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R.I. 700 *Décembre 2010*

Supercritical fluid Thermodynamics from equations of state

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Abstract

Supercritical multicomponent fluid thermodynamics are often built from equations of state. We investigate mathematically such a construction of a Gibbsian thermodynamics compatible at low density with that of ideal gas mixtures starting from a pressure law. We further study the structure of chemical production rates obtained from nonequilibrium statistical thermodynamics. As a typical application, we consider the Soave-Redlich-Kwong cubic equation of state and investigate mathematically the corresponding thermodynamics. This thermodynamics is then used to study the stability of H_2-O_2-N_2 mixtures at high pressure and low temperature as well as to illustrate the rôle of nonidealities in a transcritical H_2-O_2-N_2 flame.

1 Introduction

Supercritical reactive fluids arise in laboratory experiments and engineering applications as for instance Ariane's rocket engines [1, 2, 3]. This is a strong motivation for investigating the mathematical structure of supercritical multicomponent fluid thermodynamics as well as the corresponding nonideal chemical kinetics. Although the mathematical structure of multicomponent fluid thermodynamics and chemical kinetics has already been investigated [5, 4, 6, 7], notably for perfect gas mixtures and chemical kinetics of mass action type, it neither seems to be the case for thermodynamics built from equations of state nor for supercritical reactive fluids. A second motivation is that thermodynamic studies are requisites prior to analyze the mathematical structure of hyperbolic-parabolic symmetrizable systems of partial differential equations modeling fluids [8, 11, 12, 13, 14, 15].

We first discuss the mathematical structure and properties of thermodynamic functions in terms of intensive variables as required for fluid models. We discuss smoothness properties, homogeneity, Gibbs' relation, thermodynamic stability, as well as compatibility with perfect gases at low density. Letting $\zeta = (T, v, y_1, \dots, y_n)$ where T denotes the absolute temperature, v the volume per unit mass, $y_1, \dots, y_n$ the species mass fractions supposed to be independent, and n the number of species, thermodynamic models are specified as $e(\zeta)$, $p(\zeta)$, and $s(\zeta)$, where e denotes the energy per unit mass, p the pressure, and s the entropy per unit mass. We also address a different mathematical structure obtained with the thermodynamic variable $(T, \rho_1, \dots, \rho_n)$ where $\rho_1, \dots, \rho_n$ denote the species mass per unit volume. Considering the state variable $\zeta = (T, v, y_1, \dots, y_n)$ leads to Gibbsian thermodynamics with singular entropy Hessian matrices whereas using the state variable $(T, \rho_1, \dots, \rho_n)$ leads to nonhomogeneous thermodynamic functions and nonsingular entropy Hessian matrices. Both formalisms are useful—depending on the context—and have been investigated in the literature generally for perfect gas mixtures [4, 5, 6, 7, 13, 16]. We establish the mathematical equivalence between these thermodynamic formalisms under proper transformation rules. In comparison with other fluid thermodynamic studies, the thermodynamic functions are not defined for all states because of real gas effects and thermodynamic instabilities at low temperature and high pressure [17]. We also specify the compatibility with perfect gases at low density and give a complete mathematical description of both Gibbsian and non Gibbsian formalisms,

We then present the mathematical construction of thermodynamics from an equation of state. Such a procedure is often used to model supercritical fluids starting typically from the Soave-Redlich-Kwong or the Peng-Robinson equation of state [17, 18, 19, 20, 21, 22]. We investigate when an equation of state may define a Gibbsian thermodynamics compatible at low density with that of perfect gas mixtures under natural structural assumptions on the pressure law. The structural assumptions are notably 0-homogeneity of the pressure $p(\zeta)$ with respect to $(v, y_1, \dots, y_n)$ as well as a quadratic estimate of $p - p^{\mathrm{PG}}$

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*Corresponding author. E-mail: vincent.giovangigli@polytechnique.fr at low density where p^{PG} denotes the perfect gas pressure. We first identify the energy and entropy per unit mass and next investigate necessary and sufficient conditions. These conditions are essentially bounds on $p - p^{\mathrm{PG}}$ insuring that entropy has the required concavity properties insuring thermodynamic stability. Among the stability conditions, chemical thermodynamic stability may indeed decrease the domain of validity of the resulting thermodynamics because of possible unstable states. We further give mathematically equivalent formulations of stability conditions involving matrices which behave more smoothly for vanishing mass fractions than entropy Hessian matrices and allow to investigate thermodynamic stability for all mixtures. To the Authors' knowledge, it is the first time that such a construction of a thermodynamics from an equation of state is analyzed mathematically.

We next specify the mathematical assumptions concerning the nonideal chemical production rates deduced from statistical physics [23, 24, 25]. These rates are compatible with the symmetric forms of rates of progress derived from the kinetic theory of dilute reactive gases [7, 26]. We establish that entropy production due to chemical reactions is nonnegative and investigate chemical equilibrium states in atom conservation manifolds. Assuming that thermodynamic stability holds, equilibrium states are obtained by a minimization technique and detailed balance is obtained at equilibrium as for ideal mixtures [4, 7]. We further discuss inconsistent chemical production rates often used to model high pressure reactions.

We then specifically investigate the Soave-Redlich-Kwong equation of state and discuss the corresponding Gibbsian thermodynamics compatible with that of perfect gases. This equation of state gives accurate results over the range of pressures, temperatures and mixture states of interest for supercritical combustion [17, 20, 22]. All the required conditions to define a thermodynamics are easily established except for thermodynamic stability. Thermal and mechanical thermodynamic stability are first discussed for such a cubic equation of state and generally hold at supercritical conditions which are precisely defined mathematically. On the other hand, chemical thermodynamic stability generally not holds at low temperature and high pressure. The domain of validity of the resulting thermodynamics may thus have a complex shape which depends on the mixture under consideration and must be investigated numerically. To the best of Authors' knowledge, it is also the first time that supercritical multicomponent thermodynamics are investigated mathematically.

In order to illustrate the applicability of the resulting supercritical thermodynamics and nonideal chemical kinetics, we investigate H_2-O_2-N_2 mixtures. At sufficiently low temperature and high pressure, fresh mixtures of H_2-O_2-N_2 may be chemically unstable. These mixtures may split between a hydrogen-rich gaseous-like phase and a hydrogen-poor liquid-like phase in agreement with experimental results [17, 27, 28]. We also present the structure of a typical transcritical H_2-N_2-O_2 flames with complex kinetics and nonideal transport. We finally analyze the rôle of nonidealities in such a such a transcritical H_2-N_2-O_2 flame, by studying the repulsive and attractive contributions to pressure, the species activity coefficients and the nonideal high pressure chemical production rates.

Thermodynamics in terms of intensive variables is investigated in Section 2. The construction of a thermodynamics starting from a pressure law is discussed in Section 3 and chemical production rates are analyzed in Section 4. The Soave-Redlich-Kwong equation of state is investigated in Section 5. Finally, H_2-N_2-O_2 mixtures as well as transcritical H_2-N_2-O_2 flames are considered in Section 6.

2 Thermodynamics with intensive variables

We investigate in this section the mathematical structure of multicomponent fluid thermodynamics compatible at low density with that of perfect gases. Since we are interested in spatially non homogeneous fluids, we only investigate thermodynamics in terms of intensive variables. Both Gibbsian and non Gibbsian formalisms, which are useful for applications and can be found in the literature [4, 5, 6, 7, 16], are considered.

The origin of these multiple formalisms is that, in nonhomogeneous flows, extensivity is associated with volume integration and state variables can only be intensive variables or densities, either volumetric, molar, or per unit mass [7]. As a consequence, any set of $n+2$ intensive state variables—which are associated with independent extensive state variables after volume integration in homogeneous flows—are now a priori *dependent* variables. Considering then the a priori dependent mass fractions as formally independent lead to homogeneous Gibbsian thermodynamics investigated in the Section 2.1. On the other hand, eliminating one of these intensive state variables leads to $n+1$ independent intensive state variables and to negative definite entropy Hessians as investigated in Section 2.2.

2.1 Gibbsian thermodynamics

We investigate in Section 2.1.1 a Gibbsian thermodynamics for multicomponent fluids in terms of the natural variable $\zeta = (T, v, y_1, \dots, y_n)^t$ and the thermodynamic variable $\xi = (e, v, y_1, \dots, y_n)^t$. We next address in Section 2.1.2 the case of the pressure variable $\pi = (T, p, y_1, \dots, y_n)^t$ which is useful in constant pressure frameworks. We finally address the situation of perfect gas mixtures and discuss molar properties in Sections 2.1.3 and 2.1.4 respectively.

2.1.1 The natural and thermodynamic variables

We investigate thermodynamics in terms of the variable $\zeta = (T, v, y_1, \dots, y_n)^t$ where T denotes the absolute temperature, v the volume per unit mass, $y_1, \dots, y_n$ the species mass fractions, $n \geqslant 1$ the number of species and $\mathfrak{S}$ the species indexing set $\mathfrak{S} = \{1, \dots, n\}$. The thermodynamic model is specified as $e(\zeta)$, $p(\zeta)$, and $s(\zeta)$, where e denotes the energy per unit mass, p the pressure, and s the entropy per unit mass, In the discussion, we also use the thermodynamic variable $\xi = (e, v, y_1, \dots, y_n)^t$ and the pressure based variable $\pi = (T, p, y_1, \dots, y_n)^t$. In order to avoid notational complexities, we often commit the traditional abuse of notation of denoting by the same symbol a given quantity as function of different state variables. The superscript $^{\mathrm{PG}}$ is also associated with thermodynamic properties of perfect gas mixtures.

We denote by ∂ the derivation operator with respect to the variable $\xi = (e, v, y_1, \dots, y_n)^t$, by $\widetilde{\partial}$ the derivation operator with respect to the variable $\zeta = (T, v, y_1, \dots, y_n)^t$, and by d the total differential operator. For any $\lambda > 0$, we define for convenience $\xi_\lambda = (\lambda e, \lambda v, \lambda y_1, \dots, \lambda y_n)^t$ and $\zeta_\lambda = (T, \lambda v, \lambda y_1, \dots, \lambda y_n)^t$. We denote by y the mass fraction vector $y = (y_1, \dots, y_n)^t$, u the vector with unity components $u = (1, \dots, 1)^t$, $\langle , \rangle$ the Euclidean scalar product, and define $\Sigma = \{y \in (0, \infty)^n;\ \langle y, u \rangle = 1\}$. Physically, the mass fraction vector is such that $y \in \Sigma$. However, as usual in the modeling of reactive flows, we assume that the mass fractions are independent and the mass constraint $\langle y, u \rangle = 1$ then results from the governing equations and boundary conditions [7, 16]. We denote by $\varkappa \in \mathbb{N}$, $\varkappa \geqslant 2$, the regularity of thermodynamics functions and by f^e, f^v, $\mathsf{f}^1, \dots, \mathsf{f}^n$ the natural basis vector of $\mathbb{R}^{2+n}$.

Definition 2.1. *Let e, p, and s, be $C^\varkappa$ functions of the natural variable $\zeta = (T, v, y_1, \dots, y_n)^t$, defined on an open set $\mathcal{O}_\zeta \subset (0, \infty)^{2+n}$. These functions are said to define a thermodynamics if they satisfy Properties* (T_1-T_4).

(T_1) *The maps $\zeta \to \xi$ and $\zeta \to \pi$ are $C^\varkappa$ diffeomorphisms from the open set $\mathcal{O}_\zeta \subset (0, +\infty)^{2+n}$ onto open sets $\mathcal{O}_\xi$ and $\mathcal{O}_\pi$ respectively. For any $(\lambda, \zeta) \in (0, \infty) \times \mathcal{O}_\zeta$, we have $\zeta_\lambda \in \mathcal{O}_\zeta$, and $e(\zeta_\lambda) = \lambda e(\zeta)$, $p(\zeta_\lambda) = p(\zeta)$, $s(\zeta_\lambda) = \lambda s(\zeta)$.*

(T_2) *For any $\zeta \in \mathcal{O}_\zeta$, defining $g_k = \widetilde{\partial}_{y_k} e - T \widetilde{\partial}_{y_k} s$, $k \in \mathfrak{S}$, we have Gibbs' relation*

$$T \mathrm{d}s = \mathrm{d}e + p \mathrm{d}v - \sum_{k \in \mathfrak{S}} g_k \mathrm{d}y_k. \tag{2.1}$$

(T_3) *For any $\zeta \in \mathcal{O}_\zeta$, the Hessian matrix $\partial^2_{\xi\xi} s$ is negative semi-definite with nullspace $\mathbb{R}\xi$.*

(T_4) *For any $(T, y_1 \dots, y_n)^t \in (0, \infty)^{1+n}$ there exists v_{m} such that $(T, v, y_1 \dots, y_n)^t \in \mathcal{O}_\zeta$ for $v > v_{\mathrm{m}}$ and*

$$\lim_{v \to \infty} (e - e^{\mathrm{PG}}) = 0, \qquad \lim_{v \to \infty} v(p - p^{\mathrm{PG}}) = 0, \qquad \lim_{v \to \infty} (s - s^{\mathrm{PG}}) = 0. \tag{2.2}$$

Property (T_1) is associated with the natural changes of variables traditionally encountered in thermodynamics as well as with homogeneity properties. Temperature is naturally assumed to be positive in the model since $\mathcal{O}_\zeta \subset (0, +\infty)^{2+n}$ but not the pressure which may be negative for fluids [29]. Property (T_2) is Gibbs' relation for mixtures with a simplified definition of the species Gibbs functions g_k, $k \in \mathfrak{S}$, and Property (T_3) is the natural thermodynamic stability condition. From the second principle of thermodynamics, the evolution of an isolated system indeed tends to maximize its entropy. The entropy of a stable isolated system should thus be a concave function of its volume, composition variables, and internal energy. Whenever it is not the case, the system loses its homogeneity and splits between two or more phases in order to reach equilibrium. In particular, the open set $\mathcal{O}_\zeta$ may have a complex shape because of real gas effects and thermodynamic instabilities at high pressure and low temparture. Property (T_4) is finally the compatibility condition with perfect gases since for large v we must recover the perfect gas regime. Note that the multiplication by v is required for the pressure since as $v \to \infty$ both p and p^{PG} goes to zero. Moreover, the compatibility with perfect gases *must naturally be written in term of densities.* It is mathematically absurd to formulate such compatibility it in terms of extensive absolute quantities with a volume going to infinity, since then all thermodynamic extensive functions are exploding.

Since $\zeta \to \xi$ and $\zeta \to \pi$ are diffeomorphisms, we may equally define the thermodynamics with $T(\xi)$, $p(\xi)$ and $s(\xi)$ such that (T_1-T_4) are satisfied, or with $e(\pi)$, $v(\pi)$, and $s(\pi)$, such that (T_1-T_4) hold. These three variables are practical and useful since ξ is associated with Gibbs' relation, ζ to the natural form for equations of state or for compatibility conditions with perfect gases and π is useful in constant pressure frameworks. In the following proposition, we establish that homogeneity properties may equivalently be written in terms of the thermodynamic variable ξ and we next obtain an expression of the mixture Gibbs function per unit mass g.

Lemma 2.2. *Assume that the map $\zeta \to \xi$ is a $C^{\varkappa}$ diffeomorphism from the open set $\mathcal{O}_\zeta$ onto an open set $\mathcal{O}_\xi$. Then the following properties are equivalent*

(i) $\forall(\lambda, \zeta) \in (0,\infty)\times\mathcal{O}_\zeta,\ \ \zeta_\lambda \in \mathcal{O}_\zeta,\ \ e(\zeta_\lambda) = \lambda e(\zeta),\ \ p(\zeta_\lambda) = p(\zeta),\ \ s(\zeta_\lambda) = \lambda s(\zeta).$

(ii) $\forall(\lambda, \xi) \in (0,\infty)\times\mathcal{O}_\xi,\ \ \xi_\lambda \in \mathcal{O}_\xi,\ \ T(\xi_\lambda) = T(\xi),\ \ p(\xi_\lambda) = p(\xi),\ \ s(\xi_\lambda) = \lambda s(\xi).$

Corollary 2.3. *Assuming* (T_1-T_2) *and defining the mixture Gibbs function by $g = e + pv - Ts$ we have $g = \sum_{k\in\mathfrak{S}} y_k g_k$.*

Proof. Assume that (i) holds and denote by $\sigma : \mathcal{O}_\zeta \to \mathcal{O}_\xi$ the diffeomorphism such that $\xi = \sigma(\zeta)$. In more precise terms we have to establish that when $(\lambda, \xi) \in (0,\infty)\times\mathcal{O}_\xi$, then $\xi_\lambda \in \mathcal{O}_\xi$ and $T\circ\sigma^{-1}(\xi_\lambda) = T\circ\sigma^{-1}(\xi)$, $p\circ\sigma^{-1}(\xi_\lambda) = p\circ\sigma^{-1}(\xi)$, and $s\circ\sigma^{-1}(\xi_\lambda) = \lambda s\circ\sigma^{-1}(\xi)$. Consider thus $(\lambda, \xi) \in (0,\infty)\times\mathcal{O}_\xi$ and let $\zeta = \sigma^{-1}(\xi) \in \mathcal{O}_\zeta$. We know from (i) that $\zeta_\lambda \in \mathcal{O}_\zeta$ and that e is 1-homogeneous, so that $e(\zeta_\lambda) = \lambda e(\zeta)$. Therefore, we deduce that $\sigma(\zeta_\lambda) = (e(\zeta_\lambda), \lambda v, \lambda y_1, \dots, \lambda y_n)^t$ is simply $\sigma(\zeta_\lambda) = \xi_\lambda$ so that $\zeta_\lambda = \sigma^{-1}(\xi_\lambda)$. This establishes that $\xi_\lambda \in \mathcal{O}_\xi$ since σ is a diffeomorphism from $\mathcal{O}_\zeta$ onto $\mathcal{O}_\xi$. In addition, since $T(\zeta_\lambda) = T(\zeta)$, $p(\zeta_\lambda) = p(\zeta)$, and $s(\zeta_\lambda) = \lambda s(\zeta)$, we directly obtain that $T\circ\sigma^{-1}(\xi_\lambda) = T\circ\sigma^{-1}(\xi)$, $p\circ\sigma^{-1}(\xi_\lambda) = p\circ\sigma^{-1}(\xi)$, and $s\circ\sigma^{-1}(\xi_\lambda) = \lambda s\circ\sigma^{-1}(\xi)$ and (ii) is established. The proof that (ii) implies (i) is similar and omitted and Lemma 2.2 is established. Corollary 2.3 is then a consequence of Gibbs' relation (2.1) and Euler equation for homogeneous functionals since s is 1-homogeneous in ξ. ☐

We now establish a few technical statements in order to recast (T_1-T_4) into a more practical form involving the single variable $\zeta = (T, v, y_1, \dots, y_n)^t$. In the following proposition, we establish an equivalent formulation of (T_3) which is very useful in practice.

Proposition 2.4. *Assume that* (T_1-T_2) *are satisfied and denote by Λ the matrix of size n with coefficients $\Lambda_{kl} = \widetilde{\partial}_{y_k} g_l/T = \widetilde{\partial}_{y_l} g_k/T$. Then, for any $\zeta \in \mathcal{O}_\zeta$, the following statements are equivalent :*

(i) $\partial^2_{\xi\xi} s$ *is negative semi-definite with nullspace* $N(\partial^2_{\xi\xi} s) = \mathbb{R}\xi$.

