in the following sections.

II. EQUILIBRIUM PRINCIPLE AND CONSTRAINTS

The principle of thermodynamic equilibrium in its axiomatic form was established by Gibbs [16] on arguments of physical nature and has been dealt with at length by Tisza [14], Callen [15], and Napolitano [17]. It affirms [16,17] that the values attained at equilibrium by the independent state parameters of a thermodynamic system are those that minimize the energy [Eq. (1)] or, equivalently, maximize the entropy [Eq. (2)] of the system in the domain defined by its "virtual" states that are compatible with the physical constraints (Gibbs' "equations of condition" [16]) affecting the variations of its independent state parameters. Alternative viewpoints and corresponding formulations in line with the philosophy of axiomatic thermodynamics can be found in Refs. [14, 15, 18].

An essential feature associated with any state of equilibrium is the existence of a minimum set of constraints (Napolitano's "isolation conditions" [17]; see also Ref. [16]) that must be necessarily accounted for in the minimization or maximization procedure. In the energetic representation [Eq. (1)], these constraints are expressed by the conservation of entropy, volume, and mass

$$S = S^a, \quad (3)$$

$$V = V^a, \quad (4)$$

$$m = m^a. \quad (5)$$

The superscript a on the right-hand sides of Eqs. (3)–(5) denotes assigned values of the variables in question; this notation will be retained hereinafter. In the alternative entropic representation [Eq. (2)], the prescription [Eq. (3)] of the entropy is replaced with the conservation of the energy

$$U = U^a. \quad (6)$$

With regard to gas mixtures in thermochemical nonequilibrium, additional constraints (Callen's "internal constraints" [15]) may arise from the physical modalities that govern mass and energy exchanges during the molecular collisions. The r independent chemical reactions associated with the species present in the mixture represent an example of such constraints; their occurrence restrains the component masses to vary according to linear combinations

$$m_\epsilon = m_\epsilon^0 + \sum_{\kappa=1}^r \xi_\kappa \nu_{\kappa\epsilon} M_\epsilon, \quad \epsilon = 1, \dots, n, \quad (7)$$

of the reaction progress variables ξ_κ . In Eq. (7), m_ϵ^0 , $\nu_{\kappa\epsilon}$, and M_ϵ are, respectively, the initial mass, stoichiometric coefficient in the κ th reaction, and molecular mass of the ϵ th component. The stoichiometric relations

$$\sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_\epsilon = 0, \quad \kappa = 1, \dots, r, \quad (8)$$

enforce the mass conservation across the chemical reactions and permit the convenient disposal of the mass conservation [Eq. (5)]

$$m = \sum_{\epsilon=1}^n m_\epsilon = \sum_{\epsilon=1}^n m_\epsilon^0 = m^a. \quad (9)$$

Thus a rigorous analysis should proceed by considering the masses as state parameters and the linear combinations (7) as constraint equations. However, much simplification and clarity are achieved by interpreting the linear combinations (7) as enforcing a change of variables in the set of independent state parameters and by incorporating them, as such, directly into the fundamental relations. In this manner, the component masses lose their prerogative of independence as state parameters and are replaced with the reaction progress variables. Every occurrence of “ m_ϵ ” in the functional dependence of energy and entropy can be formally replaced with the array ξ of the r progress variables $\{\xi_1, \xi_2, \dots\}$

$$U = \sum_{\epsilon,\delta} U_{\epsilon\delta}(S_{\epsilon\delta}, V, \xi) = U(\mathbf{S}, V, \xi), \quad (10)$$

$$S = \sum_{\epsilon,\delta} S_{\epsilon\delta}(U_{\epsilon\delta}, V, \xi) = S(\mathbf{U}, V, \xi). \quad (11)$$

Other typical constraints met in the applications can be the inhibition of a chemical reaction ($\xi_\kappa = \xi_\kappa^a$), the restraint of the energy ($U_{\epsilon\delta} = U_{\epsilon\delta}^a$) distributed over a degree of freedom, etc. Explicit examples are the lack of chemical reactivity between H_2 and O_2 at standard temperature and pressure or the lack of thermalization of the free electrons with neutral and ionized species in partially ionized gases [19].

The internal constraints represent additional restrictions imposed on the independent state parameters. In general, they appear in the form of mathematical relations

$$\phi_j \text{ (independent state parameters)} = 0, \quad j = 1, 2, \dots, \quad (12)$$

which supplement the conservation constraints [Eq. (3) or (4) and Eq. (4)]. In this regard, particular attention [20] should be paid to select the appropriate functional dependence in Eq. (12) according to the chosen thermodynamic representation. For example, the energetic freezing constraint $U_{\epsilon\delta} - U_{\epsilon\delta}^a = 0$ reads as such in the entropic scheme, but it must be interpreted as $U_{\epsilon\delta}(S_{\epsilon\delta}, V, \xi) - U_{\epsilon\delta}^a = 0$ in the energetic scheme. This aspect should never be overlooked when performing equilibrium analyses.

III. EQUIVALENCE OF ENERGY MINIMIZATION AND ENTROPY MAXIMIZATION

The equivalence between energy minimization and entropy maximization finds its expression in the equilibrium principle recalled in Sec. II and is founded upon rigorous mathematical proof. For single-temperature gas mixtures, the specification of the detailed distribution of energy and entropy among the degrees of freedom is not necessary and the knowledge of the functional dependence between their total amounts is sufficient for thermodynamic purposes. The fundamental relations (10) and (11) simplify to the more familiar forms

$$U = U(S, V, \xi), \quad (13)$$

$$S = S(U, V, \xi), \quad (14)$$

whose differentials compatible with the conservation constraints [Eq. (3) or (6) and Eq. (4)] read

$$(dU)_{S,V} = \sum_{\kappa=1}^r \mathcal{A}_\kappa d\xi_\kappa = -T(dS)_{U,V}. \quad (15)$$

In Eq. (15),

$$\mathcal{A}_\kappa = (\partial U / \partial \xi_\kappa)_{S,V,\text{all } \xi_{\alpha \neq \kappa}} = -T(\partial S / \partial \xi_\kappa)_{U,V,\text{all } \xi_{\alpha \neq \kappa}}$$

is the affinity of the κ th reaction, given by the linear combination

$$\mathcal{A}_\kappa = \sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_\epsilon \mu_\epsilon \quad (16)$$

of the chemical potentials $\mu_\epsilon = (\partial U / \partial m_\epsilon)_{S,V,\text{all } m_{\alpha \neq \epsilon}} = -T(\partial S / \partial m_\epsilon)_{U,V,\text{all } m_{\alpha \neq \epsilon}}$ associated with the components, and $T = (\partial U / \partial S)_{V,\xi} = 1 / (\partial S / \partial U)_{V,\xi}$ is the temperature of the gas mixture. The equivalence between energy minimization and entropy maximization is easily understood from Eq. (15), which can also be rewritten in the convenient form

$$(dU)_{S,V} + T(dS)_{U,V} = 0. \quad (17)$$

A more formal and detailed proof of Eq. (15) has been given by Callen [15].

The equivalence property holds also for multitemperature gas mixtures, although it seems to be not as easily perceived as in the former case. An elegant proof is achieved with the method of the Lagrange multipliers [14]. The conservation constraints (3) and (6) play a key role in this case because they introduce in the Lagrangian functions

$$\mathcal{L}[U] = \sum_{\epsilon, \delta} U_{\epsilon\delta}(S_{\epsilon\delta}, V, \xi) - \underbrace{\lambda_S (\sum_{\epsilon, \delta} S_{\epsilon\delta} - S^a)}_{\text{Eqs. (2) and (3)}} + \lambda_V (V - V^a) + \sum_j \lambda_j \phi_j \quad (18)$$

$$\mathcal{L}[S] = \sum_{\epsilon, \delta} S_{\epsilon\delta}(U_{\epsilon\delta}, V, \xi) - \underbrace{\lambda_U (\sum_{\epsilon, \delta} U_{\epsilon\delta} - U^a)}_{\text{Eqs. (1) and (6)}} + \lambda'_V (V - V^a) + \sum_j \lambda'_j \phi_j \quad (19)$$

whose minimization and maximization lead, respectively, to the conditions of equilibrium, the symmetry necessary for their equivalence. The differentials of $\mathcal{L}[U]$ and $\mathcal{L}[S]$ read, respectively,

$$d\mathcal{L}[U] = \sum_{\epsilon, \delta} dU_{\epsilon\delta} - \lambda_S \sum_{\epsilon, \delta} dS_{\epsilon\delta} + \lambda_V dV + \sum_j \lambda_j d\phi_j, \quad (20)$$

$$d\mathcal{L}[S] = \sum_{\epsilon, \delta} dS_{\epsilon\delta} - \lambda_U \sum_{\epsilon, \delta} dU_{\epsilon\delta} + \lambda'_V dV + \sum_j \lambda'_j d\phi_j. \quad (21)$$