(ii) $\widetilde{\partial}_T e > 0$ *and Λ is positive definite.*

Moreover, denoting by y the mass fraction vector $y = (y_1, \dots, y_n)^t$, we have the relations

$$\Lambda y = -\frac{v}{T}(\widetilde{\partial}_v g_1, \dots, \widetilde{\partial}_v g_n)^t, \tag{2.3}$$

$$\langle \Lambda y, y\rangle = -\frac{v^2}{T}\widetilde{\partial}_v p. \tag{2.4}$$

Proof. We first derive some useful differential relations. From Gibbs' relation (2.1) we have

$$\partial_e s = \frac{1}{T}, \qquad \partial_v s = \frac{p}{T}, \qquad \partial_{y_k} s = -\frac{g_k}{T},$$

and this implies the compatibility relations

$$\partial_e\Big(\frac{p}{T}\Big) = \partial_v\Big(\frac{1}{T}\Big), \qquad \partial_e\Big(\frac{-g_k}{T}\Big) = \partial_{y_k}\Big(\frac{1}{T}\Big), \qquad \partial_v\Big(\frac{-g_k}{T}\Big) = \partial_{y_k}\Big(\frac{p}{T}\Big). \tag{2.5}$$

Similarly, from Gibbs' relation written in term of the variables $(T, v, y_1, \dots, y_n)$ we obtain that

$$\widetilde{\partial}_T s = \frac{\widetilde{\partial}_T e}{T}, \qquad \widetilde{\partial}_v s = \frac{\widetilde{\partial}_v e + p}{T}, \qquad \widetilde{\partial}_{y_k} s = \frac{\widetilde{\partial}_{y_k} e - g_k}{T},$$

and this implies after some algebra the compatibility relations

$$\widetilde{\partial}_T\big(\frac{p}{T}\big) = \frac{\widetilde{\partial}_v e}{T^2}, \qquad \widetilde{\partial}_T\big(\frac{-g_k}{T}\big) = \frac{\widetilde{\partial}_{y_k} e}{T^2}, \qquad -\widetilde{\partial}_v g_k = \widetilde{\partial}_{y_k} p. \tag{2.6}$$

The matrix Λ is symmetric since $\widetilde{\partial}_{y_l} g_k = -T\widetilde{\partial}^2_{y_k y_l} s$ and in order to establish (2.3) and (2.4), we note that $g_k(\zeta)$ is 0-homogeneous in $(v, y_1, \dots, y_n)$ since $g_k = T\widetilde{\partial}_{y_k} s$, T is 0-homogeneous, and s is 1-homogeneous. This implies the relation $\sum_{l\in\mathfrak{S}} y_l \widetilde{\partial}_{y_l} g_k = -v\widetilde{\partial}_v g_k$ and thus $\sum_{k\in\mathfrak{S}} \Lambda_{kl} y_l = -v\widetilde{\partial}_v g_k/T$ and (2.3) is established. Upon multiplying by y_k and summing over k we next obtain that $T\langle \Lambda y, y\rangle = -v\sum_{k\in\mathfrak{S}} y_k \widetilde{\partial}_v g_k$. However, from the compatibility relation (2.6) we get $\widetilde{\partial}_v g_k = -\widetilde{\partial}_{y_k} p$ and thanks to the 0-homogeneity of $p(\zeta)$ with respect to $(v, y_1, \dots, y_n)$ we conclude that $\sum_{k\in\mathfrak{S}} y_k \widetilde{\partial}_v g_k = -\sum_{k\in\mathfrak{S}} y_k \widetilde{\partial}_{y_k} p = v\widetilde{\partial}_v p$ and (2.4) is established.

We next evaluate the coefficients of the entropy Hessian matrix $\partial^2_{\xi\xi} s$. From $\partial_e s = 1/T$ we obtain that $T^2\partial^2_{ee} s = -\partial_e T$ and $T^2\partial^2_{ev} s = -\partial_v T$. Moreover, for any function χ we have the differential relations

$$\partial_e \chi = \widetilde{\partial}_T \chi\, \partial_e T, \qquad \widetilde{\partial}_T \chi = \partial_e \chi\, \widetilde{\partial}_T e, \tag{2.7}$$

$$\partial_v \chi = \widetilde{\partial}_v \chi + \widetilde{\partial}_T \chi\, \partial_v T, \qquad \widetilde{\partial}_v \chi = \partial_v \chi + \partial_e \chi\, \widetilde{\partial}_v e, \tag{2.8}$$

$$\partial_{y_k} \chi = \widetilde{\partial}_{y_k} \chi + \widetilde{\partial}_T \chi\, \partial_{y_k} T, \qquad \widetilde{\partial}_{y_k} \chi = \partial_{y_k} \chi + \partial_e \chi\, \widetilde{\partial}_{y_k} e, \tag{2.9}$$

and upon letting $\chi = T$ in (2.8) we obtain that $\partial_v T = -(\partial_e T)\widetilde{\partial}_v e$ and finally $T^2\partial^2_{ev} s = (\partial_e T)\widetilde{\partial}_v e$. Similarly, we have $T^2\partial^2_{ey_k} s = -\partial_{y_k} T$, and letting $\chi = T$ in (2.9) we obtain $\partial_{y_k} T = -(\partial_e T)\widetilde{\partial}_{y_k} e$ so that $T^2\partial^2_{ey_k} s = (\partial_e T)\widetilde{\partial}_{y_k} e$. Furthermore, we have $\partial^2_{vv} s = \partial_v\big(\frac{p}{T}\big)$, and thanks to (2.8), we have $\partial_v\big(\frac{p}{T}\big) = \widetilde{\partial}_v\big(\frac{p}{T}\big) + \widetilde{\partial}_T\big(\frac{p}{T}\big)\partial_v T$. From the compatibility conditions (2.6) and $\partial_v T = -(\partial_e T)\widetilde{\partial}_v e$, we thus obtain

$$\partial^2_{vv} s = \widetilde{\partial}_v\big(\frac{p}{T}\big) - (\partial_e T)\frac{(\widetilde{\partial}_v e)^2}{T^2}.$$

Similarly, $\partial^2_{vy_k} s = \partial_{y_k}\big(\frac{p}{T}\big)$, and thanks to (2.9) we have $\partial_{y_k}\big(\frac{p}{T}\big) = \widetilde{\partial}_{y_k}\big(\frac{p}{T}\big) + \widetilde{\partial}_T\big(\frac{p}{T}\big)\partial_{y_k} T$. From the compatibility conditions (2.6) and $\partial_{y_k} T = -(\partial_e T)\widetilde{\partial}_{y_k} e$ and we get

$$\partial^2_{vy_k} s = \widetilde{\partial}_v\big(\frac{-g_k}{T}\big) - (\partial_e T)\frac{(\widetilde{\partial}_v e)(\widetilde{\partial}_{y_k} e)}{T^2}.$$

Since $\partial^2_{y_k y_l} s = \partial_{y_l}\big(\frac{-g_k}{T}\big)$ and letting $\chi = \frac{-g_k}{T}$ in (2.9) we also obtain that

$$\partial^2_{y_k y_l} s = \widetilde{\partial}_{y_l}\big(\frac{-g_k}{T}\big) - (\partial_e T)\frac{(\widetilde{\partial}_{y_k} e)(\widetilde{\partial}_{y_l} e)}{T^2}.$$

Defining

$$\widehat{\mathsf{f}}^e = \Big(1, -\widetilde{\partial}_v e, -\widetilde{\partial}_{y_1} e, \dots, -\widetilde{\partial}_{y_n} e\Big)^t, \tag{2.10}$$

we have established that for any $\mathsf{x} = (\mathsf{x}_e, \mathsf{x}_v, \mathsf{x}_1, \dots, \mathsf{x}_n)^t \in \mathbb{R}^{2+n}$

$$\big\langle(\partial^2_{\xi\xi} s)\mathsf{x}, \mathsf{x}\big\rangle = -\frac{\partial_e T}{T^2}\,\langle \widehat{\mathsf{f}}^e, \mathsf{x}\rangle^2 + \frac{\widetilde{\partial}_v p}{T}\,\mathsf{x}_v^2 - 2\sum_{k\in\mathfrak{S}} \widetilde{\partial}_v\big(\frac{g_k}{T}\big)\,\mathsf{x}_v\mathsf{x}_k - \sum_{k,l\in\mathfrak{S}} \widetilde{\partial}_{y_l}\big(\frac{g_k}{T}\big)\,\mathsf{x}_k\mathsf{x}_l. \tag{2.11}$$

We now establish that (i) implies (ii). Since $\xi = e\mathsf{f}^e + v\mathsf{f}^v + \sum_{i\in\mathfrak{S}} y_i \mathsf{f}^{y_i}$ and f^e are not proportional we deduce that $\big\langle(\partial^2_{\xi\xi} s)\mathsf{f}^e, \mathsf{f}^e\big\rangle < 0$ so that $\partial_e T = -T^2\big\langle(\partial^2_{\xi\xi} s)\mathsf{f}^e, \mathsf{f}^e\big\rangle > 0$, and this implies $\widetilde{\partial}_T e > 0$ since $\partial_e T\ \widetilde{\partial}_T e = 1$. Letting then $\mathsf{f} = \mathsf{f}^v + (\widetilde{\partial}_v e)\mathsf{f}^e$, we have $\langle \widehat{\mathsf{f}}^e, \mathsf{f}\rangle = 0$, and $\mathsf{f} = \mathsf{f}^v + (\widetilde{\partial}_v e)\mathsf{f}^e$ and ξ cannot be proportional since the mass fractions are positive. Therefore $\widetilde{\partial}_v p/T = \big\langle(\partial^2_{\xi\xi} s)\mathsf{f}, \mathsf{f}\big\rangle < 0$ and we have established that $\widetilde{\partial}_v p < 0$. Similarly, assume that $\mathsf{x}_1, \dots, \mathsf{x}_n$ are arbitrary with $(\mathsf{x}_1, \dots, \mathsf{x}_n) \neq (0, \dots, 0)$, consider $\mathsf{f} = \sum_{i\in\mathfrak{S}} \mathsf{x}_i \mathsf{f}^i + \mathsf{x}_e \mathsf{f}^e$ and select x_e such that $\langle \widehat{\mathsf{f}}^e, \mathsf{f}\rangle = 0$, that is, $\mathsf{x}_e = \sum_{i\in\mathfrak{S}} \mathsf{x}_i \widetilde{\partial}_{y_i} e$. Then f and ξ cannot be proportional since the volume per unit mass is positive, so that $\big\langle(\partial^2_{\xi\xi} s)\mathsf{f}, \mathsf{f}\big\rangle < 0$. This shows that $\sum_{k,l\in\mathfrak{S}} \widetilde{\partial}_{y_l}\big(\frac{g_k}{T}\big)\,\mathsf{x}_k\mathsf{x}_l = -\big\langle(\partial^2_{\xi\xi} s)\mathsf{f}, \mathsf{f}\big\rangle > 0$ so that the matrix Λ is positive definite.

We now establish that (*ii*) implies (*i*). From the identity (2.4), we first obtain that $\widetilde{\partial}_v p < 0$. We may thus introduce

$$\widehat{\mathsf{f}}^v = \Big(0, 1, -\frac{\widetilde{\partial}_v g_1}{\widetilde{\partial}_v p}, \ldots, -\frac{\widetilde{\partial}_v g_n}{\widetilde{\partial}_v p}\Big)^t, \tag{2.12}$$

and using (2.11) we easily obtain that for $\mathsf{x} = (\mathsf{x}_e, \mathsf{x}_v, \mathsf{x}_1, \ldots, \mathsf{x}_n)^t$

$$\big\langle (\partial^2_{\xi\xi} s)\mathsf{x}, \mathsf{x} \big\rangle = -\partial_e T \frac{\langle \widehat{\mathsf{f}}^e, \mathsf{x}\rangle^2}{T^2} + \widetilde{\partial}_v p \frac{\langle \widehat{\mathsf{f}}^v, \mathsf{x}\rangle^2}{T} - \sum_{k,l \in \mathfrak{S}} \Big(\widetilde{\partial}_{y_l}\big(\frac{g_k}{T}\big) + \frac{\widetilde{\partial}_v g_k \, \widetilde{\partial}_v g_l}{T \widetilde{\partial}_v p} \Big) \mathsf{x}_k \mathsf{x}_l. \tag{2.13}$$

Thanks to (2.3) and (2.4), this identity is rewritten in the form

$$\big\langle (\partial^2_{\xi\xi} s)\mathsf{x}, \mathsf{x} \big\rangle = -\partial_e T \frac{\langle \widehat{\mathsf{f}}^e, \mathsf{x}\rangle^2}{T^2} + \widetilde{\partial}_v p \frac{\langle \widehat{\mathsf{f}}^v, \mathsf{x}\rangle^2}{T} - \Big\langle \big(\Lambda - \frac{\Lambda y \otimes \Lambda y}{\langle \Lambda y, y\rangle}\big) \mathsf{x}_y, \mathsf{x}_y \Big\rangle, \tag{2.14}$$

where $\mathsf{x}_y = (\mathsf{x}_1, \ldots, \mathsf{x}_n)^t$. Since Λ is positive definite, we first note that $\Lambda - \frac{\Lambda y \otimes \Lambda y}{\langle \Lambda y, y\rangle}$ is positive semi-definite with nullspace $\mathbb{R}y$ since for any $\mathsf{x}_y = (\mathsf{x}_1, \ldots, \mathsf{x}_n)^t$ we have

$$\Big\langle \big(\Lambda - \frac{\Lambda y \otimes \Lambda y}{\langle \Lambda y, y\rangle}\big) \mathsf{x}_y, \mathsf{x}_y \Big\rangle = \Big\langle \Lambda \big(\mathsf{x}_y - \tfrac{\langle \Lambda \mathsf{x}_y, y\rangle}{\langle \Lambda y, y\rangle} y \big), \ \big(\mathsf{x}_y - \tfrac{\langle \Lambda \mathsf{x}_y, y\rangle}{\langle \Lambda y, y\rangle} y \big) \Big\rangle.$$

Since $\widetilde{\partial}_T e > 0$, $\widetilde{\partial}_v p < 0$, and $\Lambda - \frac{\Lambda y \otimes \Lambda y}{\langle \Lambda y, y\rangle}$ is positive semi-definite with nullspace $\mathbb{R}y$, we deduce from (2.14) that $\partial^2_{\xi\xi} s$ is negative semi-definite. Moreover, any vector x in the nullspace of $\partial^2_{\xi\xi} s$ is such that $\langle \widehat{\mathsf{f}}^e, \mathsf{x}\rangle = 0$, $\langle \widehat{\mathsf{f}}^v, \mathsf{x}\rangle = 0$, $(\Lambda - \frac{\Lambda y \otimes \Lambda y}{\langle \Lambda y, y\rangle})\mathsf{x}_y = 0$. Since $\mathsf{x}_y = (\mathsf{x}_1, \ldots, \mathsf{x}_n)^t$ is in the nullspace of $\Lambda - \frac{\Lambda y \otimes \Lambda y}{\langle \Lambda y, y\rangle}$ we first deduce that $\mathsf{x}_y = \lambda y$ for some $\lambda \in \mathbb{R}$. From the expression (2.12) of $\widehat{\mathsf{f}}^v$, we first obtain that $\mathsf{x}_v = \sum_{i \in \mathfrak{S}} \mathsf{x}_i \widetilde{\partial}_v g_i / \widetilde{\partial}_v p$ so that $\mathsf{x}_v = \lambda \sum_{i \in \mathfrak{S}} y_i \widetilde{\partial}_v g_i / \widetilde{\partial}_v p$. Using then the compatibility relations (2.6) we have $-\widetilde{\partial}_v g_i = \widetilde{\partial}_{y_i} p$ so that $\mathsf{x}_v = -\lambda \sum_{i \in \mathfrak{S}} y_i \widetilde{\partial}_{y_i} p / \widetilde{\partial}_v p$ and finally $\mathsf{x}_v = \lambda v$ thanks to the 0-homogeneity of p. Moreover, from the expression (2.10) of $\widehat{\mathsf{f}}^e$, we now obtain that $\mathsf{x}_e = \mathsf{x}_v \widetilde{\partial}_v e + \sum_{i \in \mathfrak{S}} \mathsf{x}_i \widetilde{\partial}_{y_i} e_i$ so that $\mathsf{x}_e = \lambda v \widetilde{\partial}_v e + \lambda \sum_{i \in \mathfrak{S}} y_i \widetilde{\partial}_{y_i} e_i$ and $\mathsf{x}_e = \lambda e$ thanks to the 1-homogeneity of e. We thus conclude that x is proportional to ξ so that $N(\partial^2_{\xi\xi} s) = \mathbb{R}\xi$ and the proof is complete. □

From a practical point of view we now deduce from Proposition 2.4 that $(\mathsf{T}_1$-$\mathsf{T}_3)$ are globally equivalent to a simplified set of assumptions involving only the variable $\zeta = (T, v, y_1, \ldots, y_n)^t$.

Proposition 2.5. *Properties* $(\mathsf{T}_1$-$\mathsf{T}_3)$ *are globally equivalent to the simplified Properties* $(\mathsf{T}'_1$-$\mathsf{T}'_3)$.

(T'_1) $\forall(\lambda, \zeta) \in (0, \infty) \times \mathcal{O}_\zeta$, $\zeta_\lambda \in \mathcal{O}_\zeta$, $e(\zeta_\lambda) = \lambda e(\zeta)$, $p(\zeta_\lambda) = p(\zeta)$, *and* $s(\zeta_\lambda) = \lambda s(\zeta)$.

(T'_2) *For any* $\zeta \in \mathcal{O}_\zeta$, *we have* $T \widetilde{\partial}_T s = \widetilde{\partial}_T e$ *and* $T \widetilde{\partial}_v s = \widetilde{\partial}_v e + p$.

(T'_3) *For any* $\zeta \in \mathcal{O}_\zeta$, $\widetilde{\partial}_T e > 0$ *and the matrix* Λ *is positive definite.*

Proof. From Proposition 2.4, we deduce that $(\mathsf{T}_1$-$\mathsf{T}_3)$ implies $(\mathsf{T}'_1$-$\mathsf{T}'_3)$. Conversely, from (T'_3) and Equation (2.4) we obtain that $\widetilde{\partial}_T e > 0$ and $\widetilde{\partial}_v p < 0$ so that $\zeta \to \xi$ and $\zeta \to \pi$ are one to one. From the inverse function theorem, these functions are $C^{\varkappa}$ diffeomorphisms onto open sets $\mathcal{O}_\xi$ and $\mathcal{O}_\pi$ and (T_1) is established. On the other hand, (T_2) is a direct consequence of (T'_2) thanks to the definition $g_k = \widetilde{\partial}_{y_k} e - T \widetilde{\partial}_{y_k} s$, $k \in \mathfrak{S}$. Finally, (T_3) is also a consequence of (T'_3) thanks from Proposition 2.4 and the proof is complete. □

Remark 2.6. *As will be seen in Section 5, it is sometimes the case that the thermodynamic functions* e, p, *and* s, *are defined over an open set* $\mathcal{O}'_\zeta$ *such that* $(\mathsf{T}'_1$-$\mathsf{T}'_2)$ *and* (T_4) *hold. It is then necessary to consider an open subset* $\mathcal{O}_\zeta \subset \mathcal{O}'_\zeta$ *such that* (T'_3) *holds in order to obtain a thermodynamic in the sense of Definition 2.1 such that* $(\mathsf{T}_1$-$\mathsf{T}_4)$ *hold.*

2.1.2 The pressure variable

We discuss in this section how thermodynamic functions may be expressed in terms of the pressure variable $\pi = (T, p, y_1, \dots, y_n)^t$ where the mass fractions are independent. We denote by $\widehat{\partial}$ the derivation operator with respect to the variable $\pi = (T, p, y_1, \dots, y_n)^t$ and for any $\lambda > 0$ we define for convenience $\pi_\lambda = (T, p, \lambda y_1, \dots, \lambda y_n)^t$.

Lemma 2.7. *Assume that the map $\zeta \to \pi$ is a $C^\varkappa$ diffeomorphism from the open set $\mathcal{O}_\zeta$ onto an open set $\mathcal{O}_\pi$. Then the following properties are equivalent*

(i) $\forall(\lambda, \zeta) \in (0,\infty)\times\mathcal{O}_\zeta,\ \ \zeta_\lambda \in \mathcal{O}_\zeta,\ \ e(\zeta_\lambda) = \lambda e(\zeta),\ \ p(\zeta_\lambda) = p(\zeta),\ \ s(\zeta_\lambda) = \lambda s(\zeta).$

(ii) $\forall(\lambda, \pi) \in (0,\infty)\times\mathcal{O}_\pi,\ \ \pi_\lambda \in \mathcal{O}_\pi,\ \ e(\pi_\lambda) = \lambda e(\pi),\ \ v(\pi_\lambda) = \lambda v(\pi),\ \ s(\pi_\lambda) = \lambda s(\pi).$

Proof. The proof is similar to that of Lemma 2.2 and is omitted. ☐

Proposition 2.8. *Assume that $(\mathsf{T}_1\text{-}\mathsf{T}_2)$ are satisfied and define $g = e + pv - Ts$. Then we have the differential relations $g_k = \widehat{\partial}_{y_k} g$, $k \in \mathfrak{S}$, and*

$$\mathrm{d}g = -s\mathrm{d}T + v\mathrm{d}p + \sum_{k\in\mathfrak{S}} g_k \mathrm{d}y_k. \tag{2.15}$$

Proof. For any smooth function χ we have the following differential relations associated with the variables π and ζ

$$\widehat{\partial}_T\chi = \widetilde{\partial}_T\chi + \widetilde{\partial}_v\chi\, \widehat{\partial}_T v, \qquad \widetilde{\partial}_T\chi = \widehat{\partial}_T\chi + \widehat{\partial}_p\chi\, \widetilde{\partial}_T p, \tag{2.16}$$

$$\widehat{\partial}_p\chi = \widetilde{\partial}_v\chi\, \widehat{\partial}_p v, \qquad \widetilde{\partial}_v\chi = \widehat{\partial}_p\chi\, \widetilde{\partial}_v p, \tag{2.17}$$

$$\widehat{\partial}_{y_k}\chi = \widetilde{\partial}_{y_k}\chi + \widetilde{\partial}_v\chi\, \widehat{\partial}_{y_k} v, \qquad \widetilde{\partial}_{y_k}\chi = \widehat{\partial}_{y_k}\chi + \widehat{\partial}_p\chi\widetilde{\partial}_{y_k} p. \tag{2.18}$$

Letting $g = e + pv - Ts$, we first obtain that $\widehat{\partial}_T g = \widehat{\partial}_T e + p\widehat{\partial}_T v - s - T\widehat{\partial}_T s$ and from (2.16) we obtain the relations $\widehat{\partial}_T s = \widetilde{\partial}_T s + \widetilde{\partial}_v s\, \widehat{\partial}_T v$ and $\widehat{\partial}_T e = \widetilde{\partial}_T e + \widetilde{\partial}_v e\, \widehat{\partial}_T v$. However, Property (T_2) implies Property (T_2'). We thus get that $\widehat{\partial}_T e + p\widehat{\partial}_T v - T\widehat{\partial}_T s = 0$ since the $\widetilde{\partial}_T$ derivative contribution is $\widetilde{\partial}_T e - T\widetilde{\partial}_T s = 0$ from (T_2') and since the terms $(\widetilde{\partial}_v e + p - T\widetilde{\partial}_v s)\widehat{\partial}_T v$ associated with $\widehat{\partial}_T v$ also vanish from (T_2'). We have thus established that $\widehat{\partial}_T g = -s$. Similarly, we have $\widehat{\partial}_p g = \widehat{\partial}_p e + v + p\widehat{\partial}_p v - T\widehat{\partial}_p s$ and from (2.17) the relations $\widehat{\partial}_p e = \widetilde{\partial}_v e\, \widehat{\partial}_p v$ and $\widehat{\partial}_p s = \widetilde{\partial}_v s\, \widehat{\partial}_p v$. Regrouping the $\widehat{\partial}_p v$ factors we get $(\widetilde{\partial}_v e + p - T\widetilde{\partial}_v s)\widehat{\partial}_p v$ which vanishes from (T_2') and we have established that $\widehat{\partial}_p g = v$. Finally, we have $\widehat{\partial}_{y_k} g = \widehat{\partial}_{y_k} e + p\widehat{\partial}_{y_k} v - T\widehat{\partial}_{y_k} s$ and from (2.18) the relations $\widehat{\partial}_{y_k} e = \widetilde{\partial}_{y_k} e + \widetilde{\partial}_v e\, \widehat{\partial}_{y_k} v$ and $\widehat{\partial}_{y_k} s = \widetilde{\partial}_{y_k} s + \widetilde{\partial}_v s\, \widehat{\partial}_{y_k} v$. Regrouping the $\widehat{\partial}_{y_k} v$ factors we get $(\widetilde{\partial}_v e + p - T\widetilde{\partial}_v s)\widehat{\partial}_{y_k} v$ which vanishes thanks to (T_2') and we have established that $\widehat{\partial}_{y_k} g = \widetilde{\partial}_{y_k} e - T\widetilde{\partial}_{y_k} s$ so that $\widehat{\partial}_{y_k} g = g_k$ from (T_2) and (2.15) is established. ☐

Proposition 2.9. *Assume that $(\mathsf{T}_1\text{-}\mathsf{T}_2)$ hold. Then for any $\zeta \in \mathcal{O}_\zeta$, the following statements are equivalent :*

(i) $\partial^2_{\xi\xi} s$ *is negative semi-definite with nullspace* $N(\partial^2_{\xi\xi} s) = \mathbb{R}\xi$.

(ii) $\widetilde{\partial}_T e > 0$, $\widetilde{\partial}_v p < 0$, *and* $\widehat{\partial}^2_{yy} g$ *is positive semidefinite with nullspace* $N(\widehat{\partial}^2_{yy} g) = \mathbb{R}y$.

In this situation, we have the matrix identity

$$\widehat{\partial}^2_{yy} g = T\Big(\Lambda - \frac{\Lambda y\otimes\Lambda y}{\langle\Lambda y, y\rangle}\Big). \tag{2.19}$$

Proof. We first derive useful differential relations. From (2.15) we deduce that

$$\widehat{\partial}_T g = -s, \qquad \widehat{\partial}_p g = v, \qquad \widehat{\partial}_{y_k} g = g_k,$$

and this implies the compatibility relations

$$\widehat{\partial}_T v = -\widehat{\partial}_p s, \qquad \widehat{\partial}_T g_k = -\widehat{\partial}_{y_k} s, \qquad \widehat{\partial}_p g_k = \widehat{\partial}_{y_k} v. \tag{2.20}$$

Assume now that (i) holds. Upon letting $\chi = g_l$ in (2.18) we obtain that $\widehat{\partial}^2_{y_k y_l} g = \widehat{\partial}_{y_k} g_l = \widehat{\partial}_{y_l} g_k$ can be written $\widehat{\partial}_{y_k} g_l = \widetilde{\partial}_{y_k} g_l - \widehat{\partial}_p g_l \widetilde{\partial}_{y_k} p$ so that from (2.6) and (2.17) $\widehat{\partial}_{y_k} g_l = \widetilde{\partial}_{y_k} g_l + \widetilde{\partial}_v g_k \widetilde{\partial}_v g_l \widehat{\partial}_p v$.

This implies the identity (2.19) thanks to $\widetilde{\partial}_v p \; \widehat{\partial}_p v = 1$, (2.3) and (2.4). From (2.19) we then obtain that $\widehat{\partial}_{yy} g$ is positive semi-definite with nullspace $\mathbb{R}y$.

Conversely, assuming that (*ii*) holds, we only have to establish that Λ is positive definite from Proposition 2.4. However, upon letting $\chi = g_l$ in (2.18) and thanks to (2.20) and (2.17) we obtain that $\widehat{\partial}_{y_k} g_l = \widetilde{\partial}_{y_k} g_l + \widehat{\partial}_p g_k \widehat{\partial}_p g_l \widetilde{\partial}_v p$. This implies that $\Lambda_{kl} = (\widehat{\partial}_{y_k y_l} g - \widehat{\partial}_p g_l \widehat{\partial}_p g_k \widetilde{\partial}_v p)/T$. From (*ii*) we thus deduce that Λ is positive semi-definite and if x_y is in the nullspace of Λ, we must have $(\widehat{\partial}_{yy} g)\mathsf{x}_y = 0$ and $\sum_{k\in\mathfrak{S}} (\widehat{\partial}_p g_k)\mathsf{x}_k = 0$. Since the nullspace of $\widehat{\partial}_{yy} g$ is $\mathbb{R}y$, we have $\mathsf{x}_y = \lambda y$ for $\lambda \in \mathbb{R}$ and thus $\lambda \sum_{k\in\mathfrak{S}} y_k \widehat{\partial}_p g_k = 0$. Using then the compatibility relation $\widehat{\partial}_p g_k = \widehat{\partial}_{y_k} v$ and the Euler relation $\sum_{k\in\mathfrak{S}} y_k \widehat{\partial}_{y_k} v = v$, we obtain $\lambda v = 0$ and $\lambda = 0$ so that Λ is positive definite and the proof is complete. ☐

Remark 2.10. *The property* $\widetilde{\partial}_T e > 0$ *is usually the thermodynamic thermal stability condition, the property* $\widetilde{\partial}_v p < 0$ *the thermodynamic mechanical stability condition, and the condition that* $\widehat{\partial}^2_{yy} g$ *is positive semidefinite with nullspace* $N(\widehat{\partial}^2_{yy} g) = \mathbb{R}y$ *is usually termed the thermodynamic chemical stability condition. In particular, the property that* Λ *is positive definite encompasses both the mechanical and chemical stability conditions.*

2.1.3 Ideal gas mixtures

As a typical example, and for completeness, we present in this section the situation of ideal gas mixtures. The corresponding thermodynamic properties are denoted with the superscript ${}^{\rm PG}$. In terms of the state variables $\zeta = (T, v, y_1, \dots, y_n)^t$, the pressure of an ideal gas mixture can be written

$$p^{\rm PG} = \frac{RT}{v} \sum_{k\in\mathfrak{S}} \frac{y_k}{m_k}. \tag{2.21}$$

The energy per unit mass of an ideal gas mixture can be written

$$e^{\rm PG} = \sum_{k\in\mathfrak{S}} y_k e_k^{\rm PG}, \qquad e_k^{\rm PG} = e_k^{\rm st} + \int_{T^{\rm st}}^{T} c_{{\rm v}k}^{\rm PG}(\theta)\, d\theta, \tag{2.22}$$

where $e_k^{\rm PG}$ denotes the internal energy per unit mass of the kth species and $c_{{\rm v}k}^{\rm PG}$ the specific heat per unit mass of the k species. The quantity $e_k^{\rm st}$ is the formation energy of the kth species per unit mass at the standard temperature $T^{\rm st}$. The entropy per unit mass is given by

$$s^{\rm PG} = \sum_{k\in\mathfrak{S}} y_k s_k^{\rm PG}, \qquad s_k^{\rm PG} = s_k^{\rm st} + \int_{T^{\rm st}}^{T} \frac{c_{{\rm v}k}^{\rm PG}(\theta)}{\theta}\, d\theta - \frac{R}{m_k} \log \frac{y_k}{v m_k \gamma^{\rm st}}, \tag{2.23}$$

where $s_k^{\rm st}$ is the formation entropy of the kth species per unit mass at the standard temperature $T^{\rm st}$ and standard pressure $p^{\rm st}$, and $\gamma^{\rm st} = p^{\rm st}/RT$ is the standard concentration. The enthalpy $h^{\rm PG} = e^{\rm PG} + p^{\rm PG}/v$, Gibbs function $g^{\rm PG} = e^{\rm PG} + p^{\rm PG}/v - Ts^{\rm PG}$, and free energy $f^{\rm PG} = e^{\rm PG} - Ts^{\rm PG}$ are then easily evaluated. The perfect gas specific heat and the formation energies and entropies satisfy the following assumptions.

- **(PG)** *The formation energies* $e_i^{\rm st}$, $i \in \mathfrak{S}$, *and entropies* $s_i^{\rm st}$, $i \in \mathfrak{S}$, *are real constants. The species mass per unit mole* m_i, $i \in \mathfrak{S}$, *and the gas constant* R *are positive constants. The species heat per unit mass* $c_{{\rm v}i}^{\rm PG}$, $i \in \mathfrak{S}$, *are* C^∞ *functions over* $[0,\infty)$, *and there exist constants* $\underline{c}_{\rm v}$ *and* $\overline{c}_{\rm v}$ *such that* $0 < \underline{c}_{\rm v} \leqslant c_{{\rm v}i}^{\rm PG} \leqslant \overline{c}_{\rm v}$ *for all* $T \geqslant 0$ *and* $i \in \mathfrak{S}$.

We assume throughout the paper that Property (PG) holds. The extension up to zero temperature of specific heats, energies and enthalpies is commonly used in thermodynamics. The specific heats that are considered remain bounded away from zero since we consider perfect gases governed by Boltzmann statistics [7]. In the following Proposition, we investigate the mathematical properties of ideal gas mixture thermodynamics. Of course (T_4) is trivial in the situation of perfect gas mixtures.

Proposition 2.11. *The energy par unit mass* $e^{\rm PG}$, *the ideal gas mixture pressure* $p^{\rm PG}$, *and the entropy per unit mass* $s^{\rm PG}$, *are* C^∞ *functions defined on the open set* $\mathcal{O}_\zeta^{\rm PG} = (0,\infty)^{2+n}$ *which satisfy* (T_1-T_4). *Moreover we have* $\mathcal{O}_\pi = (0,\infty)^{2+n}$ *and*

$$\mathcal{O}_\xi = \{\xi = (\xi_e, \xi_v, \xi_1, \dots, \xi_n)^t \ \textit{with}\ \xi_v > 0, \xi_1 > 0, \dots, \xi_n > 0, \xi_e > \sum_{i\in\mathfrak{S}} \xi_i e_i^0\},$$

where e_i^0 *denotes the energy of the* i*th species at zero temperature* $e_k^0 = e_k^{\rm st} - \int_0^{T^{\rm st}} c_{{\rm v}k}^{\rm PG}(\theta)\, d\theta$, $k \in \mathfrak{S}$.

Proof. The proof is straightforward and we refer to Giovangigli [7]. ☐

2.1.4 Molar framework

We essentially consider in this paper thermodynamics properties per unit mass or per unit volume generally used to model multicomponent fluids. Indeed, the equations governing fluid mixtures notably express the conservation of mass and momentum so that mass based variables are often practical. Nevertheless, thermodynamic properties may equivalently be expressed per unit mole and the transformation from molar properties to properties per unit mass is easily performed *mutatis mutandis*.

The species mole fractions $x_1, \dots, x_n$ are first defined by

$$x_i = \frac{y_i m}{m_i}, \quad i \in \mathfrak{S}, \qquad \frac{\sum_{i\in\mathfrak{S}} y_i}{m} = \sum_{i\in\mathfrak{S}} \frac{y_i}{m_i}, \tag{2.24}$$

where m is the molar mass of the mixture. The factor $\sum_{i\in\mathfrak{S}} y_i$ in the definition of the mixture molar mass m insures that the mole/mass relations are invertible and that m is 0-homogeneous [7]. It is easily established in particular that $\sum_{i\in\mathfrak{S}} y_i = \sum_{i\in\mathfrak{S}} x_i$ and that $\big(\sum_{i\in\mathfrak{S}} x_i\big) m = \sum_{i\in\mathfrak{S}} x_i m_i$.

Considering the case of Gibbs functions as a typical example, we then define the mixture Gibbs function per unit mole $\textsc{g}$ and the species Gibbs function per unit mole $\textsc{g}_i$, $i \in \mathfrak{S}$, from

$$\textsc{g} = m g, \qquad \textsc{g}_i = m_i g_i, \qquad i \in \mathfrak{S}. \tag{2.25}$$

Using the relation $g = \sum_{i\in\mathfrak{S}} g_i y_i$, it is then easily deduced that $\textsc{g} = \sum_{i\in\mathfrak{S}} x_i \textsc{g}_i$. All thermodynamic properties per unit mass may similarly be rewritten as molar properties. In an analogous way, the molar variables $(\textsc{e}, \textsc{v}, x_1, \dots, x_n)^t$, $(T, \textsc{v}, x_1, \dots, x_n)^t$, or $(T, p, x_1, \dots, x_n)^t$ may also be used, instead of ξ, ζ or π, where $\textsc{e}$ denotes the energy per unit mole and $\textsc{v}$ the volume per unit mole, and the details are omitted.

2.2 Non Gibbsian thermodynamics

Beside the natural intensive variable $\zeta = (T, v, y_1, \dots, y_n)^t$, where the mass fractions are independent, it is also customary in multicomponent fluid models to use the variables $z = (T, \rho_1, \dots, \rho_n)^t$, where $\rho_1, \dots, \rho_n$ denotes the species mass per unit volume, also termed species partial densities. We discuss in this section the mathematical properties of the thermodynamics in the z variable.

We generally denote with calligraphic letters the properties per unit volume. In particular, we denote by $\mathcal{S}$ the entropy per unit volume, $\mathcal{E}$ the energy per unit volume, $\mathcal{P}$ the pressure as function of z and will use the volumetric variable $x = (\mathcal{E}, \rho_1, \dots, \rho_n)^t$. We also denote by $\mathfrak{d}$ the derivation operator with respect to the variable x and by $\widetilde{\mathfrak{d}}$ the derivation operator with respect to the variable z. We remind that $\varkappa \in \mathbb{N}$, $\varkappa \geqslant 2$, is the regularity class of thermodynamic functionals.

2.2.1 From $(T, v, y_1, \dots, y_n)$ to $(T, \rho_1, \dots, \rho_n)$

We assume that a thermodynamics is available in terms of the natural variable $\zeta = (T, v, y_1, \dots, y_n)^t$ and we investigate the definition and properties of thermodynamic functions in terms of the variable $z = (T, \rho_1, \dots, \rho_n)^t$.

Theorem 2.12. *Assume that e, p, and s satisfy Properties $(\mathsf{T}_1$-$\mathsf{T}_4)$. Let $\mathcal{E}$, $\mathcal{P}$, and $\mathcal{S}$, be given by*

$$\mathcal{E}(T, \rho_1, \dots, \rho_n) = \Big(\sum_{i\in\mathfrak{S}} \rho_i\Big)\, e\Big(T, \frac{1}{\sum_{i\in\mathfrak{S}} \rho_i}, \frac{\rho_1}{\sum_{i\in\mathfrak{S}} \rho_i}, \dots, \frac{\rho_n}{\sum_{i\in\mathfrak{S}} \rho_i}\Big), \tag{2.26}$$

$$\mathcal{P}(T, \rho_1, \dots, \rho_n) = p\Big(T, \frac{1}{\sum_{i\in\mathfrak{S}} \rho_i}, \frac{\rho_1}{\sum_{i\in\mathfrak{S}} \rho_i}, \dots, \frac{\rho_n}{\sum_{i\in\mathfrak{S}} \rho_i}\Big), \tag{2.27}$$

$$\mathcal{S}(T, \rho_1, \dots, \rho_n) = \Big(\sum_{i\in\mathfrak{S}} \rho_i\Big)\, s\Big(T, \frac{1}{\sum_{i\in\mathfrak{S}} \rho_i}, \frac{\rho_1}{\sum_{i\in\mathfrak{S}} \rho_i}, \dots, \frac{\rho_n}{\sum_{i\in\mathfrak{S}} \rho_i}\Big), \tag{2.28}$$

and defined on the open set

$$\mathcal{O}_z = \Big\{\, (T, \rho_1, \dots, \rho_n) \in (0,\infty)^{1+n};\ \Big(T, \frac{1}{\sum_{i\in\mathfrak{S}} \rho_i}, \frac{\rho_1}{\sum_{i\in\mathfrak{S}} \rho_i}, \dots, \frac{\rho_n}{\sum_{i\in\mathfrak{S}} \rho_i}\Big) \in \mathcal{O}_\zeta \,\Big\}. \tag{2.29}$$

Then $\mathcal{E}$, $\mathcal{P}$, and $\mathcal{S}$ are $C^\varkappa$ functions of the variable $z = (T, \rho_1, \dots, \rho_n)^t$ on the open set $\mathcal{O}_z \subset (0,\infty)^{1+n}$ and satisfy Properties $(\mathcal{T}_1$-$\mathcal{T}_4)$.