Equations (20) and (21) can always be turned into each other by appropriate algebraic manipulation. For example, multiplying Eq. (20) by $-1/\lambda_S$ and rearranging gives

$$-\frac{1}{\lambda_S} d\mathcal{L}[U] = \sum_{\epsilon, \delta} dS_{\epsilon\delta} - \frac{1}{\lambda_S} \sum_{\epsilon, \delta} dU_{\epsilon\delta} - \frac{\lambda_V}{\lambda_S} dV - \sum_j \frac{\lambda_j}{\lambda_S} d\phi_j. \quad (22)$$

The formal coincidence ($\lambda_U = 1/\lambda_S$, $\lambda'_V = -\lambda_V/\lambda_S$, $\lambda'_j = -\lambda_j/\lambda_S$) between the right-hand sides of Eqs. (21) and (22) yields the linear dependence

$$d\mathcal{L}[U] + \lambda_S d\mathcal{L}[S] = 0. \quad (23)$$

Equation (23) is the generalization of Eq. (17). It proves the equivalence between energy minimization and entropy maximization in multitemperature situations, regardless of the explicit form assumed by the internal constraints [Eq. (12)]. Thus either the minimization of the Lagrangian (18) or the maximization of the Lagrangian (19) will return the same equilibrium equations. These equations, however, will contain the derivatives of the functions ϕ_j with respect to the independent state parameters in the chosen representation and therefore their mathematical form will depend on the explicit form of the internal constraints. In other words, there is no generalized (in the thermodynamic sense) form of the equilibrium equations, and of the law of mass action in particular, that fulfills the task of producing the conditions of equilibrium irrespective of the constraining occurrences of the case being considered, as the antithetical opinions ex-

pressed in the literature seem to imply, but the applicable form of the equations varies according to the kind of internal constraints active in the gas mixture.

IV. EQUIVALENCE PROPERTY AND THERMODYNAMIC POTENTIALS

A. Introductory remarks

When dealing with single-temperature gas mixtures, it is customary to think that any (habitually used) thermodynamic potential can serve the purpose of finding the conditions of equilibrium, i.e., the chemical equilibrium composition, provided the appropriate couple of state parameters is held constant [21]. The equivalence of Helmholtz-potential, enthalpy, and Gibbs-potential minimization is enforced, respectively, by the relations

$$(dF)_{T,V} = (dH)_{S,p} = (dG)_{T,p} = (dU)_{S,V}. \quad (24)$$

In Eq. (24), p is the thermodynamic pressure. Relations similar to Eq. (24) exist also for the entropic potentials [22] defined as

$$\varphi = S - \frac{1}{T} U, \quad (25)$$

$$\Phi = S - \frac{p}{T} V, \quad (26)$$

$$\Psi = S - \frac{1}{T} U - \frac{p}{T} V. \quad (27)$$

They read

$$(d\varphi)_{1/T,V} = (d\Phi)_{U,p/T} = (d\Psi)_{1/T,p/T} = (dS)_{U,V} \quad (28)$$

and enforce the equivalence of φ -, Φ -, and Ψ -potential maximization. Now, inconsistencies arise when the idea is exported as such to multitemperature situations. The generalization of the mentioned energetic and entropic potentials to the latter situations is considered, apparently, rather straightforward [1,5–7]. On the other hand, the minimization of the multitemperature counterparts of the Helmholtz and Gibbs potentials appears to succeed or fail [23] in predicting the conditions of equilibrium according to the particular problem being investigated. At the same time, the minimization of van de Sanden's generalized free energy [5,6,11] leads to equilibrium equations unexpectedly at variance with those obtained from the minimization of the generalized Helmholtz and Gibbs potentials. Thus, why does the latter procedure

fail in some cases? Why do generalized energetic and entropic potentials lead to distinct equilibrium equations, notwithstanding the unconditional equivalence of energy and entropy (Sec. III)? Whether or not the theoretical arguments adduced to provide definite answers to these questions are sufficiently convincing, the applications remains somewhat pervaded by a vague sense of uncertainty and hesitation [24].

In the author's opinion, equilibrium analyses will inevitably be plagued by confusion and a lack of clear understanding until it will be realized that the equivalence relations (24) and (28) reflect only a partial view of a more general discourse and that their extension to multitemperature gas mixtures is not as straightforward as hurriedly assumed. Interestingly enough, the underlying limitations can be made evident even in single-temperature circumstances. Taking into account Eqs. (15) and (16), the vanishing of the differentials in Eqs. (24) and (28) generates the r chemical equilibrium equations

$$\sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_{\epsilon} \mu_{\epsilon} = 0, \quad \kappa=1, \dots, r, \quad (29)$$

which, together with the prescription of the appropriate couple of state parameters [subscripts in Eqs. (24) and (28)], can be solved for the equilibrium values of the r reaction progress variables. On the other hand, it is immediately verified that the perfectly legitimate potential

$$L = U - \mathcal{A}_1 \xi_1 = L(S, V, \mathcal{A}_1, \xi_2, \dots, \xi_r) \quad (30)$$

does not attain a minimum when calculated in correspondence to the solution of the system (29) for the same prescribed entropy and volume. The potential L attains an extremum when

$$\left(\frac{\partial L}{\partial \mathcal{A}_1} \right)_{S, V, \text{all } \xi_{\kappa \neq 1}} = -\xi_1(S, V, \mathcal{A}_1, \xi_2, \dots, \xi_r) = 0, \quad (31)$$

$$\sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_{\epsilon} \mu_{\epsilon} = 0, \quad \kappa=2, \dots, r. \quad (32)$$

The solution provided by Eqs. (31) and (32) does not coincide with the (chemical, in this case) equilibrium solution yielded by the system (29). However, under the particular circumstance of partially constrained equilibrium in which the reaction $\kappa=1$ is inhibited, the potential L becomes equivalent to, for instance, the energy U because in this case their differentials come to coincide

$$(dL)_{S, V, \mathcal{A}_1} = (dU)_{S, V, \xi_1}. \quad (33)$$

The supplemental condition $\mathcal{A}_1 = \mathcal{A}_1^a$ enforces the inhibition of the reaction $\kappa=1$ in the L -potential representation and replaces the analogous condition $\xi_1 = \xi_1^a$ of the energetic representation [25].

This simple example points out two important aspects: (a) There can be thermodynamic potentials that do not attain an extremum in conditions of equilibrium and (b) the internal constraints seem to play a role in conferring the equivalence property to the potentials. Thus, for a given situation of partially constrained equilibrium, how can the potentials pos-

sessing the equivalence property be selected and how do the internal constraints intervene in the selection process? Answering is not a straightforward endeavor but requires careful reconsideration and adequate generalization of established notions involving, at the same time, mathematical aspects and physical interpretation. The logical way to embark on such a task is to revisit some mathematical properties of the potentials that lead to answer the posed questions.

B. Some mathematical properties of the Legendre transforms

In mathematical language, the thermodynamic potentials are the Legendre transforms of a fundamental relation [Eqs. (10) and (11)]. Detailed expositions on the subject have been given by Tisza [14], Callen [15], and Napolitano [17]. The considerations of this section take advantage and are built upon the exposition of the latter author.