$(\mathcal{T}_1)$ *The applications $z \to x$ is a $C^\varkappa$ diffeomorphism from the set $\mathcal{O}_z$ onto an open set $\mathcal{O}_x$.*

$(\mathcal{T}_2)$ *For any $z \in \mathcal{O}_z$, defining $\mathcal{G}_k = \widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E} - T\,\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{S}$ $k \in \mathfrak{S}$, we have Gibbs' relation for volumetric functionals*

$$T\mathrm{d}\mathcal{S} = \mathrm{d}\mathcal{E} - \sum_{k\in\mathfrak{S}} \mathcal{G}_k \mathrm{d}\rho_k. \tag{2.30}$$

and the constraint $\sum_{k\in\mathfrak{S}} \rho_k \mathcal{G}_k = \mathcal{E} + \mathcal{P} - T\mathcal{S}$.

$(\mathcal{T}_3)$ *For any $z \in \mathcal{O}_z$, the Hessian matrix $\mathfrak{d}^2_{xx}\mathcal{S}$ is negative definite.*

$(\mathcal{T}_4)$ *For any $(T, y_1, \dots, y_n) \in (0,\infty)^{1+n}$, these exists $v_\mathrm{m} > 0$ such that $(T, y_1/v, \dots, y_n/v)^t \in \mathcal{O}_z$ for $v > v_\mathrm{m}$. Moreover, letting $v = 1/\sum_{i\in\mathfrak{S}} \rho_i$, and for fixed temperature and species mass fractions $y_i = \rho_i\, v$, $i \in \mathfrak{S}$, we have the compatibility conditions*

$$\lim_{v\to\infty} v(\mathcal{E} - \mathcal{E}^{\mathrm{PG}}) = 0, \qquad \lim_{v\to\infty} v(\mathcal{P} - \mathcal{P}^{\mathrm{PG}}) = 0, \qquad \lim_{v\to\infty} v(\mathcal{S} - \mathcal{S}^{\mathrm{PG}}) = 0. \tag{2.31}$$

Note that there are not anymore homogeneity properties for thermodynamic functionals in terms of the variable z in $(\mathcal{T}_1)$. There is also a constraint associated with Gibbs' relation (2.30) in terms of $\mathcal{S}$, $\mathcal{E}$, and $\rho_1, \dots, \rho_n$, which is essentially the second relation of (T_2'). The entropy Hessian matrix $\mathfrak{d}^2_{xx}\mathcal{S}$ is invertible with $(\mathcal{T}_3)$ unlike in the homogeneous case where $N(\partial^2_{\xi\xi}s) = \mathbb{R}\xi$. Finally, the compatibility with perfect gases $(\mathcal{T}_4)$ must be written at fixed temperature and mass fractions $y_k = \rho_k/\rho$, $k \in \mathfrak{S}$.

Proof. We define $\rho = \sum_{k\in\mathfrak{S}} \rho_k$, $v = 1/\rho$ and $y_k = \rho_k/\rho$, $k \in \mathfrak{S}$, and all functions per unit mass are evaluated at $\zeta = (T, v, y_1, \dots, y_n)$. The fact that $\mathcal{O}_z$ is an open set is a direct consequence of the continuity of $z \to \zeta$ and the smoothness of $\mathcal{S}$, $\mathcal{E}$, and $\mathcal{P}$ is straightforward. After some algebra, thanks to the 1-homogeneity of $e(\zeta)$ in $(v, y_1, \dots, y_n)$, it is established that

$$\mathrm{d}\mathcal{E} = \rho\,\widetilde{\partial}_T e\,\mathrm{d}T + \sum_{k\in\mathfrak{S}} \widetilde{\partial}_{y_k} e\,\mathrm{d}\rho_k. \tag{2.32}$$

This implies that $\widetilde{\mathfrak{d}}_T\mathcal{E} = \rho\,\widetilde{\partial}_T e > 0$ from (T_3) and Proposition 2.4 so that $z \to x$ is one to one, and thanks to the inverse function theorem, it is easily obtained that $z \to x$ is a $C^\varkappa$ diffeormorphism and that $\mathcal{O}_x$ is open and $(\mathcal{T}_1)$ is established.

As for the energy per unit volume, we also have

$$\mathrm{d}\mathcal{S} = \rho\,\widetilde{\partial}_T s\,\mathrm{d}T + \sum_{k\in\mathfrak{S}} \widetilde{\partial}_{y_k} s\,\mathrm{d}\rho_k. \tag{2.33}$$

However, thanks to (T_2), we know that $T\widetilde{\partial}_T s = \widetilde{\partial}_T e$, and $T\widetilde{\partial}_{y_k} s = \widetilde{\partial}_{y_k} e - g_k$ and this now implies Gibbs' relation for volumetric densities (2.30) with $g_k = \mathcal{G}_k$, $k \in \mathfrak{S}$. In addition, the relation $\sum_{k\in\mathfrak{S}} \rho_k \mathcal{G}_k = \mathcal{E} + \mathcal{P} - T\mathcal{S}$ is a consequence of Corollary 2.3 and $(\mathcal{T}_2)$ is established.

From Gibbs' relation (2.30) we obtain that

$$\mathfrak{d}_\mathcal{E}\mathcal{S} = \frac{1}{T}, \qquad \mathfrak{d}_{\rho_k}\mathcal{S} = -\frac{g_k}{T} = -\frac{\mathcal{G}_k}{T},$$

and this implies the compatibility relations

$$\mathfrak{d}_\mathcal{E}\Big(\frac{-\mathcal{G}_k}{T}\Big) = \mathfrak{d}_{\rho_k}\Big(\frac{1}{T}\Big). \tag{2.34}$$

Moreover, for any function χ we have the differential relations

$$\mathfrak{d}_\mathcal{E}\chi = \widetilde{\mathfrak{d}}_T\chi\;\mathfrak{d}_\mathcal{E}T, \qquad \widetilde{\mathfrak{d}}_T\chi = \mathfrak{d}_\mathcal{E}\chi\;\widetilde{\mathfrak{d}}_T\mathcal{E}, \tag{2.35}$$

$$\mathfrak{d}_{\rho_k}\chi = \widetilde{\mathfrak{d}}_{\rho_k}\chi + \widetilde{\mathfrak{d}}_T\chi\;\mathfrak{d}_{\rho_k}T, \qquad \widetilde{\mathfrak{d}}_{\rho_k}\chi = \mathfrak{d}_{\rho_k}\chi + \mathfrak{d}_\mathcal{E}\chi\;\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E}. \tag{2.36}$$

We can now evaluate the volumetric entropy Hessian matrix. We first note that $\mathfrak{d}^2_{\mathcal{E}\mathcal{E}}\mathcal{S} = \mathfrak{d}_\mathcal{E}(\frac{1}{T})$ so that $\mathfrak{d}^2_{\mathcal{E}\mathcal{E}}\mathcal{S} = -\mathfrak{d}_\mathcal{E}T/T^2$. Similarly, we have $\mathfrak{d}^2_{\mathcal{E}\rho_k}\mathcal{S} = \mathfrak{d}_{\rho_k}(\frac{1}{T})$ so that $\mathfrak{d}^2_{\mathcal{E}\rho_k}\mathcal{S} = -\mathfrak{d}_{\rho_k}T/T^2$. Upon letting $\chi = T$ in (2.36) we obtain that $\mathfrak{d}_{\rho_k}T = -\mathfrak{d}_\mathcal{E}T\,\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E}$ and since $\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E} = \widetilde{\partial}_{y_k} e$ we have established that $\mathfrak{d}^2_{\mathcal{E}\rho_k}\mathcal{S} = \mathfrak{d}_\mathcal{E}T\,\widetilde{\partial}_{y_k} e/T^2$. In addition, from $\mathfrak{d}^2_{\rho_k\rho_l}\mathcal{S} = -\mathfrak{d}_{\rho_k}(\frac{\mathcal{G}_l}{T}) = -\mathfrak{d}_{\rho_k}(\frac{g_l}{T})$ and from (2.36) we deduce that $\mathfrak{d}^2_{\rho_k\rho_l}\mathcal{S} = -\widetilde{\mathfrak{d}}_{\rho_k}(\frac{g_l}{T}) - \widetilde{\mathfrak{d}}_T(\frac{g_l}{T})\,\mathfrak{d}_{\rho_k}T$ so that $\mathfrak{d}^2_{\rho_k\rho_l}\mathcal{S} = -\frac{\widetilde{\partial}_{y_k} g_l}{\rho\, T} - \frac{\mathfrak{d}_{\mathcal{E}}T\,\widetilde{\partial}_{y_k}e\,\widetilde{\partial}_{y_l}e}{T^2}$, $k,l\in\mathfrak{S}$. We have thus established that

$$\mathfrak{d}^2_{\mathcal{E}\mathcal{E}}\mathcal{S} = -\frac{\mathfrak{d}_{\mathcal{E}}T}{T^2}, \qquad \mathfrak{d}^2_{\mathcal{E}\rho_k}\mathcal{S} = \frac{\mathfrak{d}_{\mathcal{E}}T\,\widetilde{\partial}_{y_k}e}{T^2}, \quad k\in\mathfrak{S}, \tag{2.37}$$

$$\mathfrak{d}^2_{\rho_k\rho_l}\mathcal{S} = -\frac{\widetilde{\partial}_{y_k} g_l}{T} - \frac{\mathfrak{d}_{\mathcal{E}}T\,\widetilde{\partial}_{y_k}e\,\widetilde{\partial}_{y_l}e}{T^2}, \quad k,l\in\mathfrak{S}. \tag{2.38}$$

Denoting $\mathfrak{f}^{\mathcal{E}} = (1, -\widetilde{\partial}_{y_1}e, \dots, -\widetilde{\partial}_{y_1}e)^t$ we obtain that for any $\mathsf{x} = (\mathsf{x}_{\mathcal{E}}, \mathsf{x}_1, \dots, \mathsf{x}_n)^t \in \mathbb{R}^{1+n}$

$$\big\langle(\mathfrak{d}^2_{xx}\mathcal{S})\,\mathsf{x},\mathsf{x}\big\rangle = -\mathfrak{d}_{\mathcal{E}}T\frac{\langle\mathfrak{f}^{\mathcal{E}},\mathsf{x}\rangle^2}{T^2} - \frac{1}{\rho}\big\langle\Lambda\mathsf{x}_y,\mathsf{x}_y\big\rangle, \tag{2.39}$$

where $\Lambda_{kl} = \widetilde{\partial}_{y_k} g_l/T$, $k,l\in\mathfrak{S}$ and $\mathsf{x}_y = (\mathsf{x}_1,\dots,\mathsf{x}_n)^t$. As a consequence, since Λ is positive definite from Proposition 2.4, we deduce that $\mathfrak{d}^2\mathcal{S}$ is negative definite and ($\mathcal{T}_3$) is established. Finally, ($\mathcal{T}_4$) is a simple rewritting of (T_4) with e, p, and s evaluated at $T, v, y_1, \dots, y_n$ and the proof is complete. ☐

Proposition 2.13. *Assume that ($\mathcal{T}_1$-$\mathcal{T}_2$) are satisfied and denote by Λ the matrix of size n with coefficients $\Lambda_{kl} = \rho\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{G}_l/T = \rho\widetilde{\mathfrak{d}}_{\rho_l}\mathcal{G}_k/T$. Then, for any $z\in\mathcal{O}_z$, the following statements are equivalent :*

- *(i) $\partial^2_{zz}\mathcal{S}$ is negative definite.*
- *(ii) $\widetilde{\mathfrak{d}}_T\mathcal{E} > 0$ and Λ is positive definite.*

Proof. This proposition is a straighforward consequence of Equation (2.39). ☐

Remark 2.14. *The functions $\mathcal{E}$, $\mathcal{P}$, and $\mathcal{S}$, may also be defined by*

$$\mathcal{E}(T,\rho_1,\dots,\rho_n) = e\big(T,1,\rho_1,\dots,\rho_n\big), \tag{2.40}$$

$$\mathcal{P}(T,\rho_1,\dots,\rho_n) = p\big(T,1,\rho_1,\dots,\rho_n\big), \tag{2.41}$$

$$\mathcal{S}(T,\rho_1,\dots,\rho_n) = s\big(T,1,\rho_1,\dots,\rho_n\big), \tag{2.42}$$

on the open set

$$\mathcal{O}_z = \{\ (T,\rho_1,\dots,\rho_n)\in(0,\infty)^{1+n};\ \big(T,1,\rho_1,\dots,\rho_n\big)\in\mathcal{O}_\zeta\ \}. \tag{2.43}$$

Thanks to the homogeneity properties of e, s, p, and $\mathcal{O}_\zeta$, it is easily established that these definitions coincide with the natural definitions of Proposition 2.12.

2.2.2 From $(T,\rho_1,\dots,\rho_n)$ to $(T,v,y_1,\dots,y_n)$

We assume that a thermodynamics is available in terms of the variable $z = (T,\rho_1,\dots,\rho_n)^t$ and we investigate the definition and properties of thermodynamic functions in terms of $\zeta = (T,v,y_1,\dots,y_n)^t$.

Theorem 2.15. *Assume that $\mathcal{E}$, $\mathcal{P}$, and $\mathcal{S}$, satisfy Properties ($\mathcal{T}_1$-$\mathcal{T}_4$). Let the functions e, p, and s, be given by*

$$e(T,v,y_1,\dots,y_n) = v\ \mathcal{E}\Big(T,\frac{y_1}{v},\dots,\frac{y_n}{v}\Big), \tag{2.44}$$

$$p(T,v,y_1,\dots,y_n) = \mathcal{P}\Big(T,\frac{y_1}{v},\dots,\frac{y_n}{v}\Big), \tag{2.45}$$

$$s(T,v,y_1,\dots,y_n) = v\ \mathcal{S}\Big(T,\frac{y_1}{v},\dots,\frac{y_n}{v}\Big), \tag{2.46}$$

and defined on the open set

$$\mathcal{O}_\zeta = \{\ (T,v,y_1,\dots,y_n)\in(0,\infty)^{2+n};\ \Big(T,\frac{y_1}{v},\dots,\frac{y_n}{v}\Big)\in\mathcal{O}_z\ \}. \tag{2.47}$$

Then e, p, and s are $C^\varkappa$ functions of the variable $\zeta = (T,v,y_1,\dots,y_n)^t$ on the open set $\mathcal{O}_\zeta\subset(0,\infty)^{2+n}$ and satisfy the properties (T_1-T_4).

Proof. The fact that $\mathcal{O}_\zeta$ is open and that e, p, and s are smooth if straightforward to establish. The homogeneity properties of $\mathcal{O}_\zeta$, e, p, and s are also a direct consequence of their definition and (T_1) is established.

In order to establish Gibbs relation (2.1) we note that

$$\mathrm{d}s = v\widetilde{\mathfrak{d}}_T\mathcal{S}\,\mathrm{d}T + \big(\mathcal{S} - \sum_{k\in\mathfrak{S}} \rho_k\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{S}\big)\,\mathrm{d}v + \sum_{k\in\mathfrak{S}} \widetilde{\mathfrak{d}}_{\rho_k}\mathcal{S}\,\mathrm{d}y_k,$$

$$\mathrm{d}e = v\widetilde{\mathfrak{d}}_T\mathcal{E}\,\mathrm{d}T + \big(\mathcal{E} - \sum_{k\in\mathfrak{S}} \rho_k\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E}\big)\,\mathrm{d}v + \sum_{k\in\mathfrak{S}} \widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E}\,\mathrm{d}y_k,$$

However, from Gibbs' relation in $(\mathcal{T}_2)$ we obtain that $T\widetilde{\mathfrak{d}}_T\mathcal{S} = \widetilde{\mathfrak{d}}_T\mathcal{E}$, from the definition of $\mathcal{G}_k = \widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E} - T\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{S}$, $k \in \mathfrak{S}$, and from the natural constraint $\sum_{k\in\mathfrak{S}} \rho_k\mathcal{G}_k = \mathcal{E} + \mathcal{P} - T\mathcal{S}$ we obtain that

$$T(\mathcal{S} - \sum_{k\in\mathfrak{S}} \rho_k\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{S}_k) - (\mathcal{E} - \sum_{k\in\mathfrak{S}} \rho_k\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E}_k) = \mathcal{P}, \qquad T\widetilde{\mathfrak{d}}_{\rho_k}\mathcal{S} - \widetilde{\mathfrak{d}}_{\rho_k}\mathcal{E} = -\mathcal{G}_k,$$

so that forming $T\mathrm{d}s - \mathrm{d}e$ we directly obtain (T_2).

In Proposition 2.13 we have established that $(\mathcal{T}_3)$ is equivalent to $\widetilde{\mathfrak{d}}_T\mathcal{E} = \rho\,\widetilde{\partial}_T e > 0$ and the matrix Λ is positive definite so that (T_3) is established thanks to Proposition 2.4. Finally, (T_4) is a simple transformation of $(\mathcal{T}_4)$ and the proof is complete. ☐

2.2.3 Ideal gas mixtures

As a typical example of non Gibbsian thermochemistry, we address in this section the situation of perfect gas mixtures in terms of the variables $z = (T, \rho_1, \ldots, \rho_n)^t$ [7]. The state law then reads

$$\mathcal{P}^{\mathrm{PG}} = RT \sum_{k\in\mathfrak{S}} \frac{\rho_k}{m_k}, \tag{2.48}$$

and the energy per unit volume

$$\mathcal{E}^{\mathrm{PG}} = \sum_{k\in\mathfrak{S}} \rho_k\mathcal{E}_k^{\mathrm{PG}}, \qquad \mathcal{E}_k^{\mathrm{PG}} = e^{\mathrm{st}} + \int_{T^{\mathrm{st}}}^{T} c_{\mathrm{v}k}^{\mathrm{PG}}(\theta)\,d\theta, \tag{2.49}$$

where $\mathcal{E}_k$ denotes the internal energy per unit mass of the kth species and $c_{\mathrm{v}k}$ the specific heat per unit mass of the k species. Similarly, the entropy per unit volume is given by

$$\mathcal{S}^{\mathrm{PG}} = \sum_{k\in\mathfrak{S}} \rho_k\mathcal{S}_k^{\mathrm{PG}}, \qquad \mathcal{S}_k^{\mathrm{PG}} = s^{\mathrm{st}} + \int_{T^{\mathrm{st}}}^{T} \frac{c_{\mathrm{v}k}^{\mathrm{PG}}(\theta)}{\theta}\,d\theta - \frac{RT}{m_k}\log\frac{\rho_k}{m_k\gamma^{\mathrm{st}}}. \tag{2.50}$$

The enthalpy $\mathcal{H}^{\mathrm{PG}} = \mathcal{E}^{\mathrm{PG}} + \mathcal{P}^{\mathrm{PG}}$, Gibbs function $\mathcal{G}^{\mathrm{PG}} = \mathcal{E}^{\mathrm{PG}} + \mathcal{P}^{\mathrm{PG}} - T\mathcal{S}^{\mathrm{PG}}$, and free energy $\mathcal{F}^{\mathrm{PG}} = \mathcal{E}^{\mathrm{PG}} - T\mathcal{S}^{\mathrm{PG}}$ are then easily evaluated. The assumptions required for perfect gas in such a volumetric framework are still Property (PG).

3 Thermodynamics from equations of state

We investigate in this section when an equation of state may define a Gibbsian thermodynamics compatible with that of perfect gas mixtures at low density under natural structural assumptions. The structural assumptions are essentially 0-homogeneity of pressure as well as a quadratic estimate $p - p^{\mathrm{PG}} = O(\rho^2)$ valid for small densities ρ or large volume per unit mass $v = 1/\rho$. We first identify the energy and entropy per unit mass in Section 3.1 and next investigate necessary and sufficient conditions in Section 3.2. According to Beattie [30], the matching with perfect gases is due to Van der Waals and Gillespie [31].

3.1 Construction of the thermodynamics

We investigate in this section the energy, entropy, and species Gibbs functions associated with an equation of state in the framework of a Gibbsian thermodynamics compatible at low density with that of perfect gases. We consider a pressure law $p(\zeta)$ as function of $\zeta = (T, v, y_1, \dots, y_n)^t$ defined of an open set $\mathcal{O}'_\zeta \subset (0,\infty)^{n+2}$ and write for convenience

$$p = p^{\mathrm{PG}} + \phi, \tag{3.1}$$

so that ϕ denotes the pressure corrector $\phi(\zeta) = p(\zeta) - p^{\mathrm{PG}}(\zeta)$. We make the following structural assumptions concerning the pressure law (3.1).

(P_0) *The open set $\mathcal{O}'_\zeta \subset (0,\infty)^{n+2}$ is such that for any $(T, v, y_1, \dots, y_n) \in \mathcal{O}'_\zeta$ and any $v' > v$ we have $(T, v', y_1, \dots, y_n) \in \mathcal{O}'_\zeta$, and the function ϕ is $C^{\varkappa+1}$ over the open set $\mathcal{O}'_\zeta$. There exist $\underline{v} > 0$ such that for any $(T, y_1, \dots, y_n) \in (0,\infty)^{1+n}$ with $\sum_{i\in\mathfrak{S}} y_i = 1$, and any $v \geqslant \underline{v}$, we have $\zeta = (T, v, y_1, \dots, y_n)^t \in \mathcal{O}'_\zeta$. In addition, the function ϕ and all its partial derivatives $\widetilde{\partial}_\zeta^\beta \phi$ of order $|\beta| \leqslant 1 + \varkappa$ admits a smooth extension to the set $T > 0$, $v \geqslant \underline{v}$, $y_i \geqslant 0$, $\langle y, u \rangle = 1$. There exist positive continuous functions of temperature $\mathsf{c}(\beta, T)$ depending on the multiindex $\beta \in \mathbb{N}^{2+n}$, $|\beta| \leqslant 1 + \varkappa$, such that for any $T > 0$, $v \geqslant \underline{v}$, and $y_i \geqslant 0$, $i \in \mathfrak{S}$, $\langle y, u \rangle = 1$, we have the estimates*

$$|\widetilde{\partial}_\zeta^\beta \phi| \leqslant \frac{\mathsf{c}(\beta, T)}{v^{\beta_v + 2}}. \tag{3.2}$$

(P_1) *The open set $\mathcal{O}'_\zeta$ is such that for any $\zeta = (T, v, y_1, \dots, y_n) \in \mathcal{O}'_\zeta$ and any $\lambda \in (0,\infty)$ we have $\zeta_\lambda = (T, \lambda v, \lambda y_1, \dots, \lambda y_n) \in \mathcal{O}'_\zeta$ and p is 0-homogeneous in the sense that $p(\zeta_\lambda) = p(\zeta)$.*

We have used here the traditional notation $\widetilde{\partial}^\beta = \widetilde{\partial}_T^{\beta_T} \widetilde{\partial}_v^{\beta_v} \widetilde{\partial}_{y_1}^{\beta_1} \cdots \widetilde{\partial}_{y_n}^{\beta_n}$ where β is a multiindex and $\beta = (\beta_T, \beta_v, \beta_1, \dots, \beta_n) \in \mathbb{N}^{2+n}$. The condition (P_0) guarantees that ϕ and its partial derivatives of order lower or equal to $1 + \varkappa$ decrease at least quadratically with respect to v at ∞ insuring convergence of various integrals. The estimates (3.2) are easily extended by homogeneity and the resulting inequalities are omitted for the sake of simplicity. The quadratic estimates (3.2) are naturally obtained by expanding the pressure law in a series in $\rho = 1/v$ in the neighborhood of the origin, keeping in mind that the linear term is associated with the perfect gas contribution p^{PG} in p and by deriving. The structure of the open set $\mathcal{O}'_\zeta$ is also required in order to integrate with respect to the volume per unit mass v and to recover the compatibility at low density with perfect gases. Finally, the homogeneity property (P_1) is also natural since we seek to obtain a thermodynamics such that (T_1) holds.

Proposition 3.1. *Let p be a pressure law in the form (3.1) with ϕ satisfying (P_0) and assume that there exists a corresponding Gibbsian thermodynamics as in Definition 2.1. Then the energy e, entropy s, and species Gibbs functions g_k, $k \in \mathfrak{S}$, are given by*

$$e = e^{\mathrm{PG}} - \int_v^\infty T^2 \widetilde{\partial}_T \big(\frac{\phi}{T}\big)\, dv', \tag{3.3}$$

$$s = s^{\mathrm{PG}} - \int_v^\infty \widetilde{\partial}_T \phi \, dv', \tag{3.4}$$

$$g_k = g_k^{\mathrm{PG}} - \int_v^\infty \widetilde{\partial}_{y_k} \phi \, dv', \qquad k \in \mathfrak{S}, \tag{3.5}$$

where the integrands are evaluated at $(T, v', y_1, \dots, y_n)$. Moreover, e, s, and g_k, $k \in \mathfrak{S}$, are $C^\varkappa$ functions over $\mathcal{O}'_\zeta$, and if Property (P_1) also holds, then e and s are 1-homogeneous and g_k, $k \in \mathfrak{S}$, are 0-homogeneous over $\mathcal{O}'_\zeta$ in the sense that $e(\zeta_\lambda) = \lambda e(\zeta)$, $s(\zeta_\lambda) = \lambda s(\zeta)$, and $g_k(\zeta_\lambda) = g_k(\zeta)$, $k \in \mathfrak{S}$ for any $\zeta \in \mathcal{O}'_\zeta$ and any $\lambda \in (0,\infty)$.

Proof. We first obtain from the compatibility relations (2.6) that $\widetilde{\partial}_v e = T^2 \widetilde{\partial}_T \big(\frac{p}{T}\big)$ so that $\widetilde{\partial}_v e = T^2 \widetilde{\partial}_T \big(\frac{\phi}{T}\big)$ since $\widetilde{\partial}_T \big(p^{\mathrm{PG}}/T\big) = 0$ from (2.21). Integrating with respect to v' over $[v, v'']$, thanks to the structure of $\mathcal{O}'_\zeta$, we obtain that

$$e(T, v, y_1, \dots, y_n) - e(T, v'', y_1, \dots, y_n) = -\int_v^{v''} T^2 \widetilde{\partial}_T \big(\frac{\phi}{T}\big)(T, v', y_1, \dots, y_n)\, dv'.$$

Using then the integrability properties (3.2) from (P_0) and noting that

$$\lim_{v''\to\infty} e(T, v'', y_1, \dots, y_n) = e^{\mathrm{PG}}(T, y_1, \dots, y_n),$$

from (T_4) and (2.22) we may let $v'' \to \infty$ and deduce that (3.3) holds.

Similarly, from Gibbs' relation, we obtain that $\widetilde{\partial}_v(Ts-e)=p$ and since $\widetilde{\partial}_v(Ts^{\text{PG}}-e^{\text{PG}})=p^{\text{PG}}$ we deduce that $\widetilde{\partial}_v(Ts-e)-\widetilde{\partial}_v(Ts^{\text{PG}}-e^{\text{PG}})=\phi$. Integrating with respect to v' over $[v,v'']$ we obtain that

$$\begin{aligned}\big(Ts-Ts^{\text{PG}}-e+e^{\text{PG}}\big)&(T,v,y_1,\dots,y_n)\\ -\big(Ts-Ts^{\text{PG}}-e+e^{\text{PG}}\big)&(T,v'',y_1,\dots,y_n)=-\int_v^{v''}\phi(T,v',y_1,\dots,y_n)\,dv'.\end{aligned} \tag{3.6}$$

Letting $v''\to\infty$, thanks to the estimates (3.2) of (P_0) and the compatibility condition (T_4), we obtain that $\big(Ts-Ts^{\text{PG}}-e+e^{\text{PG}}\big)(T,v'',y_1,\dots,y_n)$ goes to zero as $v''\to\infty$, and we deduce after some algebra that (3.4) holds.

The regularity assumptions on ϕ and the estimates (3.2) then allow to differentiate the identities (3.3) and (3.4) with respect to T, v, and y_k, $k\in\mathfrak{S}$, and it is easily established that e and s are $C^{\varkappa}$ functions over $\mathcal{O}'_\zeta$. Upon deriving with respect to y_k, we can evaluate $g_k=\widetilde{\partial}_{y_k}e-T\widetilde{\partial}_{y_k}s$ to obtain that

$$g_k=g_k^{\text{PG}}-\int_v^{\infty}\widetilde{\partial}_{y_k}\phi\,dv,$$

and it is easily established that g_k, $k\in\mathfrak{S}$, are $C^{\varkappa-1}$ functions over $\mathcal{O}'_\zeta$. Moreover, taking into account the homogeneity properties of e^{PG}, s^{PG}, and g_k^{PG}, $k\in\mathfrak{S}$, and assuming (P_1), we easily deduce that e and s are 1-homogeneous over $\mathcal{O}'_\zeta$ and g_k, $k\in\mathfrak{S}$, are 0-homogeneous over $\mathcal{O}'_\zeta$. Indeed the pressure corrector ϕ is 0-homogeneous, so that $\widetilde{\partial}_T\phi$ and $T\widetilde{\partial}_T\phi-\phi$ are 0-homogeneous, and the corresponding integrals $\int_v^\infty\widetilde{\partial}_T\phi\,dv'$ and $\int_v^\infty(T\widetilde{\partial}\phi-\phi)\,dv'$ are then 1-homogeneous. Similarly, $\widetilde{\partial}_{y_k}\phi$ is (-1)-homogeneous so that $\int_v^\infty\widetilde{\partial}_{y_k}\phi\,dv'$ is 0-homogeneous and the proof is complete. □

3.2 Necessary and sufficient conditions

The open set $\mathcal{O}'_\zeta$ where the pressure p, the energy per unit mass e, and the entropy per unit mass s are defined and smooth enough, may be too large for the thermodynamic stability condition (T_3). This open set $\mathcal{O}'_\zeta$ will contain as a subset the domain $\mathcal{O}_\zeta$ where the thermodynamic functions satisfy $(\mathsf{T}_1$-$\mathsf{T}_4)$ as established in the following theorem.

Theorem 3.2. *Assume that the structural conditions* $(\mathsf{P}_0$-$\mathsf{P}_1)$ *hold. If there exists a thermodynamics compatible with* p *and satisfying* $(\mathsf{T}_1$-$\mathsf{T}_4)$ *over the open set* $\mathcal{O}_\zeta\subset\mathcal{O}'_\zeta$ *then the following Properties* $(\mathsf{P}_2$-$\mathsf{P}_3)$ *hold.*

(P_2) *For any* $\zeta\in\mathcal{O}_\zeta$, *we have*

$$T\int_v^{\infty}\widetilde{\partial}^2_T\phi\,dv' \quad < \quad \sum_{k\in\mathfrak{S}} y_k c_{vk}^{\text{PG}}. \tag{3.7}$$

(P_3) *For any* $\zeta\in\mathcal{O}_\zeta$, *the matrix* Λ *with coefficients*

$$\Lambda_{kl}=\frac{R}{y_k m_k}\delta_{kl}+\frac{1}{T}\int_v^{\infty}\widetilde{\partial}^2_{y_k y_l}\phi\,dv',\qquad k,l\in\mathfrak{S}, \tag{3.8}$$

is positive definite.

Conversely, define the open set $\mathcal{O}_\zeta$ *as the subset of* $\mathcal{O}'_\zeta$ *such that* $(\mathsf{P}_2$-$\mathsf{P}_3)$ *hold. Then the energy per unit mass* e *given by* (3.3), *the pressure* p *given by* (5.1), *and the entropy per unit mass* s *given by* (3.4), *satisfy* $(\mathsf{T}_1$-$\mathsf{T}_4)$ *over* $\mathcal{O}_\zeta$, *and the species Gibbs functions are also given by* (3.5).

Proof. Assume first that there exists a thermodynamics compatible with p satisfying $(\mathsf{T}_1$-$\mathsf{T}_4)$ over an open set $\mathcal{O}_\zeta\subset\mathcal{O}'_\zeta$. From Propostion 3.1 we know that the energy e, the entropy s and the species Gibbs functions g_k, $k\in\mathfrak{S}$, are given by (3.3), (3.4), and (3.5) and that the proper homogeneity properties (P_1) hold.

Deriving the energy e with respect to temperature we further obtain that

$$\widetilde{\partial}_T e=\widetilde{\partial}_T e^{\text{PG}}-T\int_v^{\infty}\widetilde{\partial}^2_T\phi\,dv'. \tag{3.9}$$

Then (P_2) is a consequence of Proposition 2.4 and of the expression of $\widetilde{\partial}_T e^{\mathrm{PG}}$. Similarly, deriving (3.5), it is easily checked that the matrix Λ with coefficients $\Lambda_{kl} = \widetilde{\partial}_{y_l} g_k / T$ is given by (3.8) so that (P_3) is a consequence of Proposition 2.4.

Conversely, define the open set $\mathcal{O}_\zeta$ as the subset of $\mathcal{O}'_\zeta$ such that $(\mathsf{P}_2\text{-}\mathsf{P}_3)$ hold. We know from Proposition 3.1 that the energy e is given by (3.3) and the entropy s is given by (3.4), and we have to establish that Properties $(\mathsf{T}_1\text{-}\mathsf{T}_4)$ hold, or, equivalently, that $(\mathsf{T}'_1\text{-}\mathsf{T}'_3)$ and (T_4) hold.

The 1-homogeneity properties of e and s have been established in Proposition 3.1 as well as the regularity properties $e, s \in C^{\varkappa}(\mathcal{O}'_\zeta)$. Moreover, it is easily checked that for any $\zeta \in \mathcal{O}_\zeta$, we have $\zeta_\lambda \in \mathcal{O}_\zeta$ by homogeneity. Similarly p is 0-homogeneous and $p \in C^{1+\varkappa}(\mathcal{O}'_\zeta)$, and we obtain that (T'_1) holds since $\mathcal{O}_\zeta$ is an open subset of $\mathcal{O}'_\zeta$.

In order to establish Gibbs relation, we have to establish (T'_2). From (3.3)(3.4), and the estimates (3.2), we first obtain that

$$\widetilde{\partial}_T e = \widetilde{\partial}_T e^{\mathrm{PG}} - T \int_v^\infty \widetilde{\partial}^2_T \phi \, dv', \qquad \widetilde{\partial}_T s = \widetilde{\partial}_T s^{\mathrm{PG}} - \int_v^\infty \widetilde{\partial}^2_T \phi \, dv',$$

and since $\widetilde{\partial}_T e^{\mathrm{PG}} = T \widetilde{\partial}_T s^{\mathrm{PG}}$ we obtain that $\widetilde{\partial}_T e = T \widetilde{\partial}_T s$. Similarly, from (3.3), (3.4), and the estimates (3.2), we have

$$\widetilde{\partial}_v e = \widetilde{\partial}_v e^{\mathrm{PG}} + T \widetilde{\partial}_T \phi - \phi, \qquad \widetilde{\partial}_v s = \widetilde{\partial}_v s^{\mathrm{PG}} + \widetilde{\partial}_T \phi.$$

Using now $\widetilde{\partial}_v e^{\mathrm{PG}} = T \widetilde{\partial}_v s^{\mathrm{PG}} - p^{\mathrm{PG}}$, we deduce that $\widetilde{\partial}_v e = T \widetilde{\partial}_v s^{\mathrm{PG}} - p^{\mathrm{PG}} + T \widetilde{\partial}_T \phi - \phi$, and thus $\widetilde{\partial}_v e = T \widetilde{\partial}_v s - p$ and (T'_2) is established. Properties (T'_3) is then a direct consequence of (P_2) and (P_3) and of the relations (3.3) and (3.5) derived with respect to temperature and species mass fractions. Finally, (T_4) is guaranteed by construction of the thermodynamics (5.1)(3.3)(3.4) and from the estimates (3.2) which implies in particular that $(T, v, y_1, \dots, y_n)^t$ belongs to $\mathcal{O}_\zeta$ for v large enough. ☐

In practice, once a pressure law is available, we first have to check that $(\mathsf{P}_0\text{-}\mathsf{P}_1)$ are satisfied. We may then calculate the energy, entropy and species Gibbs functions per unit mass according to the expressions (3.3), (3.4), and (3.5). We finally have to investigate the open set $\mathcal{O}_\zeta$ where thermodynamic stability holds. This may be the most difficult part in practice since *thermodynamic stability may not hold* at high pressure and low temperature [17].

Remark 3.3. *The inequalities associated with* $(\mathsf{P}_2\text{-}\mathsf{P}_3)$ *are homogeneous with respect to* $(v, y_1, \dots, y_n)$ *so that it is sufficient in practice to solely the physical case* $\langle y, u \rangle = 1$.

3.3 More on thermodynamic stability

From Theorem 3.2 the thermodynamic stability domain, where the mixture is locally stable, is the domain where $\widetilde{\partial}_T e > 0$ and the matrix Λ is positive definite. The mixture is also globally stable on every convex set—with respect to the variable ξ—included in this stability domain. The condition $\widetilde{\partial}_T e > 0$ is the thermal stability condition whereas the positive definiteness of the matrix Λ includes both the mechanical stability condition $\widetilde{\partial}_v p < 0$ and the chemical stability condition that $\widehat{\partial}^2_{yy} g$ is positive semi-definite with nullspace $\mathbb{R}y$. The mechanical stability condition $\widetilde{\partial}_v p < 0$ is generally satisfied above a critical pressure as discussed in Section 5. We establish in this section a few result about the matrix Λ which have practical implications for the determination of the stability domain.

We first relate the spectrum of the matrix Λ to that of matrices $\overline{\Lambda}$, $\widehat{\Lambda}_{\mathsf{r}}$, and $\widehat{\Lambda}_{\mathsf{l}}$, which behave more regularly for zero mass fractions. For any diagonalizable matrix A, we denote by $\mathsf{d}^+(A)$, $\mathsf{d}^0(A)$, and $\mathsf{d}^-(A)$, the number of positive, zero and negative eigenvalues of A, respectively.