Consider a function $f = f(x_1, \dots, x_v)$ of v variables and its derivatives

$$u_i = \frac{\partial f}{\partial x_i} = u_i(x_1, \dots, x_v), \quad i = 1, \dots, v. \quad (34)$$

Moreover, assume that the variations of t ($t < v$) variables are affected by c ($c \leq t$) constraints. After an inessential permutation, it is always possible to enumerate the variables in such a way that the constrained ones are grouped for i ranging from 1 to t . Thus, in general, the constraints can be expressed as

$$\beta_j(x_1, \dots, x_t) = 0, \quad j = 1, \dots, c. \quad (35)$$

The search of the extrema of the function f with the constraints (35) calls for the Lagrangian function

$$\mathcal{L}[f] = f + \sum_{j=1}^c \lambda_j \beta_j \quad (36)$$

and leads to the v equations

$$u_i(x_1, \dots, x_v) + \sum_{j=1}^c \lambda_j \frac{\partial \beta_j}{\partial x_i} = 0, \quad i = 1, \dots, t \quad (37)$$

$$u_i(x_1, \dots, x_v) = 0, \quad i = t+1, \dots, v. \quad (38)$$

These equations, the derivative definitions [Eq. (34)], and the constraint equations [Eq. (35)] constitute a system of $2v + c$ equations for the v variables x_i , the v derivative values u_i , and the c Lagrange multipliers λ_j . The values x_i^e, u_i^e ($i = 1, \dots, v$) provided by the solution of such a system may conveniently be referred to as "equilibrium" conditions.

The function f generates $2^v - 1$ Legendre transforms. Among these, the one defined as

$$g = f - \sum_{i=1}^t u_i x_i \quad (39)$$

deserves particular attention in connection with the existence of the constraints (35). In the g -potential representation the first t derivatives (34) replace their conjugate variables x_i ($i = 1, \dots, t$) and assume the role of independent variables. The function g reads

$$g = g(u_1, \dots, u_t, x_{t+1}, \dots, x_v) \quad (40)$$

and yields the derivatives

$$-x_i = \frac{\partial g}{\partial u_i} = -x_i(u_1, \dots, u_t, x_{t+1}, \dots, x_v), \quad i = 1, \dots, t \quad (41)$$

$$u_i = \frac{\partial g}{\partial x_i} = u_i(u_1, \dots, u_t, x_{t+1}, \dots, x_v), \quad i = t+1, \dots, v. \quad (42)$$

The transform (39) is characterized by the following noticeable property [17]: Its extrema compatible with the constraints

$$u_i - u_i^e = 0, \quad i = 1, \dots, t, \quad (43)$$

coincide with the extrema of the function f compatible with the constraints (35). In fact, the search of the extrema of the transform (39) with the constraints (43) requires the Lagrangian function

$$\mathcal{L}[g] = g + \sum_{i=1}^t \lambda'_i (u_i - u_i^e) \quad (44)$$

and produces the v equations

$$x_i(u_1, \dots, u_t, x_{t+1}, \dots, x_v) - \lambda'_i = 0, \quad i = 1, \dots, t \quad (45)$$

$$u_i(u_1, \dots, u_t, x_{t+1}, \dots, x_v) = 0, \quad i = t+1, \dots, v. \quad (46)$$

The former equations [Eq. (45)] yield the t Lagrange multipliers λ'_i and are therefore inessential. The latter equations [Eq. (46)] coincide with those [Eq. (38)] found previously, although the functional dependence is different because they have been generated within the g -potential representation. With the aid of Eq. (43), it is easy to verify that Eqs. (41) and (46) reduce to identities when the equilibrium values x_i^e ($i = 1, \dots, v$) are substituted into them. Thus the function f and its transform (39) share the same extrema and, in this sense, they are equivalent for the purpose of finding the equilibrium conditions.

Whether the equivalence property belongs exclusively to the transform (39) or it is owned by other transforms of the function f depends on the possibility of decoupling offered by the constraints (35). Constraint decoupling occurs when the constraint equations do not share simultaneously all the constrained variables. As a first step towards the understanding of this important mathematical aspect with far-reaching physical significance, consider the circumstance in which the first t' ($t' < t$) constrained variables appear only in the first c' ($c' < c$; $c' \leq t'$) constraint equations

$$\beta_j(x_1, \dots, x_{t'}) = 0, \quad j = 1, \dots, c', \quad (47)$$

while the remaining $t - t'$ constrained variables appear only in the remaining $c - c'$ ($c - c' \leq t - t'$) constraint equations

$$\beta_j(x_{t'+1}, \dots, x_t) = 0, \quad j = c'+1, \dots, c. \quad (48)$$

There is no loss of generality in assuming this ordering of constraints and variables because it can always be arrived at after adequate, and inessential, permutations; what really matters is that Eqs. (47) and (48) do not have any variable in common. The separation of Eq. (35) into Eqs. (47) and (48) makes block-diagonal [26] the Jacobian of the constraints

$$\left(\frac{\partial \beta_j}{\partial x_i} \right)_{c \times t} = \left(\begin{array}{c|c} \left(\frac{\partial \beta_j}{\partial x_i} \right)_{c' \times t'} & 0 \\ \hline 0 & \left(\frac{\partial \beta_j}{\partial x_i} \right)_{(c-c') \times (t-t')} \end{array} \right). \quad (49)$$

The appearance of two noncommunicating, independent blocks in Eq. (49) suggests that the equivalence property featured by the transform (39) may have been passed on to the transforms

$$\hat{g} = f - \sum_{i=1}^{t'} u_i x_i, \quad (50)$$

$$\tilde{g} = f - \sum_{i=t'+1}^t u_i x_i \quad (51)$$

in connection with the constraints (47) and (48), respectively. As a matter of fact, this turns out to be the case. In particular, the determination of the extrema of the transform (50) compatibly with the constraints

$$u_i - u_i^e = 0, \quad i = 1, \dots, t' \quad (52)$$

$$\beta_j(x_{t'+1}, \dots, x_t) = 0, \quad j = c'+1, \dots, c \quad (53)$$

returns the same equilibrium conditions obtained by the extremization of the function f compatible with the constraints (47) and (48). The same holds for the transform (51), but with the constraints

$$\beta_j(x_1, \dots, x_{t'}) = 0, \quad j = 1, \dots, c' \quad (54)$$

$$u_i - u_i^e = 0, \quad i = t'+1, \dots, t. \quad (55)$$

The proof of these equivalence statements starts, respectively, from the Lagrangian functions

$$\mathcal{L}[\hat{g}] = \hat{g} + \sum_{i=1}^{t'} \hat{\lambda}'_i (u_i - u_i^e) + \sum_{j=c'+1}^c \hat{\lambda}_j \beta_j, \quad (56)$$

$$\mathcal{L}[\tilde{g}] = \tilde{g} + \sum_{j=1}^{c'} \tilde{\lambda}_j \beta_j + \sum_{i=t'+1}^t \tilde{\lambda}'_i (u_i - u_i^e) \quad (57)$$

and proceeds along arguments similar to those used to establish the equivalence of the transform (39). The algebraic passages are somewhat lengthy and therefore are omitted.

The recursive application to the constraints (35) of the separability concept permits a straightforward generalization of the conclusions drawn for the introductory case and leads to the definition of an unambiguous selection procedure to single out the transforms of the function f that possess the

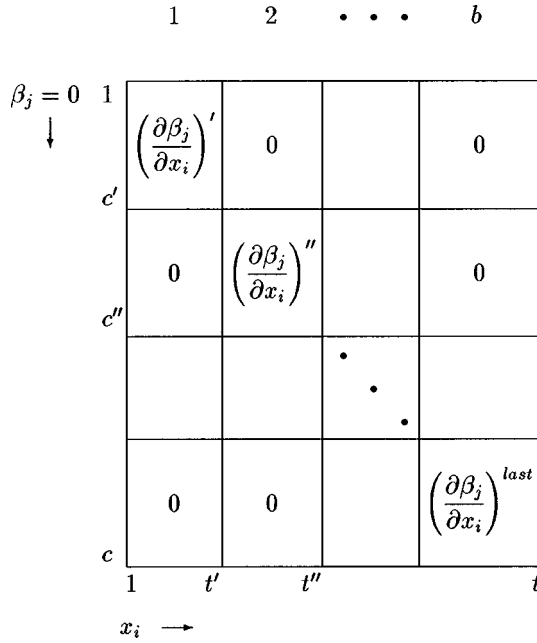


FIG. 1. Reduction of the Jacobian $(\partial\beta_j/\partial x_i)_{c \times t}$ to a block-diagonal form.

equivalence property. The basic step is to operate a reduction of the Jacobian $(\partial\beta_j/\partial x_i)_{c \times t}$ to a block-diagonal form, schematically represented in the diagram of Fig. 1, by inspection of the constraint equations (35). Then every transform of the function f obtained by selecting a block (say, $i=t'+1, \dots, t''$) and by making the Legendre transformation with respect to *all* the variables x_i included in the selected block is equivalent to the function f for the purpose of finding the equilibrium conditions provided that the subset of the $c''-c'$ constraints

$$\beta_j(x_{t'+1}, \dots, x_{t''}) = 0, \quad j=c'+1, \dots, c'', \quad (58)$$

corresponding to the selected block is replaced with the prescription of the $t''-t'$ first derivatives

$$u_i - u_i^e = 0, \quad i=t'+1, \dots, t'', \quad (59)$$

of the function f . Multiple blocks can be simultaneously selected for transformation. Thus, if b ($b \leq t$) is the number of blocks in which the Jacobian $(\partial\beta_j/\partial x_i)_{c \times t}$ can be decomposed (see Fig. 1) then the number of equivalent transforms is $2^b - 1$. For example, in the introductory case the Jacobian reduces to $b=2$ blocks [Eq. (49)] and gives rise to the $2^2 - 1 = 3$ equivalent transforms (39), (50), and (51). If the Jacobian cannot be reduced to a block-diagonal form, then $b=1$ and the transform (39) is the only equivalent transform available.

C. Representative cases of equilibrium

1. Basic definitions

The considerations of Sec. IV B resolve the questions expressed at the end of Sec. IV A and give evidence of the importance that the knowledge of the constraints imposed on the gas mixture has for the purpose of identifying the equivalent thermodynamic potentials. In order to remove math-

ematical abstraction and to reintroduce physical significance, those considerations will be applied in the following sections to representative cases of equilibrium, namely, in the absence of internal constraints and in the presence of energetic freezing. A more concrete example of the application of the ideas expounded in this work is illustrated in Ref. [27] and, in a more elaborate manner, in Ref. [13], where the Saha equation for a two-temperature partially ionized gas is derived for both the constraining circumstances in which the energy or the entropy, respectively, of the free electron translational degree of freedom are frozen.

There are diverse motivations behind the choice of the equilibrium cases dealt with in the following sections. The equilibrium analysis relative to the absence of internal constraints shows unequivocally that the application of the selection rule described in Sec. IV B leads invariably to agreement with the equivalence relations (24) and (28) when multitemperature mixtures reduce to single-temperature ones; it also represents a case in which the minimization of the generalized Helmholtz and Gibbs potentials and the maximization of van de Sanden's generalized free energy do not exclude each other but lead to concurring equilibrium equations. Equilibria in the presence of energetic freezing are reported to be observed in applications and experimental setups (see Ref. [5] and Refs. [19, 20] therein; see also Ref. [24]); the corresponding equilibrium analysis evidences that the selection rule of Sec. IV B interdicts the use of the generalized Helmholtz and Gibbs potentials and favors the applicability of van de Sanden's generalized free energy, in accordance with Refs. [5, 6], although, at the same time, it reveals the lack of generality otherwise claimed for the latter potential. However, before plunging in the mathematical detail, it is convenient to recall and summarize some basic definitions [13] in view of the Legendre-transforming operations that will be carried out on the fundamental relations (10) and (11).

The $\sum_{\epsilon} I_{\epsilon}$ entropies \mathbf{S} , the volume V , and the r progress variables $\boldsymbol{\xi}$ are the independent state parameters ($v = \sum_{\epsilon} I_{\epsilon} + 1 + r$) in the energetic representation. The first derivatives of the energy (10) represent, by definitions, the state equations [14,15,17] of the gas mixture in that scheme. The derivatives taken with respect to the entropies define the corresponding temperatures

$$T_{\epsilon\delta} = \left(\frac{\partial U}{\partial S_{\epsilon\delta}} \right)_{\text{all } S_{\alpha\eta \neq \epsilon\delta}, V, \boldsymbol{\xi}} \quad \text{for all } \epsilon, \delta \quad (60)$$

associated with the degrees of freedom of the components. The derivative taken with respect to the volume defines the pressure

$$-p = \left(\frac{\partial U}{\partial V} \right)_{\mathbf{S}, \boldsymbol{\xi}} \quad (61)$$

of the gas mixture, which, as a consequence of the energy additivity, turns out to be given by the sum $\sum_{\epsilon, \delta} p_{\epsilon\delta}$ of the partial pressures $p_{\epsilon\delta} = -(\partial U_{\epsilon\delta} / \partial V)_{S_{\epsilon\delta}, \boldsymbol{\xi}}$ (Dalton's law). The derivatives taken with respect to the progress variables define the energetic [28] affinities

$$A_\kappa = \left(\frac{\partial U}{\partial \xi_\kappa} \right)_{S, V, \text{all } \xi_{\alpha \neq \kappa}}, \quad \kappa = 1, \dots, r, \quad (62)$$

of the chemical reactions. These affinities are obtained from the linear combinations

$$A_\kappa = \sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_\epsilon \sum_{\delta=1}^{l_\epsilon} \mu_{\epsilon\delta}, \quad \kappa = 1, \dots, r, \quad (63)$$

of the partial chemical potentials

$$\mu_{\epsilon\delta} = (\partial U_{\epsilon\delta} / \partial m_\epsilon)_{S_{\epsilon\delta}, V, \text{all } m_{\alpha \neq \epsilon}}.$$

Equation (63) is the generalization of Eq. (16) in a multitemperature context.

In the entropic representation, the $\sum_\epsilon l_\epsilon$ energies \mathbf{U} assume the role of independent state parameters together with volume and progress variables. In this scheme, the state equations of the gas mixture are given by the first derivatives of the entropy (11). They define, respectively, the temperature reciprocals

$$\frac{1}{T_{\epsilon\delta}} = \left(\frac{\partial S}{\partial U_{\epsilon\delta}} \right)_{\text{all } U_{\alpha\eta \neq \epsilon\delta}, V, \xi} \quad \text{for all } \epsilon, \delta, \quad (64)$$

the sum of the ratios $p_{\epsilon\delta}/T_{\epsilon\delta}$

$$\sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} = \left(\frac{\partial S}{\partial V} \right)_{U, \xi}, \quad (65)$$

and the entropic [28] affinities

$$-\bar{A}_\kappa = \left(\frac{\partial S}{\partial \xi_\kappa} \right)_{U, V, \text{all } \xi_{\alpha \neq \kappa}}, \quad \kappa = 1, \dots, r, \quad (66)$$

of the chemical reactions. These affinities are given by the linear combinations

$$\bar{A}_\kappa = \sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_\epsilon \sum_{\delta=1}^{l_\epsilon} \frac{\mu_{\epsilon\delta}}{T_{\epsilon\delta}}, \quad \kappa = 1, \dots, r, \quad (67)$$

of the ratios $\mu_{\epsilon\delta}/T_{\epsilon\delta} = -(\partial S_{\epsilon\delta} / \partial m_\epsilon)_{U_{\epsilon\delta}, V, \text{all } m_{\alpha \neq \epsilon}}$. Energetic and entropic affinities are distinct and coexisting thermodynamic entities; the necessity to discern between them manifests itself only in multitemperature situations.

2. Equilibrium in the absence of internal constraints

The absence of internal constraints [Eq. (12)] is the macroscopic condition that settles in when the physical and dynamical properties of the molecules participating in the collisions taking place in the gas mixture allow a free redistribution of mass and energy among, respectively, components and molecular degrees of freedom. Under these circumstances, the unrestrained redistribution of energy leads to the establishment of a common temperature among all the degrees of freedom or, equivalently, to the complete thermal equilibrium of the gas mixture. When this condition prevails, the gas becomes a single-temperature mixture for which Eqs. (24) and (28) hold. The selection method described in Sec.

IV B can thus be tested by checking if its application reproduces the equivalence relations (24) and (28) when the internal constraints (12) are absent.