Proposition 3.4. *Assume that Properties* $(\mathsf{P}_0\text{-}\mathsf{P}_1)$ *hold. For any* $\zeta \in \mathcal{O}'_\zeta$, *let* Λ *be defined as in* (P_3) *and* $\mathit{\Pi}$ *be the diagonal matrix* $\mathit{\Pi} = \mathrm{diag}\big(\sqrt{m_1 y_1}, \dots, \sqrt{m_1 y_n}\big)/\sqrt{R}$. *The matrices* $\overline{\Lambda}$, $\widehat{\Lambda}_{\mathsf{r}}$, *and* $\widehat{\Lambda}_{\mathsf{l}}$, *defined by*

$$\overline{\Lambda} = \mathit{\Pi}\, \Lambda\, \mathit{\Pi}, \qquad \widehat{\Lambda}_{\mathsf{r}} = \Lambda\, \mathit{\Pi}^2, \qquad \widehat{\Lambda}_{\mathsf{l}} = \mathit{\Pi}^2\, \Lambda,$$

are then $C^{\varkappa-1}$ *function of* $\zeta \in \mathcal{O}'_\zeta$. *Furthermore, if we assume that* $v > \underline{v}$, *then* $\overline{\Lambda}$ *admits a continuous extension to nonnegative mass fractions whereas* $\widehat{\Lambda}_{\mathsf{r}}$ *and* $\widehat{\Lambda}_{\mathsf{l}}$ *admit* $C^{\varkappa-1}$ *extensions to nonnegative mass fractions. Finally, for any* $\zeta \in \mathcal{O}'_\zeta$, *we have* $\mathsf{d}^+(\Lambda) = \mathsf{d}^+(\overline{\Lambda})$, $\mathsf{d}^0(\Lambda) = \mathsf{d}^0(\overline{\Lambda})$, $\mathsf{d}^-(\Lambda) = \mathsf{d}^-(\overline{\Lambda})$, *and the matrices* $\overline{\Lambda}$, $\widehat{\Lambda}^{\mathsf{r}}$, *and* $\widehat{\Lambda}_{\mathsf{l}}$, *have the same spectrum.*

Proof. The coefficients of the matrix $\overline{\Lambda}$ are given by

$$\overline{\Lambda}_{kl} = \delta_{kl} + \sqrt{y_k y_l}\,\frac{\sqrt{m_k m_l}}{RT} \int_v^\infty \widetilde{\partial}^2_{y_k y_l} \phi \, dv', \tag{3.10}$$

so that $\overline{\Lambda}$ is $C^{\varkappa-1}$ function of $\zeta \in \mathcal{O}'_\zeta$, keeping in mind that the mass fractions remain positive when $\zeta \in \mathcal{O}'_\zeta$ and that the estimates associated with (P_0) allow to differentiate under the integral sign. Similarly, we have

$$\widehat{\Lambda}_{\mathsf{r}\,kl} = \delta_{kl} + y_l \frac{m_l}{RT} \int_v^\infty \widetilde{\partial}^2_{y_k y_l} \phi \, dv', \tag{3.11}$$

and

$$\widehat{\Lambda}_{\mathsf{l}\,kl} = \delta_{kl} + y_k \frac{m_k}{RT} \int_v^\infty \widetilde{\partial}^2_{y_k y_l} \phi \, dv', \tag{3.12}$$

so that $\widehat{\Lambda}_{\mathsf{r}}$ and $\widehat{\Lambda}_{\mathsf{l}}$ are also $C^{\varkappa-1}$ function of $\zeta \in \mathcal{O}'_\zeta$. These formulas shows that, whenever $v > \underline{v}$, the matrix $\overline{\Lambda}$ admits a continuous extension for nonnegative mass fractions, and similarly that $\widehat{\Lambda}_{\mathsf{r}}$ and $\widehat{\Lambda}_{\mathsf{l}}$ admit $C^{\varkappa-1}$ extensions to nonnegative mass fractions, since ϕ admits a $C^{\varkappa+1}$ extension to nonnegative mass fractions when $v > \underline{v}$.

Since the mass fractions are positive if $\zeta \in \mathcal{O}'_\zeta$, the matrix $\varPi$ is then invertible. From Sylvester's law of inertia we thus deduce that $\mathsf{d}^+(\Lambda) = \mathsf{d}^+(\overline{\Lambda})$, $\mathsf{d}^0(\Lambda) = \mathsf{d}^0(\overline{\Lambda})$, and $\mathsf{d}^-(\Lambda) = \mathsf{d}^-(\overline{\Lambda})$. Finally, we have $\varPi^{-1}\widehat{\Lambda}_{\mathsf{l}}\varPi = \overline{\Lambda}$ and $\varPi\widehat{\Lambda}_{\mathsf{r}}\varPi^{-1} = \overline{\Lambda}$ so that the matrices $\overline{\Lambda}$, $\widehat{\Lambda}_{\mathsf{r}}$, and $\widehat{\Lambda}_{\mathsf{l}}$, are similar and have the same spectrum. □

We deduce from Proposition 3.4 that $\mathsf{d}^+(\Lambda) = \mathsf{d}^+(\overline{\Lambda}) = \mathsf{d}^+(\widehat{\Lambda}_{\mathsf{r}}) = \mathsf{d}^+(\widehat{\Lambda}_{\mathsf{l}})$, $\mathsf{d}^0(\Lambda) = \mathsf{d}^0(\overline{\Lambda}) = \mathsf{d}^0(\widehat{\Lambda}_{\mathsf{r}}) = \mathsf{d}^0(\widehat{\Lambda}_{\mathsf{l}})$, and $\mathsf{d}^-(\Lambda) = \mathsf{d}^-(\overline{\Lambda}) = \mathsf{d}^-(\widehat{\Lambda}_{\mathsf{r}}) = \mathsf{d}^-(\widehat{\Lambda}_{\mathsf{l}})$, in such a way that any of the matrices Λ, $\overline{\Lambda}$, $\widehat{\Lambda}_{\mathsf{r}}$, or $\widehat{\Lambda}_{\mathsf{l}}$, may be used over $\mathcal{O}'_\zeta$ to determine the stability domain.

We now consider the limiting situation where some mass fractions vanish. For simplicity, we assume that, for some $1 \leqslant n^+ < n$, the positive mass fractions are the n^+ first components of y. The general case is easily reduced to this situation upon introducing permutation matrices [7]. We thus have $y_k > 0$ for $1 \leqslant k \leqslant n^+$ and $y_k = 0$ for $n^+ + 1 \leqslant k \leqslant n$. We denote by $n^0 = n - n^+$ the number of zero mass fractions, y^+ the vector of positive mass fractions and y^0 the vector of zero mass fractions. The indexing set of positive mass fractions is also denoted by $\mathfrak{S}^+$ and that of zero mass fractions by $\mathfrak{S}^0$. The decomposition $\mathbb{R}^n = \mathbb{R}^{n^+} \times \mathbb{R}^{n^0}$ induces a partitionning of vectors and any $\mathsf{x} \in \mathbb{R}^n$ can be written in the form $\mathsf{x} = (\mathsf{x}^+, \mathsf{x}^0)$ and we have for instance $u^+ \in \mathbb{R}^{n^+}$ and $u^+ = (1, \dots, 1)^t$. This partitionning of vectors induces a partitionning of matrices and for any matrix $A \in \mathbb{R}^{n,n}$, we denote by A^{++}, A^{+0}, A^{0+}, A^{00}, the corresponding blocks, in such a way that $(A\,\mathsf{x})^+ = A^{++}\mathsf{x}^+ + A^{+0}\mathsf{x}^0$, and $(A\,\mathsf{x})^0 = A^{0+}\mathsf{x}^+ + A^{00}\mathsf{x}^0$. From the relations (3.8), only the blocks Λ^{++}, Λ^{+0}, and Λ^{0+}, of the matrix Λ are defined for nonnegative mass fractions. This is in contrast with the matrices $\overline{\Lambda}$, $\widehat{\Lambda}_{\mathsf{r}}$, and $\widehat{\Lambda}_{\mathsf{l}}$, which are well defined for nonnegative mass fractions. In addition, the $++$ blocks are associated with the $\mathfrak{S}^+$ submixture, that is, would be obtained by solely considering the species subset indexed by $\mathfrak{S}^+$.

Proposition 3.5. *Assume that Properties* $(\mathsf{P}_0\text{-}\mathsf{P}_1)$ *hold. Assume that* $T > 0$, $v > \underline{v}$, *and that the mass fraction vector is in the form* $y = (y^+, y^0)$, *where* $y^+ \in \mathbb{R}^{n^+}$, $y^0 \in \mathbb{R}^{n^0}$, $y^+ = (y_1, \dots, y_{n^+})^t$, $y^0 = (0, \dots, 0)^t$, $y_i > 0$, $1 \leqslant i \leqslant n^+$, *and* $\langle y, u \rangle = \langle y^+, u^+ \rangle = 1$. *Then we have the block decompositions*

$$\overline{\Lambda} = \begin{pmatrix} \overline{\Lambda}^{++} & 0 \\ 0 & \mathbb{I} \end{pmatrix}, \qquad \widehat{\Lambda}_{\mathsf{r}} = \begin{pmatrix} \widehat{\Lambda}_{\mathsf{r}}^{++} & 0 \\ \widehat{\Lambda}_{\mathsf{r}}^{0+} & \mathbb{I} \end{pmatrix}, \qquad \widehat{\Lambda}_{\mathsf{l}} = \begin{pmatrix} \widehat{\Lambda}_{\mathsf{l}}^{++} & \widehat{\Lambda}_{\mathsf{l}}^{+0} \\ 0 & \mathbb{I} \end{pmatrix},$$

where $\mathbb{I}$ *denotes the identity matrix of size* n^0 *and the symbol* 0 *denotes various rectangular matrices with zero entries so that* $\overline{\Lambda}^{+0} = 0$, $\overline{\Lambda}^{0+} = 0$, $\widehat{\Lambda}_{\mathsf{r}}^{+0} = 0$, *and* $\widehat{\Lambda}_{\mathsf{l}}^{0+} = 0$. *Moreover, denoting by* $\varPi^{++} = \operatorname{diag}(\sqrt{m_1 y_1}, \dots, \sqrt{m_{n^+} y_{n^+}})/\sqrt{R}$ *the upper left block of the matrix* $\varPi$ *we have the relations*

$$\overline{\Lambda}^{++} = \varPi^{++}\Lambda^{++}\varPi^{++}, \qquad \widehat{\Lambda}_{\mathsf{r}}^{++} = \Lambda^{++}(\varPi^{++})^2, \qquad \widehat{\Lambda}_{\mathsf{r}}^{0+} = \Lambda^{0+}(\varPi^{++})^2,$$

$$\widehat{\Lambda}_{\mathsf{l}}^{++} = (\varPi^{++})^2\Lambda^{++}, \qquad \widehat{\Lambda}_{\mathsf{l}}^{+0} = (\varPi^{++})^2\Lambda^{+0}.$$

In particular, we have $\mathsf{d}^+(\Lambda^{++}) = \mathsf{d}^+(\overline{\Lambda}^{++})$, $\mathsf{d}^0(\Lambda^{++}) = \mathsf{d}^0(\overline{\Lambda}^{++})$, *and* $\mathsf{d}^-(\Lambda^{++}) = \mathsf{d}^-(\overline{\Lambda}^{++})$, *and the matrices* $\overline{\Lambda}^{++}$, $\widehat{\Lambda}_{\mathsf{r}}^{++}$, *and* $\widehat{\Lambda}_{\mathsf{l}}^{++}$, *have the same spectrum.*

Proof. These properties are easily obtained from (3.8), (3.10), (3.11), and (3.12), using block manipulations. ☐

An important consequence of Proposition 3.5 is that the stability of multicomponent mixtures can more conveniently be investigated with the help of the matrices $\widehat{\Lambda}_{\mathsf{r}}$ or $\widehat{\Lambda}_{\mathsf{l}}$ which behave smoothly for nonnegative mass fractions so that the whole stability diagram can be constructed over the set $y_i \geqslant 0$, $i \in \mathfrak{S}$, $\langle y, u\rangle = 1$, including automatically all mixture states with zero mass fractions. As a special case, we may also consider the limiting situation of pure species states. Denoting by $\mathsf{e}^1, \dots, \mathsf{e}^n$ the canonical base vectors of $\mathbb{R}^n$ and by ζ^i the state $\zeta^i = (T, v, \mathsf{e}^i)^t$ for $y = \mathsf{e}^i$, we investigate in the following proposition the thermodynamic stability in the neighborhood of e^i.

Proposition 3.6. *Assume that for $\zeta = \zeta^i$ we have $\widetilde{\partial}_T e(\zeta^i) = c_{\mathrm{v}i} > 0$ and $\widetilde{\partial}_v p(\zeta^i) < 0$. Then in the neighborhood of ζ^i thermodynamic stability holds.*

Proof. Denoting $\widetilde{\partial}_T e(\zeta^i) = c_{\mathrm{v}i}(T, v)$, the limit of $\widetilde{\partial}_T e$ when $\zeta \to \zeta^i$ is $c_{\mathrm{v}i}(T, v) > 0$ so that thermal stability holds in the neighborhood of ζ^i. We thus only have to investigate the positive definiteness of the matrix Λ and thus of the matrix $\overline{\Lambda}$. However, the pure state is a special case of Proposition 3.5, and we thus only have to check that the matrix $\overline{\Lambda}(\zeta^i)$ is positive definite. However, thanks to the identity

$$\sum_{i,j\in\mathfrak{S}} y_i y_j \Lambda_{ij} = -\frac{v^2}{T}\widetilde{\partial}_v p, \tag{3.13}$$

the limiting value at ζ^i of the single diagonal coefficients of $\overline{\Lambda}$ eventually different from unity is $\overline{\Lambda}_{ii} = -\frac{m_i v^2}{RT}\widetilde{\partial}_v p(\zeta^i)$ which is positive by assumptions and the proof is complete. ☐

Remark 3.7. *The mechanical stability condition will be automatically satisfied when the pressure is large enough as investigated in Section 5.*

Remark 3.8. *Another limit of interest is the low density limit $v \to \infty$. In this situation, the specific heat at constant volume $\widetilde{\partial}_T e = c_{\mathrm{v}}$ tends to $c_{\mathrm{v}}^{\mathrm{PG}}$ which is positive from* (PG) *and the matrix Λ also becomes positive definite since it asymptotically reduces to the diagonal matrix*

$$\lim_{v\to\infty} \Lambda = R \,\mathrm{diag}\Big(\frac{1}{m_1 y_1}, \dots, \frac{1}{m_n y_n}\Big).$$

A similar asymptotic limit is $\phi \to 0$, which is easily handled, since in this situation we recover the perfect gas model and thermodynamic stability holds.

4 Chemistry sources

We first present the nonideal chemical production rates in Section 4.1 and that of ideal gas mixtures in Section 4.2. We also discuss *inconsistent* production rates sometimes used to model high pressure chemistry in Section 4.3. We next investigate the mathematical structure of the corresponding chemical kinetics in Section 4.4 as well as chemical equilibrium states in Section 4.5.

4.1 Nonideal chemical production rates

We consider in this section the nonideal chemical production rates deduced from statistical physics [23, 24, 25]. These rates are compatible with the symmetric forms of rates of progress derived from the kinetic theory of dilute reactive gases [7, 26]. Note that these rates are only defined where the corresponding thermodynamic is defined. To the authors' knowledge, the nonideal rates of progress have first been derived by Marcelin from chemical and statistical physics considerations [23, 24, 32]. These nonideal rates have also been rederived by Keizer in the framework of an extended statistical theory of nonequilibrium processes [25].

We consider an arbitrary complex reaction mechanism with n^{r} reactions involving n species which may be written symbolically

$$\sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{f}} \mathcal{M}_i \rightleftarrows \sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{b}} \mathcal{M}_i, \qquad j \in \mathfrak{R}, \tag{4.1}$$

where ν_{ij}^{f} and ν_{ij}^{b} denote the forward and backward stoichiometric coefficients of the ith species in the jth reaction, $\mathcal{M}_i$ the symbol of the ith species, and $\mathfrak{R} = \{1, \dots, n^{\mathrm{r}}\}$ the reaction indexing set. Note that all chemical reactions are reversible and that the number of reactions $n^{\mathrm{r}} \geqslant 1$ is arbitrary. We are indeed interested in *elementary* chemical reactions which effectively take place in the fluid mixtures, and elementary reactions are always reversible [7, 33, 34].

The molar production rate of the ith species ω_i is then given by [23, 24, 25]

$$\omega_i = \sum_{j\in\mathfrak{R}} (\nu_{ij}^{\mathrm{b}} - \nu_{ij}^{\mathrm{f}})\tau_j, \tag{4.2}$$

where τ_j denotes the rate of progress of the jth reaction. The proper form for the rate of progress of the jth reaction τ_j is deduced from statistical physics [24, 25]

$$\tau_j = \kappa_j^{\mathrm{s}}\Big(\exp\big(\sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{f}}\mu_i\big) - \exp\big(\sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{b}}\mu_i\big)\Big), \tag{4.3}$$

where κ_j^{s} is the symmetric reaction constant of the jth reaction and μ_i, $i \in \mathfrak{S}$, the species molar dimensionless chemical potentials defined by $\mu_i = m_i g_i/RT$ where g_i denotes the Gibbs function per unit mass of the ith species. This form for rates of progress insures that entropy production due to chemical reactions is nonnegative, coincides with the ideal gas rate in the perfect gas limit [17] and is compatible with traditional nonidealities used to estimate *equilibrium constants* [35, 36].

4.2 Ideal chemical production rates

In the perfect gas limit, we recover from (4.3) the ideal gas rate of progress of the jth reaction τ_j^{PG} given by

$$\tau_j^{\mathrm{PG}} = \kappa_j^{\mathrm{f}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}})^{\nu_{ij}^{\mathrm{f}}} - \kappa_j^{\mathrm{b}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}})^{\nu_{ij}^{\mathrm{b}}}, \tag{4.4}$$

where κ_j^{f} and κ_j^{b} denote the forward and backward reaction constants of the jth reaction, respectively, $\gamma_i^{\mathrm{PG}} = y_i/(v^{\mathrm{PG}} m_i)$ the perfect gas molar concentration of the ith species, $v^{\mathrm{PG}} = (RT/p)\sum_{i\in\mathfrak{S}} \frac{y_i}{m_i}$ the perfect gas volume per unit mass, and where the superscript $^{\mathrm{PG}}$ refers to ideal solutions of perfect gases. The reaction constants κ_j^{f} and κ_j^{b} are related through the ideal gas equilibrium constant $\kappa_j^{\mathrm{e,PG}}$ of the jth reaction

$$\kappa_j^{\mathrm{f}} = \kappa_j^{\mathrm{b}}\kappa_j^{\mathrm{e,PG}}, \qquad \kappa_j^{\mathrm{e,PG}} = \exp\Big(\sum_{i\in\mathfrak{S}} (\nu_{ij}^{\mathrm{f}} - \nu_{ij}^{\mathrm{b}})\mu_i^{\mathrm{u,PG}}\Big), \tag{4.5}$$

where $\mu_i^{\mathrm{u,PG}}$ denotes the perfect gas reduced chemical potential of the ith species at unit concentration. This standard potential is given by

$$\mu_i^{\mathrm{u,PG}} = \frac{m_i g_i^{\mathrm{PG}\star}(T)}{RT} + \ln\Big(\frac{RT}{p^{\mathrm{st}}}\Big), \tag{4.6}$$

where $g_i^{\mathrm{PG}\star}$ denotes the perfect gas specific Gibbs function of the ith species at the standard pressure p^{st}. The perfect gas dimensionless potential $\mu_i^{\mathrm{PG}} = m_i g_i^{\mathrm{PG}}/RT$, where g_i^{PG} is the perfect gas Gibbs function of the ith species, is then given by $\mu_i^{\mathrm{PG}} = \mu_i^{\mathrm{u,PG}} + \ln \gamma_i^{\mathrm{PG}}$. Defining the symmetric constant κ_j^{s} of the jth reaction by

$$\kappa_j^{\mathrm{s}} = \kappa_j^{\mathrm{f}} \exp\big(-\sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{f}}\mu_i^{\mathrm{u,PG}}\big) = \kappa_j^{\mathrm{b}} \exp\big(-\sum_{i\in\mathfrak{S}} \nu_{ij}^{\mathrm{b}}\mu_i^{\mathrm{u,PG}}\big), \tag{4.7}$$

we then recover the ideal gas rate of progress (4.4) from the symmetric form (4.3) and from the relations $\mu_i^{\mathrm{PG}} = \mu_i^{\mathrm{u,PG}} + \ln \gamma_i^{\mathrm{PG}}$, $i \in \mathfrak{S}$ [7]. Identification of both forms for rates of progress (4.7) also yields a method for estimating the symmetric reaction constants κ_j^{s}, $j \in \mathfrak{R}$. In practice, the forward reaction constants κ_j^{f}, $j \in \mathfrak{R}$, are often evaluated from an Arrhenius type expression and the backward reaction constants κ_j^{b}, $j \in \mathfrak{R}$, are obtained through the equilibrium constants $\kappa_j^{\mathrm{e,PG}}$, $j \in \mathfrak{R}$. The ideal gas rates are then evaluated in the form

$$\tau_j^{\mathrm{PG}} = \kappa_j^{\mathrm{f}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}})^{\nu_{ij}^{\mathrm{f}}} - \frac{\kappa_j^{\mathrm{f}}}{\kappa_j^{\mathrm{e,PG}}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}})^{\nu_{ij}^{\mathrm{b}}}, \tag{4.8}$$

and for each reaction $j \in \mathfrak{R}$, the Arrhenius expression reads $\kappa_j^{\mathrm{f}}(T) = \mathfrak{A}_j T^{\mathfrak{b}_j} \exp\big(-\mathfrak{E}_j/RT\big)$ where $\mathfrak{A}_j$ is the preexponential constant, $\mathfrak{b}_j$ the temperature exponent, and $\mathfrak{E}_j$ the activation energy.