The equilibrium analysis in the energetic representation starts from the fundamental relation (10). The prescriptions of entropy [Eq. (3)] and volume [Eq. (4)] are the sole constraints ($c=2$) to account for; they are conveniently rephrased here as

$$\beta_S = \sum_{\epsilon, \delta} S_{\epsilon\delta} - S^a = 0, \quad (68)$$

$$\beta_V = V - V^a = 0 \quad (69)$$

for formal consistency with Eq. (35). The entropies and the volume constitute the set of the constrained variables ($t = \sum_\epsilon l_\epsilon + 1$). The minimization of the Lagrangian function

$$\mathcal{L}[U] = \sum_{\epsilon, \delta} U_{\epsilon\delta}(S_{\epsilon\delta}, V, \xi) - \lambda_S \left(\sum_{\epsilon, \delta} S_{\epsilon\delta} - S^a \right) + \lambda_V (V - V^a) \quad (70)$$

leads to the equilibrium equations

$$T_{\epsilon\delta} - \lambda_S = 0 \quad \text{for all } \epsilon, \delta, \quad (71)$$

$$-p + \lambda_V = 0, \quad (72)$$

$$A_\kappa = 0, \quad \kappa = 1, \dots, r. \quad (73)$$

The set of equations (71) enforces the mutual thermal equilibrium of the degrees of freedom: They all share a common temperature given by the value of the Lagrange multiplier λ_S , which represents, therefore, the thermal-equilibrium temperature T^e . The latter is the familiar temperature of the single-temperature mixtures; the superscript e is kept for notational consistency. The Lagrange multiplier λ_V obtained from Eq. (72) represents the equilibrium value p^e of the pressure. The vanishing [Eq. (73)] of the energetic affinities (63), in turn, characterizes the chemical equilibrium. The simultaneous solution of Eqs. (71)–(73), supplemented with Eqs. (68) and (69), provides the conditions of thermodynamic equilibrium of the gas mixture in the absence of internal constraints.

The identification among the $(2^{(r+1+\sum_\epsilon l_\epsilon)} - 1)$ thermodynamic potentials generable by Legendre transforming the energy (10) of those possessing the equivalence property is determined by the structure of the Jacobian

$$\frac{\partial(\beta_S, \beta_V)}{\partial(\mathbf{S}, V)} = \left(\begin{array}{cccc|c} 1 & 1 & \cdots & 1 & 0 \\ 0 & 0 & \cdots & 0 & 1 \end{array} \right) \quad (74)$$

of the constraints (68) and (69). The decoupling of the latter makes their Jacobian block-diagonal with $b=2$ independent blocks; there are then only $2^2 - 1 = 3$ thermodynamic potentials equivalent to the energy (10). The selection of the top-left block of the Jacobian (74) calls for the Legendre transformation with respect to all the entropies $S_{\epsilon\delta}$ and, taking into account the temperature definitions (60), it identifies the complete Helmholtz potential [29]

TABLE I. Equivalent thermodynamic potentials, and associated constraints, generated by Legendre transforming the energy (10) in the absence of internal constraints.

Block selected from diagonal of Jacobian (74)	Potential	Constraints
top left	$F=U-\sum_{\epsilon,\delta} T_{\epsilon\delta} S_{\epsilon\delta}$	$T_{\epsilon\delta}-T^e=0$ (for all ϵ, δ) $V-V^a=0$
bottom right	$H=U+pV$	$\sum_{\epsilon,\delta} S_{\epsilon\delta}-S^a=0$ $p-p^e=0$
both	$G=U-\sum_{\epsilon,\delta} T_{\epsilon\delta} S_{\epsilon\delta}+pV$	$T_{\epsilon\delta}-T^e=0$ (for all ϵ, δ) $p-p^e=0$

$$F=U-\sum_{\epsilon,\delta} T_{\epsilon\delta} S_{\epsilon\delta}=F(\mathbf{T}, V, \boldsymbol{\xi}). \quad (75)$$

In Eq. (75), \mathbf{T} represents the array of the $\sum_{\epsilon} l_{\epsilon}$ temperatures $\{T_{11}, T_{12}, \dots, T_{21}, \dots\}$. Consistently with the chosen selection, the entropy constraint (68) must be discarded and replaced with the prescription of the temperatures

$$T_{\epsilon\delta}-T^e=0 \quad \text{for all } \epsilon, \delta. \quad (76)$$

The latter equations assume the role of constraints ($T_{\epsilon\delta}^a = T^e$ for all ϵ, δ) in the representation based on the potential (75). The volume constraint (69) is unrelated to the top-left block and therefore must be retained as such. Taking into account the pressure definition (61), the selection of the bottom-right block of the Jacobian (74) leads to the enthalpy

$$H=U+pV=H(\mathbf{S}, p, \boldsymbol{\xi}). \quad (77)$$

In this case, the entropy constraint (68) must be retained and the volume constraint (69) must be replaced with the prescription of the pressure

$$p-p^e=0, \quad (78)$$

which therefore assumes the role of constraint ($p^a = p^e$) in the enthalpy representation. The simultaneous selection of both the diagonal blocks in the Jacobian (74) leads to the complete Gibbs potential

$$G=U-\sum_{\epsilon,\delta} T_{\epsilon\delta} S_{\epsilon\delta}+pV=G(\mathbf{T}, p, \boldsymbol{\xi}) \quad (79)$$

and the relevant constraints are Eqs. (76) and (78). Table I summarizes the identified potentials and the associated constraints. The minimization of any Lagrangian function constructed from those potentials and their associated constraints provides the same equilibrium conditions found from the minimization of the Lagrangian function (70). Thus the application of the selection procedure described in Sec. IV B leads to a result that confirms and generalizes the equivalences expressed in Eq. (24).

According to the property of equivalence between energy and entropy discussed in Sec. III, the same conditions of

thermodynamic equilibrium provided by the minimization of the Lagrangian function (70) are obtained also from the equilibrium analysis in the entropic representation. In this representation, the analysis is based on the fundamental relation (11). The entropy conservation [Eq. (3) or (68)] is replaced with the energy prescription [Eq. (6)], which is consistently rephrased here as

$$\beta_U = \sum_{\epsilon,\delta} U_{\epsilon\delta} - U^a = 0. \quad (80)$$

The maximization of the Lagrangian function

$$\mathcal{L}[S] = \sum_{\epsilon,\delta} S_{\epsilon\delta}(U_{\epsilon\delta}, V, \boldsymbol{\xi}) - \lambda_U \left(\sum_{\epsilon,\delta} U_{\epsilon\delta} - U^a \right) + \lambda'_V (V - V^a) \quad (81)$$

leads to the equilibrium equations

$$\frac{1}{T_{\epsilon\delta}} - \lambda_U = 0 \quad \text{for all } \epsilon, \delta, \quad (82)$$

$$\sum_{\epsilon,\delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} + \lambda'_V = 0, \quad (83)$$

$$\bar{A}_{\kappa} = 0, \quad \kappa = 1, \dots, r. \quad (84)$$

The set of equations (82) reaffirms the complete thermal equilibrium of the degrees of freedom. The Lagrange multiplier λ'_V obtained from Eq. (83) represents, apart from the sign, the equilibrium value of the entropic (nameless) state equation $\sum_{\epsilon,\delta} p_{\epsilon\delta}/T_{\epsilon\delta}$, which, because of the complete thermal equilibrium, reduces to the ratio p^e/T^e . The vanishing [Eq. (84)] of the entropic affinities (67) governs the chemical equilibrium. In spite of their different mathematical structure, energetic [Eq. (63)] and entropic [Eq. (67)] affinities become equivalent in the case, and only in this case, of absent internal constraints because the complete thermal equilibrium [Eqs. (71) and (82)] implies the relationship ($1/\lambda_U = \lambda_S = T^e$)

TABLE II. Equivalent thermodynamic potentials, and associated constraints, generated by Legendre transforming the entropy (11) in the absence of internal constraints.

Block selected from diagonal of Jacobian (86)	Potential	Constraints
top left	$\varphi = S - \sum_{\epsilon, \delta} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta}$	$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0$ (for all ϵ, δ) $V - V^a = 0$
bottom right	$\Phi = S - \sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} V$	$\sum_{\epsilon, \delta} U_{\epsilon\delta} - U^a = 0$ $\sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} - \frac{p^e}{T^e} = 0$
both	$\Psi = S - \sum_{\epsilon, \delta} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta} - \sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} V$	$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0$ (for all ϵ, δ) $\sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} - \frac{p^e}{T^e} = 0$

$$\bar{\mathcal{A}}_{\kappa} = \frac{1}{T^e} \mathcal{A}_{\kappa}. \quad (85)$$

Therefore, the vanishing of one presupposes the vanishing of the other. In conclusion, the set of equations (82)–(84), supplemented with Eqs. (69) and (80), is equivalent to that composed by Eqs. (71)–(73), supplemented with Eqs. (68) and (69); they both yield the same equilibrium conditions.