The nonideal rates of progress derived from statistical physics (4.3) may equivalently be obtained by defining the activity coefficient a_i of the ith species

$$\mathsf{a}_i = \exp\big(\mu_i - \mu_i^{\mathrm{u,PG}}\big), \tag{4.9}$$

and by replacing γ_i^{PG} by a_i in the classical form of the rates of progress (4.4), keeping in mind that in the ideal gas limit we have $\gamma_i^{\mathrm{PG}} = \exp\bigl(\mu_i^{\mathrm{PG}} - \mu_i^{\mathrm{u,PG}}\bigr)$, $i \in \mathfrak{S}$. Defining for convenience the species activity coefficient $\widetilde{\mathsf{a}}_i$, $i \in \mathfrak{S}$, by $\widetilde{\mathsf{a}}_i = \exp(\mu_i - \mu_i^{\mathrm{PG}})$ so that $\mathsf{a}_i = \gamma_i^{\mathrm{PG}}\, \widetilde{\mathsf{a}}_i$, $i \in \mathfrak{S}$, we may thus evaluate the nonideal rates τ_j, $j \in \mathfrak{R}$, in the form

$$\tau_j = \kappa_j^{\mathrm{f}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{f}}} - \frac{\kappa_j^{\mathrm{f}}}{\kappa_j^{\mathrm{e,PG}}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{b}}}. \tag{4.10}$$

4.3 Hybrid chemical production rates

We further discuss in this section two other forms for rates of progress, intermediate between the ideal gas rates τ_j^{PG}, $j \in \mathfrak{R}$, and the nonideal rates deduced from statistical physics τ_j, $j \in \mathfrak{R}$. These intermediate forms for rates of progress have already been used to model high pressure chemistry.

A first intermediate model—referred to as PG-HP—uses the the perfect gas formulation (4.4) with the same reaction constants but with concentrations evaluated from the high pressure volume per unit mass v

$$\gamma_j = \frac{y_j}{m_j v}. \tag{4.11}$$

Noting that $\gamma_i = \gamma_i^{\mathrm{PG}} \frac{v^{\mathrm{PG}}}{v}$, the equilibrium displacement is then a consequence of the Le Chatellier's principle. These rates, denoted by $\tau_j^{\mathrm{HP-PG}}$, $j \in \mathfrak{R}$, can then be written in the form

$$\tau_j^{\mathrm{HP-PG}} = \kappa_j^{\mathrm{f}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}} \tfrac{v^{\mathrm{PG}}}{v})^{\nu_{ij}^{\mathrm{f}}} - \frac{\kappa_j^{\mathrm{f}}}{\kappa_j^{\mathrm{e,PG}}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}} \tfrac{v^{\mathrm{PG}}}{v})^{\nu_{ij}^{\mathrm{b}}}. \tag{4.12}$$

A second intermediate model—referred to as Hybrid—is an inconsistent attempt to take into account real-gas effects in chemical source terms. It uses the perfect gas formulation (4.4) with the real-gas predicted molar concentrations (4.11), the forward reaction constant κ_j^{f} in standard Arrhenius form, the backward reaction constant in the form $\kappa_j^{\mathrm{b}} = \kappa_j^{\mathrm{f}}/\kappa_j^{\mathrm{e}}$, and the equilibrium constant κ_j^{e} takes into account nonidealities

$$\kappa_j^{\mathrm{e}} = \exp\Bigl(\sum_{l\in\mathfrak{S}} (\nu_{lj}^{f} - \nu_{lj}^{b})\mu_l^{\mathrm{u}}\Bigr), \qquad j \in \mathfrak{R}. \tag{4.13}$$

In other words, the concentrations γ_j, $j \in \mathfrak{S}$, are used in the rates whereas the activities a_j, $j \in \mathfrak{S}$, are used to define the equilibrium constants, so that this often used model is *inconsistent*, and the forward and reverse reactions do not play a symmetric rôle. In terms of the species activity coefficient $\widetilde{\mathsf{a}}_i = \exp(\mu_i - \mu_i^{\mathrm{PG}})$, $i \in \mathfrak{S}$, after some algebra, these rates are in the form

$$\tau_j^{\mathrm{HY}} = \frac{1}{\prod_{i\in\mathfrak{S}} (\frac{v}{v^{\mathrm{PG}}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{f}}}} \Bigl(\kappa_j^{\mathrm{f}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{f}}} - \frac{\kappa_j^{\mathrm{f}}}{\kappa_j^{\mathrm{e,PG}}} \prod_{i\in\mathfrak{S}} (\gamma_i^{\mathrm{PG}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{b}}} \Bigr) = \frac{\tau_j}{\prod_{i\in\mathfrak{S}} (\frac{v}{v^{\mathrm{PG}}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{f}}}}. \tag{4.14}$$

The hybrid rates τ_j^{HY}, $j \in \mathfrak{R}$, are thus found to be proportional to the nonideal rates τ_j, $j \in \mathfrak{R}$, since the equilibrium constants take into account nonidealities. However, they are quantitatively wrong by the factors $\prod_{i\in\mathfrak{S}} (\frac{v}{v^{\mathrm{PG}}} \widetilde{\mathsf{a}}_i)^{\nu_{ij}^{\mathrm{f}}}$, $j \in \mathfrak{R}$.

4.4 Mathematical structure

We describe in this section the mathematical structure of nonideal chemistry source terms. The mathematical structure of chemical kinetics has notably been investigated—generally for homogeneous systems and kinetics of mass action type—by Aris [37], Wei [38], Shapiro and Shapley [4], Pousin [6], Krambeck [5], and Giovangigli and Massot [7, 13, 15].

The species of the mixture are assumed to be constituted by atoms, and we denote by $\mathfrak{a}_{il}$ the number of lth atom in the ith species, $\mathfrak{A} = \{1, \dots, n^{\mathrm{a}}\}$ the set of atom indices, and $n^{\mathrm{a}} \geqslant 1$ the number of atoms—or elements—in the mixture. We first introduce a convenient vector notation in order to investigate the mathematical structure of chemical production rates. The forward and backward reaction vectors ν_j^{f} and ν_j^{b} of the jth reaction are defined by $\nu_j^{\mathrm{f}} = (\nu_{1j}^{\mathrm{f}}, \dots, \nu_{nj}^{\mathrm{f}})^t$ and $\nu_j^{\mathrm{b}} = (\nu_{1j}^{\mathrm{b}}, \dots, \nu_{nj}^{\mathrm{b}})^t$, and the global reaction vector ν_j by $\nu_j = \nu_j^{\mathrm{b}} - \nu_j^{\mathrm{f}}$. The atomic vectors $\mathfrak{a}_l$, $l \in \mathfrak{A}$, are similarly defined by $\mathfrak{a}_l = (\mathfrak{a}_{1l}, \dots, \mathfrak{a}_{nl})^t$ and the unit vector by $u = (1, \dots, 1)^t$. The production vector ω is defined by $\omega = (\omega_1, \dots, \omega_n)^t$ and we have the vector relation $\omega = \sum_{j\in\mathfrak{R}} \tau_j \nu_j$. We further define the vector $\mu = (\mu_1, \dots, \mu_n)^t$, where $\mu_i = m_i g_i/RT$, $i \in \mathfrak{S}$, in such a way that $\tau_j = \kappa_j^{\mathrm{s}}\bigl(\exp\langle \mu, \nu_j^{\mathrm{f}}\rangle - \exp\langle \mu, \nu_j^{\mathrm{b}}\rangle\bigr)$,

$j \in \mathfrak{R}$ where $\langle\, ,\, \rangle$ denotes the Euclidean scalar product. The vector spaces spanned by the reaction vectors and the atomic vectors are denoted by $\mathcal{R}$ and $\mathcal{A}$, respectively

$$\mathcal{R} = \mathrm{span}\{\ \nu_i,\ i \in \mathfrak{R}\ \}, \qquad \mathcal{A} = \mathrm{span}\{\ \mathfrak{a}_l,\ l \in \mathfrak{A}\ \}.$$

We denote by $\mathfrak{m}$ the mass vector $\mathfrak{m} = (m_1, \dots, m_n)^t$ where m_k denotes the molar mass of the kth species and by M the diagonal matrix $\mathsf{M} = \mathrm{diag}(m_1, \dots, m_n)$. The mathematical assumptions associated with the chemical production rates are then the following.

(C_1) *The stoichiometric coefficients* ν_{kj}^{f} *and* ν_{kj}^{b}, $k \in \mathfrak{S}$, $j \in \mathfrak{R}$, *and the atomic coefficients* $\mathfrak{a}_{kl}$, $k \in \mathfrak{S}$, $l \in \mathfrak{A}$, *are nonnegative integers. The atomic vectors* $\mathfrak{a}_l$, $l \in \mathfrak{A}$, *and the reaction vectors* ν_j, $j \in \mathfrak{R}$, *satisfy the atom conservation relations*

$$\langle \nu_j^{\mathrm{b}}, \mathfrak{a}_l\rangle - \langle \nu_j^{\mathrm{f}}, \mathfrak{a}_l\rangle = \langle \nu_j, \mathfrak{a}_l\rangle = 0, \qquad j \in \mathfrak{R}, \quad l \in \mathfrak{A}.$$

(C_2) *The atom masses* $\widetilde{m}_l$, $l \in \mathfrak{A}$, *are positive constants, and the species molar masses* m_k, $k \in \mathfrak{S}$, *are given by*

$$m_k = \sum_{l \in \mathfrak{A}} \widetilde{m}_l\, \mathfrak{a}_{kl}.$$

(C_3) *The symmetric rate constants* κ_j^{s}, $j \in \mathfrak{R}$, *are* C^∞ *positive functions of* $T > 0$.

The reaction and atomic vector spaces are thus such that $\mathcal{R} \subset \mathcal{A}^\perp$ and $\mathcal{A} \subset \mathcal{R}^\perp$. The vector of molar masses $\mathfrak{m}$ can also be written $\mathfrak{m} = \sum_{l\in\mathfrak{A}} \widetilde{m}_l\, \mathfrak{a}_l$.

Remark 4.1. *For realistic complex chemistry networks, the number of chemical reactions is always much larger than the number of chemical species and one usually has* $\mathcal{R} = \mathcal{A}^\perp$. *In other words, the chemical reactions vectors* ν_j, $j \in \mathfrak{R}$, *are spanning the largest possible space. When this is not the case, one has simply to use the space* $\mathcal{R}^\perp$ *instead of* $\mathcal{A}$ *[5].*

Remark 4.2. *The atoms vectors* $\mathfrak{a}_l$, $l \in \mathfrak{A}$, *may be assumed to be linearly independent. When this is not the case, it is first necessary to eliminate linearly dependent atomic vectors.*

Assuming that Properties (T_1-T_4) and (C_1-C_3) hold, the resulting chemical production rates, which involve the chemical potentials μ_i, $i \in \mathfrak{S}$, are thus defined over the open set $\mathcal{O}_\zeta$. From atom conservation and the definition of species masses, we now deduce the mass conservation property.

Lemma 4.3. *The vector of chemical production rates* ω *is such that* $\omega \in \mathcal{R}$ *and* $\mathsf{M}\,\omega \in \mathsf{M}\,\mathcal{R}$. *Moreover, the unity vector satisfies* $u \in (\mathsf{M}\,\mathcal{R})^\perp$ *so that we have the total mass conservation relation* $\langle u, \mathsf{M}\,\omega\rangle = \sum_{k\in\mathfrak{S}} m_k \omega_k = 0$.

Proof. We deduce from (C_1-C_3) that $u = \sum_{l\in\mathfrak{A}} \widetilde{m}_l \mathsf{M}^{-1} \mathfrak{a}_l$ so that $u \in (\mathsf{M}\,\mathcal{R})^\perp$. Moreover, $\omega \in \mathcal{R}$ since $\omega = \sum_{j\in\mathfrak{R}} \tau_j \nu_j$ and thus $\mathsf{M}\,\omega \in \mathsf{M}\,\mathcal{R}$ and finally $\langle \mathsf{M}\,\omega, u\rangle = 0$. ☐

The most important property associated with the nonideal rates is that entropy production is guaranteed to be nonnegative.

Proposition 4.4. *Assume that Properties* (T_1-T_4) *and* (C_1-C_3) *hold and let* $\zeta \in \mathcal{O}_\zeta$. *The reduced entropy production* $\mathfrak{v}(\zeta)$ *due to chemical reactions*

$$\mathfrak{v}(T, v, y_1, \dots, y_n) = -\frac{1}{RT} \sum_{k\in\mathfrak{S}} g_k m_k \omega_k = -\langle \mu, \omega\rangle,$$

is nonnegative and can be written in the form

$$\mathfrak{v} = \sum_{j\in\mathfrak{R}} \kappa_j^{\mathrm{s}} \big(\langle \mu, \nu_j^{\mathrm{f}}\rangle - \langle \mu, \nu_j^{\mathrm{b}}\rangle\big)\ \big(\exp\langle \mu, \nu_j^{\mathrm{f}}\rangle - \exp\langle \mu, \nu_j^{\mathrm{b}}\rangle\big). \tag{4.15}$$

Proof. Rewriting $\mathfrak{v}$ in the form $\mathfrak{v} = -\sum_{j\in\mathfrak{R}, i\in\mathfrak{S}} \mu_i \nu_{ij} \tau_j = \sum_{j\in\mathfrak{R}} \langle \mu, \nu_j^{\mathrm{f}} - \nu_j^{\mathrm{b}}\rangle\, \tau_j$ we directly obtain (4.15) from the expression (4.3) of τ_j, $j \in \mathfrak{R}$. Finally the right hand side of (4.15) is always nonnegative thanks to (C_3) since exp is increasing. ☐

Remark 4.5. *The entropy production associated with the hybrid rates* τ_j^{HY}, $j \in \mathfrak{R}$, *is also nonnegative although these rates are quantitatively erroneous. On the other hand, in the framework of nonideal thermodynamics, the entropy production* $-\sum_{j\in\mathfrak{R}} \langle \mu, \nu_j\rangle \tau_j^{\mathrm{PG}}$ *associated with the perfect gas rates* τ_j^{PG}, $j \in \mathfrak{R}$, *or the entropy production* $-\sum_{j\in\mathfrak{R}} \langle \mu, \nu_j\rangle \tau_j^{\mathrm{HP-PG}}$ *associate with the intermediate rates* $\tau_j^{\mathrm{HP-PG}}$, $j \in \mathfrak{R}$, *are not guaranteed to be nonnegative.*

4.5 Chemical equilibrium

We discuss in this section chemical equilibrium points in atom conservation manifolds under the structural assumptions $(\mathsf{T}_1\text{-}\mathsf{T}_4)$ and $(\mathsf{C}_1\text{-}\mathsf{C}_3)$.

Proposition 4.6. *Assume that Properties* $(\mathsf{T}_1\text{-}\mathsf{T}_4)$ *and* $(\mathsf{C}_1\text{-}\mathsf{C}_3)$ *hold. For any* $\zeta \in \mathcal{O}_\zeta$*, the following statements are equivalent :*

- (i) *The entropy production due to chemistry vanishes* $\mathfrak{v} = 0$.
- (ii) *The reactions rates of progress vanish* $\tau_j = 0$*,* $j \in \mathfrak{R}$.
- (iii) *The species production rates vanish* $\omega_k = 0$*,* $k \in \mathfrak{S}$.
- (iv) *The vector* μ *belongs to* $\mathcal{R}^\perp$.

Proof. From (4.15) and (C_3) we obtain that $\mathfrak{v} = 0$ implies $\langle \mu, \nu_j \rangle = 0$, $j \in \mathfrak{R}$, and so $\tau_j = 0$, $j \in \mathfrak{R}$, and we have established that (i) implies (ii). The fact that (ii) implies (iii) is a consequence of the relations $\omega_k = \sum_{j\in\mathfrak{R}} \tau_j \nu_{kj}$, $k \in \mathfrak{S}$. Moreover, we deduce from the definition $\mathfrak{v} = -\langle \mu, \omega \rangle$ that (iii) implies (i) so that the three statements (i), (ii), and (iii) are equivalent. Finally, it is easily established that (iv) is equivalent to $\langle \mu, \nu_j \rangle = 0$, $j \in \mathfrak{R}$, so that (ii) and (iv) are also equivalent and the proof is complete. □

Definition 4.7. *A point* $\zeta^{\mathrm{e}} \in \mathcal{O}_\zeta$ *which satisfies the equivalent properties of Proposition 4.6 will be termed an equilibrium point.*

We are only interested here in positive equilibrium states which are in the interior $(0,\infty)^n$ of the composition space. Spurious points with zero mass fractions where the source terms ω_k, $k \in \mathfrak{S}$, also vanish—termed 'boundary equilibrium points'—are of a different nature [7]. Properly structures chemical kinetic mechanisms automatically exclude such spurious points unless some element is missing in the mixture [7].

When defining chemical equilibrium states, it is necessary to use equations expressing the fact that atoms are neither created nor destroyed by chemical reactions. These atom conservation relations are typically in the form $\langle y - y^{\mathrm{f}}, \mathsf{M}^{-1}\mathfrak{a} \rangle = 0$, where $\mathfrak{a}$ is an atom vector and y^{f} is a given state, and more generally in the form $\langle y - y^{\mathrm{f}}, u \rangle = 0$, where $u \in (\mathsf{M}\,\mathcal{R})^\perp$. As a consequence, equilibrium points have to be investigated in atom conservation affine manifolds in the form $y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}$. Different equilibrium points may be obtained with various thermal properties kept fixed. We establish in this section the existence of equilibrium points at fixed temperature and volume per unit mass. Existence of equilibrium states is generally obtained by extremalizing a thermodynamic functional over an atom conservation affine subspace [4]. The thermodynamic functional to be maximized or minimized depends on which thermal properties are kept fixed and we refer to [7] for instance for equilibrium points with h and p fixed—in an ideal gas framework—typical of laminar flames.

Theorem 4.8. *Assume that Properties* $(\mathsf{T}_1\text{-}\mathsf{T}_4)$ *and* $(\mathsf{C}_1\text{-}\mathsf{C}_3)$ *hold and let* $T^{\mathrm{e}} > 0$*,* $v^{\mathrm{e}} > 0$*, and* $y^{\mathrm{f}} \in [0,\infty)^n$ *with* $\langle y^{\mathrm{f}}, u \rangle = 1$*. Assume that the reaction simplex* $(y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$ *is not empty and that*

$$\forall y \in (y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n \qquad (T^{\mathrm{e}}, v^{\mathrm{e}}, y_1, \dots, y_n)^t \in \mathcal{O}_\zeta. \tag{4.16}$$

Further assume that $f - f^{\mathrm{PG}}$ *admits a smooth extension to the closure* $(y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap [0,\infty)^n$ *of the reaction simplex. Then there exists a unique equilibrium state* y^{e} *in the simplex* $(y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$.