The constraints (69) and (80) are, once again, decoupled and their Jacobian

$$\frac{\partial(\beta_U, \beta_V)}{\partial(\mathbf{U}, V)} = \left(\begin{array}{cccc|c} 1 & 1 & \cdots & 1 & 0 \\ 0 & 0 & \cdots & 0 & 1 \end{array} \right) \quad (86)$$

features the same structure of the Jacobian (74). Thus there are also three equivalent thermodynamic potentials of the entropy (11). The complete φ potential

$$\varphi = S - \sum_{\epsilon, \delta} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta} = \varphi\left(\frac{\mathbf{1}}{\mathbf{T}}, V, \xi\right) \quad (87)$$

is obtained from the selection of the top-left block of the Jacobian (86) and depends on the array $\mathbf{1/T}$ of the $\sum_{\epsilon} l_{\epsilon}$ temperature reciprocals $\{1/T_{11}, 1/T_{12}, \dots, 1/T_{21}, \dots\}$. With its sign changed, it coincides with the generalized free energy introduced by van de Sanden and co-workers [5,6]. The potential (87) must be maximized with the volume constraint (69) and the prescription of the temperature reciprocals

$$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0 \quad \text{for all } \epsilon, \delta. \quad (88)$$

that replace the energy constraint (80). The Φ potential

$$\Phi = S - \sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} V = \Phi\left(\mathbf{U}, \sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}}, \xi\right) \quad (89)$$

derives from the selection of the right-bottom block of the Jacobian (86). Its maximization requires the energy constraint (80) and the prescription

$$\sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} - \frac{p^e}{T^e} = 0 \quad (90)$$

of the state equation (65). The complete Ψ potential

$$\Psi = S - \sum_{\epsilon, \delta} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta} - \sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}} V = \Psi\left(\frac{\mathbf{1}}{\mathbf{T}}, \sum_{\epsilon, \delta} \frac{p_{\epsilon\delta}}{T_{\epsilon\delta}}, \xi\right) \quad (91)$$

is found from the selection of both the diagonal blocks of the Jacobian (86) and must be maximized with the constraints (88) and (90). The potentials equivalent to the entropy are summarized in Table II. The equivalences expressed in Eq. (28) are thus also confirmed and generalized.

3. Equilibrium with energetic freezing

Energetic freezing refers to the situation in which the energy exchanges among some degrees of freedom are impaired during the collisions. Under such circumstances, the energies of the “frozen” degrees of freedom are restrained to remain constant. A typical example is the two-temperature equilibrium observed in partially ionized gases. In this case, the exchange of the translational energy of the free electrons is practically inhibited because the small electron mass, as compared to the mass of the heavier species, makes the elastic collisions an inefficient mechanism for the redistribution of that energy.

The equilibrium analysis in the presence of energetic freezing was carried out in Ref. [13] with the aid of the fundamental relation (11) and by assuming that, in general, each component has \bar{l}_{ϵ} ($\leq l_{\epsilon}$) frozen degrees of freedom. Thus the gas mixture is subjected to the $\sum_{\epsilon} \bar{l}_{\epsilon}$ internal constraints

$$U_{\epsilon\delta} = U_{\epsilon\delta}^a$$

for all $\epsilon; \delta$ of frozen degrees of freedom only. (92)

It was also shown in Ref. [13] that, in accordance with the equivalence property discussed in Sec. III, the equilibrium analysis based on the fundamental relation (10) leads to the same equilibrium equations. The latter can be summarized as follows. The nonfrozen degrees of freedom attain mutual thermal equilibrium, enforced by the $\sum_{\epsilon}(l_{\epsilon} - \bar{l}_{\epsilon})$ equations

$$\frac{1}{T_{\epsilon\delta}} - \lambda_U = 0$$

for all $\epsilon; \delta$ of nonfrozen degrees of freedom only. (93)

No condition exists on the temperatures $T_{\epsilon\delta}^e$ of the frozen degrees of freedom; they differ from the equilibrium temperature $T^e = 1/\lambda_U$ and must be determined from the definitions (60) or (64) after the set of equilibrium equations has been solved. Assuming, for simplicity, that the progress variables are unconstrained, the chemical equilibrium is governed by the vanishing of the entropic affinities

$$\bar{A}_{\kappa} = \sum_{\epsilon=1}^n \nu_{\kappa\epsilon} M_{\epsilon} \sum_{\delta=1}^{l_{\epsilon}} \frac{\mu_{\epsilon\delta}}{T_{\epsilon\delta}} = 0, \quad \kappa = 1, \dots, r. \quad (94)$$

It is important to notice that the incompleteness of the thermal equilibrium [Eq. (93)] due to the energetic freezing [Eq. (92)] of some degrees of freedom excludes, in general, the validity of Eq. (85). The lack of equivalence between energetic and entropic affinities stems from the fact that the linear combinations (67) include also the contributions of the frozen degrees of freedom whose temperatures cannot be factorized out of the summations; consequently, Eq. (85) cannot be arrived at in the case being considered. The energetic affinities [Eq. (63)] do not vanish at equilibrium but assume definite values \mathcal{A}_{κ}^e that can be calculated after the set of the equilibrium equations has been solved.

In the energetic representation, the constraints imposed on the gas mixture are the prescriptions of entropy [Eq. (68)] and volume [Eq. (69)]

$$\beta_S = \sum_{\epsilon, \delta} S_{\epsilon\delta} - S^a = 0, \quad (95)$$

$$\beta_V = V - V^a = 0 \quad (96)$$

supplemented with the energetic freezing constraints [Eq. (92)], which, in this representation, must be interpreted as

$$\beta_{\epsilon\delta} = U_{\epsilon\delta}(S_{\epsilon\delta}, V, \xi) - U_{\epsilon\delta}^a = 0$$

for all $\epsilon; \delta$ of frozen degrees of freedom only. (97)

The $c = 2 + \sum_{\epsilon} \bar{l}_{\epsilon}$ constraints (95)–(97) affect all the independent state parameters ($t = \sum_{\epsilon} l_{\epsilon} + 1 + r = v$) of the energetic representation. Their Jacobian presents the structure

$$\frac{\partial(\beta_S, \beta^f, \beta_V)}{\partial(\mathbf{S}^f, \mathbf{S}^e, \xi, V)} = \begin{pmatrix} \leftarrow 1 \rightarrow & \leftarrow 1 \rightarrow & \leftarrow 0 \rightarrow & 0 \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & 0 & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & 1 \end{pmatrix} \quad (98)$$

In Eq. (98), β^f , \mathbf{S}^f , and \mathbf{S}^{nf} are the arrays of, respectively, the $\sum_{\epsilon} \bar{l}_{\epsilon}$ functions $\beta_{\epsilon\delta}$, the $\sum_{\epsilon} \bar{l}_{\epsilon}$ entropies of the energetically frozen degrees of freedom, i.e., the entropies appearing in the constraints (97), and the $\sum_{\epsilon}(l_{\epsilon} - \bar{l}_{\epsilon})$ entropies of the nonfrozen degrees of freedom, i.e., the entropies occurring only in the constraint (95). Horizontal and vertical space is inserted on the right-hand side of Eq. (98) to outline the matrices composing the Jacobian; the dimensions of these matrices can be deduced from the notation on the left-hand side of Eq. (98). The presence of the diagonal matrix $\partial\beta^f/\partial\mathbf{S}^f$, the sparse matrix $\partial\beta^f/\partial\xi$, and the column matrix $\partial\beta^f/\partial V$ precludes, in general, the possibility to reduce the Jacobian (98) to the block-diagonal form illustrated in Fig. 1. Thus, in the case of energetic freezing, there is only one ($b=1$) thermodynamic potential equivalent to the energy (10) and it is obtained by Legendre transforming with respect to all the constrained variables

$$\Omega = U - \sum_{\epsilon, \delta} T_{\epsilon\delta} S_{\epsilon\delta} + pV - \sum_{\kappa=1}^r \mathcal{A}_{\kappa} \xi_{\kappa} = \Omega(\mathbf{T}, p, \mathcal{A}). \quad (99)$$

In Eq. (99), \mathcal{A} is the array of the r energetic affinities $\{\mathcal{A}_1, \mathcal{A}_2, \dots\}$. The minimization of the thermodynamic potential (99) calls for the prescription of the equilibrium temperature for the nonfrozen degrees of freedom

$$T_{\epsilon\delta} - T^e = 0$$

for all $\epsilon; \delta$ of nonfrozen degrees of freedom only, (100)

of the $\sum_{\epsilon} \bar{l}_{\epsilon}$ distinct temperatures of the energetically frozen degrees of freedom

$$T_{\epsilon\delta} - T_{\epsilon\delta}^e = 0$$

for all $\epsilon; \delta$ of frozen degrees of freedom only, (101)

of the pressure

$$p = p^e = 0, \quad (102)$$

and of the energetic affinities

$$\mathcal{A}_{\kappa} - \mathcal{A}_{\kappa}^e = 0, \quad \kappa = 1, \dots, r. \quad (103)$$

The constraints (100)–(103) relative to the Ω -potential representation replace the constraints (95)–(97) of the energy scheme. The structure of the Jacobian (98) indicates clearly that no Helmholtz- or Gibbs-like potential possesses the equivalence property when energetic freezing prevails. In general, even the enthalpy does not qualify as an equivalent potential unless the energetic freezing does not affect the

TABLE III. Equivalent thermodynamic potentials, and associated constraints, generated by Legendre transforming the energy (10) in the presence of energetic freezing of the internal degrees of freedom (DOF).

Block selected from diagonal of Jacobian (104)	Potential	Constraints
top left	$Y = U - \sum_{\epsilon, \delta} T_{\epsilon\delta} S_{\epsilon\delta} - \sum_{\kappa=1}^r \mathcal{A}_{\kappa} \xi_{\kappa}$	$T_{\epsilon\delta} - T^e = 0 \text{ (for all } \epsilon; \delta \text{ of nonfrozen DOF)}$ $T_{\epsilon\delta} - T_{\epsilon\delta}^e = 0 \text{ (for all } \epsilon; \delta \text{ of frozen DOF)}$ $\mathcal{A}_{\kappa} - \mathcal{A}_{\kappa}^e = 0 \text{ } (\kappa = 1, \dots, r)$ $V - V^a = 0$
bottom right	$H = U + pV$	$\sum_{\epsilon, \delta} S_{\epsilon\delta} - S^a = 0$ $U_{\epsilon\delta}(S_{\epsilon\delta}, V, \xi) - U_{\epsilon\delta}^a = 0 \text{ (for all } \epsilon; \delta \text{ of frozen DOF)}$ $p - p^e = 0$
both	$\Omega = U - \sum_{\epsilon, \delta} T_{\epsilon\delta} S_{\epsilon\delta} + pV - \sum_{\kappa=1}^r \mathcal{A}_{\kappa} \xi_{\kappa}$	$T_{\epsilon\delta} - T^e = 0 \text{ (for all } \epsilon; \delta \text{ of nonfrozen DOF)}$ $T_{\epsilon\delta} - T_{\epsilon\delta}^e = 0 \text{ (for all } \epsilon; \delta \text{ of frozen DOF)}$ $\mathcal{A}_{\kappa} - \mathcal{A}_{\kappa}^e = 0 \text{ } (\kappa = 1, \dots, r)$ $p - p^e = 0$

translational degrees of freedom. In this regard, it is known from statistical thermodynamics that the volume dependence of energy and entropy appears only in the contributions of the translational ($\delta=1$) degrees of freedom while all the available models of internal ($\delta>1$) degrees of freedom yield volume-independent contributions. Thus, in the particular circumstance in which the translational degrees of freedom are not energetically frozen, the column matrix $\partial\boldsymbol{\beta}^f/\partial V$ vanishes identically and the Jacobian (98) becomes block-diagonal with $b=2$ independent blocks

$$\frac{\partial(\beta_{\delta}, \beta^f, \beta_v)}{\partial(S^{\text{nf}}, S^f, \xi, V)} = \left(\begin{array}{ccc|ccc|c} \leftarrow 1 \rightarrow & \leftarrow 1 \rightarrow & \leftarrow 0 \rightarrow & & & & 0 \\ \cdot & \cdot & \cdot & \swarrow & 0 & \cdot & \cdot & \cdot & \uparrow \\ \cdot & 0 & \cdot & & T_{\delta\delta} & \cdot & \nu_{\kappa} M_{\kappa} \mu_{\kappa\delta} & \cdot & 0 \\ \cdot & \cdot & \cdot & 0 & \searrow & \cdot & \cdot & \cdot & \downarrow \\ \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & & & & & & 1 \end{array} \right) \quad (104)$$

Consequently, other two equivalent potentials appear, in addition to the potential (99), from the selection of the top-left and right-bottom blocks of the Jacobian (104). These potentials and their associated constraints are listed in Table III.

The identification of the equivalent thermodynamic potentials generated by Legendre transforming the entropy (11) turns out to be a more simplified task because the frozen energies [Eq. (92)] belong to the set of the independent state parameters in the entropic formulation. Thus the energetic freezing constraints (92) must be retained as such

$$\beta_{\epsilon\delta} = U_{\epsilon\delta} - U_{\epsilon\delta}^a = 0$$

for all $\epsilon; \delta$ of frozen degrees of freedom only. (105)

They supplement the prescription of the volume [Eq. (69)]

$$\beta_v = V - V^a = 0 \quad (106)$$

and the prescription of the energy [Eq. (80)], which, consistently with the energetic freezing enforced by Eq. (105), can be adapted to read

$$\beta_U = \sum_{\epsilon, \delta}^{\text{nf}} U_{\epsilon\delta} - \left(U^a - \sum_{\epsilon, \delta}^f U_{\epsilon\delta}^a \right) = 0. \quad (107)$$

In Eq. (107), the superscripts nf and f applied to the symbol $\sum_{\epsilon, \delta}$ indicate that the corresponding summations are extended to, respectively, nonfrozen and frozen degrees of freedom. The quantity in parentheses represents physically the energy that is available for redistribution among the nonfrozen degrees of freedom. The $c = 2 + \sum_{\epsilon} \bar{l}_{\epsilon}$ constraints (105)–(107) involve all the energies \mathbf{U} and the volume V ($t = \sum_{\epsilon} \bar{l}_{\epsilon} + 1$); the progress variables ξ are unconstrained in this formulation. The Jacobian of the constraints (105)–(107) presents the structure

$$\frac{\partial(\beta_v, \beta^f, \beta_U)}{\partial(\mathbf{U}^{\text{nf}}, \mathbf{U}^f, V)} = \left(\begin{array}{ccc|ccc|c} \leftarrow 1 \rightarrow & \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & & & & 0 \\ \cdot & \cdot & \cdot & \swarrow & 0 & \cdot & \cdot & \cdot & \uparrow \\ \cdot & 0 & \cdot & & \boxed{1} & \cdot & \cdot & \cdot & 0 \\ \cdot & \cdot & \cdot & 0 & \searrow & \cdot & \cdot & \cdot & \downarrow \\ \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & \leftarrow 0 \rightarrow & & & & & & 1 \end{array} \right) \quad (108)$$

In Eq. (108), \mathbf{U}^f and \mathbf{U}^{nf} are the arrays of, respectively, the $\sum_{\epsilon} \bar{l}_{\epsilon}$ energies of the frozen degrees of freedom, i.e., the energies appearing in the constraints (105), and the $\sum_{\epsilon} (l_{\epsilon} - \bar{l}_{\epsilon})$ energies of the nonfrozen degrees of freedom, i.e., the energies occurring only in the constraint (107). The central block is composed by the unit matrix $\partial\boldsymbol{\beta}^f/\partial\mathbf{U}^f$; the frame around the digit 1 serves to emphasize that each position on its diagonal constitutes an independent block of the Jacobian (108). The total number of independent blocks is thus $b = 2 + \sum_{\epsilon} \bar{l}_{\epsilon}$ and the number of equivalent thermodynamic poten-

TABLE IV. Some representative equivalent thermodynamic potentials, and associated constraints, generated by Legendre transforming the entropy (11) in the presence of energetic freezing of some degrees of freedom (DOF).

Blocks selected from diagonal of Jacobian (108)	Potential	Constraints
top left	$\varphi^{\text{nf}} = S - \sum_{\epsilon, \delta}^{\text{nf}} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta}$	$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0$ (for all $\epsilon; \delta$ of nonfrozen DOF) $U_{\epsilon\delta} - U_{\epsilon\delta}^a = 0$ (for all $\epsilon; \delta$ of frozen DOF) $V - V^a = 0$
central	$\varphi^{\text{f}} = S - \sum_{\epsilon, \delta}^{\text{f}} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta}$	$\sum_{\epsilon, \delta}^{\text{nf}} U_{\epsilon\delta} - \left(U^a - \sum_{\epsilon, \delta}^{\text{f}} U_{\epsilon\delta}^a \right) = 0$ $\frac{1}{T_{\epsilon\delta}} - \frac{1}{T_{\epsilon\delta}^e} = 0$ (for all $\epsilon; \delta$ of frozen DOF) $V - V^a = 0$
top left central	$\varphi = S - \sum_{\epsilon, \delta} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta}$	$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0$ (for all $\epsilon; \delta$ of nonfrozen DOF) $\frac{1}{T_{\epsilon\delta}} - \frac{1}{T_{\epsilon\delta}^e} = 0$ (for all $\epsilon; \delta$ of frozen DOF) $V - V^a = 0$
bottom right	$\Phi = S - \sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} V$	$\sum_{\epsilon, \delta}^{\text{nf}} U_{\epsilon\delta} - \left(U^a - \sum_{\epsilon, \delta}^{\text{f}} U_{\epsilon\delta}^a \right) = 0$ $U_{\epsilon\delta} - U_{\epsilon\delta}^a = 0$ (for all $\epsilon; \delta$ of frozen DOF) $\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} - \left(\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} \right)^e = 0$
top left bottom right	$\Psi^{\text{nf}} = S - \sum_{\epsilon, \delta}^{\text{nf}} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta} - \sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} V$	$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0$ (for all $\epsilon; \delta$ of nonfrozen DOF) $U_{\epsilon\delta} - U_{\epsilon\delta}^a = 0$ (for all $\epsilon; \delta$ of frozen DOF) $\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} - \left(\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} \right)^e = 0$
central bottom right	$\Psi^{\text{f}} = S - \sum_{\epsilon, \delta}^{\text{f}} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta} - \sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} V$	$\sum_{\epsilon, \delta}^{\text{nf}} U_{\epsilon\delta} - \left(U^a - \sum_{\epsilon, \delta}^{\text{f}} U_{\epsilon\delta}^a \right) = 0$ $\frac{1}{T_{\epsilon\delta}} - \frac{1}{T_{\epsilon\delta}^e} = 0$ (for all $\epsilon; \delta$ of frozen DOF) $\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} - \left(\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} \right)^e = 0$
top left central bottom right	$\Psi = S - \sum_{\epsilon, \delta} \frac{1}{T_{\epsilon\delta}} U_{\epsilon\delta} - \sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} V$	$\frac{1}{T_{\epsilon\delta}} - \frac{1}{T^e} = 0$ (for all $\epsilon; \delta$ of nonfrozen DOF) $\frac{1}{T_{\epsilon\delta}} - \frac{1}{T_{\epsilon\delta}^e} = 0$ (for all $\epsilon; \delta$ of frozen DOF) $\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} - \left(\sum_{\epsilon, \delta} \frac{P_{\epsilon\delta}}{T_{\epsilon\delta}} \right)^e = 0$

tials amount to $2^{(2+\sum \bar{e})} - 1$. The most representative ones are listed in Table IV together with their associated constraints.

The structure of the Jacobians (98) and (104) denies the equivalence property to Helmholtz and Gibbs-like potentials while the simultaneous selection of the top-left and central blocks of the Jacobian (108) grants that property to the generalized free energy $(-\varphi)$ of van de Sanden and co-workers [5,6]. Thus the application of the selection method described in Sec. IV B reaffirms partially the findings of Ref. [5] reached via arguments of classical thermodynamics. At the same time, however, it outlines the incorrectness of attaching the claimed attribute of generality to van de Sanden's thermodynamic function because it puts in evidence that such a function (a) is not the sole potential that can be used and (b) inherits the attribute of equivalence from the existence of the energetic freezing constraints. Relatively to the latter point, constraining circumstances, for example, entropic freezing [13], cannot be excluded in which the generalized free energy loses the equivalence property.

V. CONCLUSIONS

Thermodynamic equilibria settling in multitemperature gas mixtures have been observed in engineering applications and can be characterized quantitatively in a conceptually straightforward manner within the framework of the axiomatics thermodynamics initiated by Gibbs [16] and brought to the actual level of conceptual clarity by Tisza [14], Callen [15], and Napolitano [17].

The application of the general principle of energy minimization and entropy maximization leads unambiguously to the correct equilibrium equations if it is supplemented with

the adequate recognition of the importance of the role played by the physical constraints imposed on the gas mixture. The most relevant feature of multitemperature equilibria is that the equilibrium equations are not unique but their mathematical form is established by the kind of internal constraints. This feature resolves and rules out the debate in the literature concerned with the existence of a generalized law of mass action. The debate appears to be moot because it arises from comparing multitemperature equilibria that correspond to different constraining circumstances.

The equivalence between energy and entropy expressed in the equilibrium principle is enforced by rigorous mathematical proof. Conversely, not all the thermodynamic potentials possess the equivalence property; it is the kind of internal constraints that grants such an attribute to a subset of them. The selection method described in Sec. IV B permits one to single out the equivalent potentials according to the specified internal constraints. The application of the selection procedure to the case in which multitemperature mixtures reduce to single-temperature ones reconfirms results [Eqs. (24) and (28)] firmly established in thermodynamics.

Finally, it would be interesting to investigate if and how the role of the internal constraints materializes in the irreversible thermodynamics approach to the multitemperature equilibrium problem and whether or not the same, or at least concurring, conclusions obtained in the axiomatic thermodynamics approach could be arrived at. This aspect, however, has not been considered in this study.

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 [11] Conforming to the notation and terminology of Refs. [5,6], van de Sanden's generalized free energy is the opposite of an entropic potential obtained by Legendre transforming (Sec. IV B) the entropy of the considered plasma with respect to all the energies U_n of its thermodynamic subsystems, i.e., the molecular degrees of freedom. For a prescribed volume, the minimization of the generalized free energy with constant temperatures T_n is equivalent to the maximization of the entropy with constant energies U_n and therefore it describes the particular circumstance of equilibrium in which the collisions in the plasma occur in such a way as to restrain the redistribution of the energies U_n among the molecular degrees of freedom. See also Ref. [22].
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- [19] The author is grateful to H. S. Robertson for bringing these examples to his attention.
- [20] The following remark by Callen (Ref. [15], latest reference) is particularly appropriate at this point: “In performing formal manipulations in thermodynamics it is extremely important to make a definite commitment to one or the other of these choices [*energetic or entropic representations and corresponding sets of independent state parameters*] and to adhere rigorously to that choice. A great deal of confusion results from a vacillation between these two alternatives within a single problem.” (Italics have been introduced by the present author.)
- [21] Some expositions on the subject, cast in the framework of classical thermodynamics, implicitly disagree with this idea because they distinguish among the potentials in Eq. (24) according to the kind of process (isobar, isochor, etc.) followed by the gas mixture to reach the state of equilibrium. The concept of “process” stays central in this view while the axiomatic thermodynamics viewpoint relies upon the concept of “state.” Reconciliation between the different views requires a deeper conceptual analysis of the classical and axiomatic philosophies of thermodynamics. Such an analysis, however, is irrelevant in the context of the present discussion.
- [22] The entropic potentials are obtained by Legendre transforming the entropy. These state functions are also known as Massieu functions, after the thermodynamicist who introduced them in 1869 [M. F. Massieu, C. R. Acad. Sci. **69**, 858 (1869); **69**, 1057 (1869)]. The entropic potentials have been dealt with by Callen [15] and, for multitemperature gas mixtures, have been properly discussed by Napolitano [17] in 1971. However, there does not appear to be standard names and notation for them.
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- [25] The prescribed constants \mathcal{A}_1^a and ξ_1^a are obviously not arbitrary but depend on each other via, for example, the energetic state equation $\mathcal{A}_1^a = \mathcal{A}_1(S^a, V^a, \xi_1^a, \xi_2^e, \dots, \xi_r^e)$, where ξ_κ^e ($\kappa > 2$) are the equilibrium progress variables of the remaining chemical reactions.
- [26] The term “block-diagonal” is used here mainly to emphasize the structure of the Jacobian from a visual point of view. The matrices on the diagonal of the right-hand side of Eq. (49) and of the schematic diagram in Fig. 1 need not be necessarily squared.
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- [28] See note 39 on p. 280 of Ref. [13].
- [29] Complete in the sense that it is generated from the transformation with respect to all the entropies $S_{\epsilon\delta}$. In general, the energy (10) can generate $(2^{\sum \epsilon} - 1)$ Helmholtz-like or Gibbs-like potentials.