Proof. We characterize the equilibrium point as the only minimum of the free energy function

$$\varphi(y_1, \dots, y_n) = f(T^{\mathrm{e}}, v^{\mathrm{e}}, y_1, \dots, y_n),$$

over the nonempty simplex $(y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$. The boundedness of the reaction simplex is a direct consequence of $u \in (\mathsf{M}\,\mathcal{R})^\perp$ which implies that $\langle y, u \rangle = \langle y^{\mathrm{f}}, u \rangle$. It is easily deduced that the closure of $(y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$ is $(y^{\mathrm{f}} + \mathsf{M}\,\mathcal{R}) \cap [0,\infty)^n$ which is both compact and convex.

We first establish that φ admits a continuous extension on this compact convex set. The free energy function f is indeed in the form $f = f^{\mathrm{PG}} + (f - f^{\mathrm{PG}})$ and f^{PG} can be written

$$f^{\mathrm{PG}}(T^{\mathrm{e}}, v^{\mathrm{e}}, y_1, \dots, y_n) = \sum_{k\in S} y_k \big(RT \frac{\log y_k}{m_k} + r_k(T^{\mathrm{e}}, v^{\mathrm{e}}) \big),$$

where r_k only depends on T and v

$$r_k(T,v) = f_k^{\rm st} + \int_{T^{\rm st}}^{T} c_k^{\rm PG}(\theta)\,d\theta - T\int_{T^{\rm st}}^{T} \frac{c_k^{\rm PG}(\theta)}{\theta}\,d\theta + \frac{RT}{m_k}\log(v m_k \gamma^{\rm st}).$$

Therefore, $f^{\rm PG}$ admits a continuous extension for zero mass fractions on the reaction simplex as well as the nonideal part $f - f^{\rm PG}$ thanks to assumptions and we conclude that φ is continuous on the closure $(y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap [0,\infty)^n$.

The partial derivative of φ with respect to the mass density vector y over the reaction simplex $(y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$ is also given by

$$\widetilde{\partial}_y\,\varphi = \widetilde{\partial}_y\, f = (g_1,\dots,g_n)^t = RT\mathsf{M}^{-1}\mu.$$

We indeed have from Gibbs relation $f = e - Ts$ so that $\widetilde{\partial}_{y_k} f = \widetilde{\partial}_{y_k} e - T\widetilde{\partial}_{y_k} s$ and $\widetilde{\partial}_{y_k}\varphi = \widetilde{\partial}_{y_k} f = g_k$ from (T_2). We further deduce that $\widetilde{\partial}^2_{y_k y_l}\varphi = \widetilde{\partial}_{y_l} g_k = T\,\Lambda_{kl}$, $k,l \in \mathfrak{S}$, so that

$$\big\langle (\widetilde{\partial}^2_{yy}\varphi)\mathsf{x}_y, \mathsf{x}_y \big\rangle = T\big\langle \Lambda \mathsf{x}_y, \mathsf{x}_y \big\rangle,$$

and φ is strictly convex with $\widetilde{\partial}^2_{yy}\varphi$ positive definite over the simplex $(y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$ since Λ is positive definite.

The function φ admits a minimum on the compact convex set $(y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap [0,\infty)^n$ and we denote by $y_{\rm min}$ a point where φ reaches this minimum. This minimum cannot be reached at the boundaries as established by inspecting the sign of the its derivative. More specifically, assume that $y_{\rm min}$ has some zero component, and define $\mathfrak{S}^+$ and $\mathfrak{S}^0$ such that $y_{{\rm min}k} > 0$ if $k \in \mathfrak{S}^+$ and $y_{{\rm min}k} = 0$ if $k \in \mathfrak{S}^0$. Let $y_{\rm int}$ be a point interior to the simplex $(y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$, so that all components of $y_{\rm int}$ are positive. We may consider the auxiliary function $\psi(t) = \varphi\big(t y_{\rm min} + (1-t) y_{\rm int}\big)$ which is continuous over $[0,1]$ and derivable over $[0,1)$. We also have $\psi = \psi^{\rm PG} + (\psi - \psi^{\rm PG})$ where $\psi^{\rm PG}(t) = \varphi^{\rm PG}\big(t y_{\rm min} + (1-t) y_{\rm int}\big)$ and $(\psi - \psi^{\rm PG})'$ remains bounded over $[0,1]$ since $\widetilde{\partial}_{y_k}(f - f^{\rm PG})$ is defined up to the boundary of the simplex by assumptions. However, we also have

$$(\psi^{\rm PG})'(t) = \sum_{k\in\mathfrak{S}^+} (y_{{\rm min}k} - y_{{\rm int}k}) g_k^{\rm PG} - \sum_{k\in\mathfrak{S}^0} y_{{\rm int}k} g_k^{\rm PG},$$

where $g_k^{\rm PG}$ is evaluated at $t y_{\rm min} + (1-t) y_{\rm int}$ so that as $t \to 1$ the first sum is bounded since $y_{{\rm min}k} > 0$ if $k \in \mathfrak{S}^+$ whereas the second sum goes to $+\infty$ because $y_{{\rm min}k} = 0$ if $k \in \mathfrak{S}^0$. Therefore, we have $\lim_{t\to1} \psi'(t) = +\infty$ and ψ reaches its minimum at $t = 1$, an obvious contradiction. As a consequence, the miminum is reached in the interior, $y_{\rm min} \in (y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$, and, thanks to the strict convexity of φ, this minimum is unique.

We denote with the superscript $^{\rm e}$ the properties associated with the unique point $y^{\rm e}$ where φ is minimum. Since all vectors $y^{\rm e} + \mathsf{M}\,\delta\nu_j$ are in the interior of the reaction simplex $(y^{\rm f} + \mathsf{M}\,\mathcal{R}) \cap (0,\infty)^n$ for δ small enough, we obtain that $\big\langle (\partial_y\varphi)(y^{\rm e}), \mathsf{M}\,\nu_j \big\rangle = 0$, $j \in \mathfrak{R}$. As a consequence, $\mu^{\rm e}$ must be such that $\mathsf{M}^{-1}\mu^{\rm e} \in (\mathsf{M}\,\mathcal{R})^\perp$. Since $(\mathsf{M}\,\mathcal{R})^\perp = \mathsf{M}^{-1}\mathcal{R}^\perp$ we deduce that $\mu^{\rm e} \in \mathcal{R}^\perp$ and the minimum of f is an equilibrium point. Conversely, any equilibrium point on the reaction simplex is such that the quantities $\langle \mu, \nu_j \rangle$, $j \in \mathfrak{R}$, vanish, so that the partial derivatives of φ along the reaction simplex are zero. Since φ is a strictly convex function of y, it reaches a minimum at this point. Therefore, this point coincides with the unique minimum of f and the proof is complete. ☐

Remark 4.9. *Equilibrium points only depend on the vector space $\mathcal{R}$ spanned by the reaction vectors ν_j, $j \in \mathfrak{R}$. On the contrary, forward and backward reaction vectors $\nu_j^{\rm f}$, and $\nu_j^{\rm b}$, $j \in \mathfrak{R}$, are important for the production rates and in order to rule out 'boundary equilibrium points' [7].*

Remark 4.10. *In practical applications, the space $\mathcal{R}$ spanned by the reaction vectors ν_j, $j \in \mathfrak{S}$, is the maximum space $\mathcal{R} = \mathcal{A}^\perp$ so that equilibrium is achieved when $\mu \in \mathcal{A}$.*

Remark 4.11. *The smoothness of $f - f^{\rm PG}$ is a natural assumptions partially introduced by Krambeck [5] who has assumed that $f_i \sim RT\log(y_i/v)$, as $y_i \to 0$, $i \in \mathfrak{S}$. The stability condition* (4.16) *is also natural since otherwise the mixture may not even be stable and several phases may appear so that it does not make sense to look for a single phase equilibrium point.*

Remark 4.12. *Smoothness of equilibrium points is easily obtained by using the implicit function theorem [5, 7].*

5 Application to the SRK equation of state

We present the Soave-Redlich-Kwong equation of state in Section 5.1 and obtain the corresponding thermodynamics in Section 5.2. We then discuss thermodynamic stability, supercritical states, and mechanical stability in Section 5.3.

5.1 SRK equation of state

Various equations of state have been introduced to represent the behavior of dense fluids [39, 40, 41, 42, 43, 44]. The Benedict-Webb-Rubin equation of state [39] and its modified form by Soave [40] are notably accurate but are uneasy to handle. On the other hand, the Soave-Redlich-Kwong equation of state [41, 42] and the Peng-Robinson equation of state [43] yield less accuracy but allow an easier inversion by using Cardan's formula thanks to their cubic form. These cubic equations of state give accurate results over the range of pressures, temperatures and mixture states of interest for supercritical combustion [19, 20, 21, 22, 17].

In this paper, we investigate the Soave-Redlich-Kwong equation of state [41, 42]

$$p = \sum_{i \in \mathfrak{S}} \frac{y_i}{m_i} \frac{RT}{v-b} - \frac{a}{v(v+b)}, \tag{5.1}$$

where p denotes the pressure, R the perfect gas constant, v the volume per unit mass, and a and b the attractive and repulsive parameters per unit mass, respectively. These parameters $a(T, y_1, \dots, y_n)$ and $b(y_1, \dots, y_n)$ are evaluated with the usual Van der Waals mixing rules written here with a mass based formulation

$$a = \sum_{i,j \in \mathfrak{S}} y_i y_j \alpha_i \alpha_j \qquad b = \sum_{i \in \mathfrak{S}} y_i b_i. \tag{5.2}$$

The pure-component parameters $\alpha_i(T) = \sqrt{a_i(T)}$ and b_i are deduced from the corresponding macroscopic fluid behavior or from interaction potentials as discussed in Appendix B. The validity of this equation of state (5.1) and of the corresponding mixing rules (5.2) have been carefully studied by comparison with NIST data by Congiunti et al. [45] and with results of Monte Carlo simulations by Colonna and Silva [46] and Cañas-Marín et al. [47, 48]. This equation of state has been used in high pressure combustion models by Meng and Yang [20], Ribert et al. [22], and Giovangigli et al. [17].

From a mathematical point of view, we assume the following properties on the coefficients $\alpha_i(T)$, and b_i, $i \in \mathfrak{S}$, where $\varkappa \in \mathbb{N}$ and $\varkappa \geqslant 2$.

(SRK) *For any $i \in \mathfrak{S}$, $\alpha_i \in C^0[0,\infty) \cap C^{1+\varkappa}(0,\infty)$, $\alpha_i(0) > 0$, $\alpha_i \geqslant 0$, $\lim_{+\infty} \alpha_i = 0$, $\widetilde{\partial}_T \alpha_i \leqslant 0$ and $\widetilde{\partial}^2_{TT} \alpha_i \geqslant 0$ over $(0,\infty)$, and the parameters b_i, $i \in \mathfrak{S}$, are positive constants.*

The following proposition is easily deduces from (SRK).

Proposition 5.1. *Assume that* (SRK) *holds and denote $a = a(T,y)$. Then $a \in C^0[0,\infty) \times (0,\infty)^n$, $a \in C^{1+\varkappa}(0,\infty) \times (0,\infty)^n$, $a(0,y) > 0$, $a \geqslant 0$, $\lim_{T \to +\infty} a(T,y) = 0$, $\widetilde{\partial}_T a \leqslant 0$ and $\widetilde{\partial}^2_{TT} a \geqslant 0$ over $(0,\infty) \times (0,\infty)^n$.*

In practice, the attractive parameters are taken in a special form [17] analyzed in the following proposition.

Proposition 5.2. *Assume that α_i is in the form*

$$\frac{\alpha_i}{\alpha_{\mathrm{c},i}} = 1 + A\big(\mathrm{s}_i(1 - \sqrt{T}/\sqrt{T_{\mathrm{c},i}})\big), \tag{5.3}$$

where $\alpha_{\mathrm{c},i}$, s_i, and $T_{\mathrm{c},i}$ are positive constants and $A \in C^{1+\varkappa}(\mathbb{R})$. Further assume that $A' \geqslant 0$, $A'' \geqslant 0$, $A(0) = 0$, $-1 \leqslant A$, and $\lim_{-\infty} A = -1$. Then Property (SRK) *holds.*

Proof. Since A is $C^{1+\varkappa}(\mathbb{R})$ it is easily checked that, for any $i \in \mathfrak{S}$, we have $\alpha_i \in C^0[0,\infty) \cap C^{1+\varkappa}(0,\infty)$ and for $T > 0$ we have

$$\frac{\alpha_i'}{\alpha_{\mathrm{c},i}} = -\frac{\mathrm{s}_i}{2(T T_{\mathrm{c},i})^{1/2}} A'\big(\mathrm{s}_i(1 - \sqrt{T}/\sqrt{T_{\mathrm{c},i}})\big),$$

$$\frac{\alpha_i''}{\alpha_{\mathrm{c},i}} = \frac{\mathrm{s}_i}{4T^{3/2}T_{\mathrm{c},i}^{1/2}} A'\big(\mathrm{s}_i(1 - \sqrt{T}/\sqrt{T_{\mathrm{c},i}})\big) + \frac{\mathrm{s}_i^2}{4T T_{\mathrm{c},i}} A''\big(\mathrm{s}_i(1 - \sqrt{T}/\sqrt{T_{\mathrm{c},i}})\big).$$

Thanks to the properties of A, we deduce that for any positive temperature $\alpha_i'(T) \leqslant 0$ and $\alpha_i''(T) \geqslant 0$ so that α_i is decreasing and convex. Finally we have $\alpha_i(0) = \alpha_{\mathrm{c},i}\big(1 + A(\mathrm{s}_i)\big)$ and $A(\mathrm{s}_i) \geqslant 0$ since A is increasing and $A(0) = 0$ so that $\alpha_i(0) > 0$. Moreover, we also have $\lim_{T\to+\infty} \alpha_i(T) = 0$ since $\lim_{x\to-\infty} A(x) = -1$ and the proof is complete. $\square$

Remark 5.3. *As typical function A we may use*

$$A(x) = \begin{cases} x, & \textit{if } x \geqslant 0, \\ x/(1+x^4)^{1/4}, & \textit{if } x \leqslant 0. \end{cases} \tag{5.4}$$

It is easlily checked that $A \in C^4(\mathbb{R})$, $A' \geqslant 0$, $A'' \geqslant 0$, $A(0) = 0$, $-1 \leqslant A$, and $\lim_{-\infty} A = -1$, so that the assumptions of Proposition 5.2 hold.

Remark 5.4. *In the limiting situation $\varkappa = 1$, excluded from* (SRK)*, Proposition 5.1, and Proposition 5.2, smoothness with respect to ζ is not guaranteed, that is, $s(\zeta)$ may only be derived once. However, one may establish that entropy is still twice derivable with respect to the thermodynamic variable ξ so that* (T_2-T_4) *still makes sense.*

From physical considerations the coefficient $\alpha_i = \sqrt{a_i}$ should be positive for small temperature and should be a decreasing function of temperature as pointed out by Ozokwelu and Erbar [49] and Grabovski and Daubert [50]. Moreover, the coefficient $\alpha_i = \sqrt{a_i}$ should goes to zero as $T \to \infty$ since we must recover the perfect gas equation of states for increasing temperatures. The coefficients introduced by Soave, and associated with the choice $A(x) = |1+x| - 1$, do not satisfy such a property and do not satisfy the assumptions of Proposition 5.2. Even if it is possible to truncate these coefficients by using $A(x) = |1+x|^+ - 1$, where $y^+ = \max(y, 0)$, neither the Soave coefficients nor their truncated version are regular enough for mixtures of gases since they introduce small jumps in the temperature derivative of the attractive factor $\alpha_i = \sqrt{a_i}$ and thereby of the attractive parameter $a = \sum_{i,j\in\mathfrak{S}} y_i y_j \alpha_i \alpha_j$ at the crossing temperatures $T_{\mathrm{c},i}(1 + 1/\mathrm{s}_i)^2$, $i \in \mathfrak{S}$. Even though such small jumps only arise in regions where the temperature is high and where nonidealities are usually negligible, it is preferable—from a numerical as well as mathematical point of view—to have smoother attractive factors. Numerical spurious behavior has indeed been observed due to these small discontinuities of the attractive factor temperature derivative. The modifications of the Soave coefficients associated with Proposition 5.2 and Remark 5.3 have been introduced by the authors and yields thermodynamic properties that are in very close agreement [17].

5.2 SRK thermodynamics

We investigate in this section the thermodynamics associated with the SRK equation of state from Theorem 3.2. We first investigate the structural properties (P_0-P_1).

Proposition 5.5. *The pressure corrector ϕ associated with the equation of state* (5.1) *is given by*

$$\phi = \Big(\sum_{i\in\mathfrak{S}} \frac{RTy_i}{m_i}\Big) \frac{b}{v(v-b)} - \frac{a}{v(v+b)}. \tag{5.5}$$

Assuming (SRK)*, the pressure corrector ϕ satisfies Properties* (P_0-P_1) *over the domain*

$$\mathcal{O}_\zeta' = \{\, \zeta \in (0,\infty)^{2+n};\ v > b \,\}, \tag{5.6}$$

with the particular value $\underline{v} = 2\max_{i\in\mathfrak{S}} b_i$.

Proof. A calculation directly yields the expression (5.5) for the pressure corrector ϕ. Considering then any factor in the form $\chi = \mathsf{a}/\big(v(v+\mathsf{b})\big)$ where a and b are two C^k functions of $(T, y_1, \ldots, y_n)$, an easy induction shows that for any multiindex $\beta \in \mathbb{N}^{n+2}$, $\beta = (\beta_T, \beta_v, \beta_1, \ldots, \beta_n)$, with $|\beta| \leqslant k$, the derivative $\widetilde{\partial}_\zeta^\beta \chi$ is a linear combination with constant coefficients of terms in the form $\widehat{\mathsf{a}}/\big(v^\gamma (v+\mathsf{b})^\delta\big)$ where $\widehat{\mathsf{a}}$ is a product of derivatives of a and b of order lower than k and where $\gamma \geqslant 1$ and $\delta \geqslant 1$ are such that $\gamma + \delta \geqslant 2 + \beta_v$. We may now use this result first with $k = 1 + \varkappa$, $\mathsf{a} = (\sum_{i\in\mathfrak{S}} RTy_i/m_i)\, b$ and $\mathsf{b} = -b$, and next with $k = 1 + \varkappa$, $\mathsf{a} = a$ and $\mathsf{b} = b$, keeping in mind that $a = \sum_{i,j\in\mathfrak{S}} y_i y_j \alpha_i \alpha_j$, $b = \sum_{i\in\mathfrak{S}} y_i b_i$, that ($\mathsf{SRK}$) holds, and that $1/(v-b) \leqslant 2/v$ and $1/v \leqslant 1/\underline{v}$ when $v \geqslant \underline{v} \geqslant 2b$. We then obtain that for any multiindex $\beta \in \mathbb{N}^{n+2}$ with $|\beta| \leqslant 1 + \varkappa$, there exists $\mathsf{c}(\beta, T)$ depending continuously on T and on β, such that whenever $T > 0$, $v \geqslant 2\max_{i\in\mathfrak{S}} b_i$, and $y_i \geqslant 0$, $i \in \mathfrak{S}$, and $\sum_{i\in\mathfrak{S}} y_i = 1$, we have

$$|\widetilde{\partial}_\zeta^\beta \phi| \leqslant \frac{\mathsf{c}(\beta,T)}{v^{\beta_v+2}}. \tag{5.7}$$

In addition, since a is 2-homogeneous in $(y_1,\dots,y_n)$ and b is 1-homogeneous, we directly deduce that p and ϕ are 0-homogeneous in $(v, y_1,\dots,y_n)$. □

Properties (P_0-P_1) are thus established and, following Proposition 3.1, the thermodynamic functions can then be evaluated. Thanks to the special form of the SRK equation of state, it is further possible to evaluate these properties explicitly. From (5.5), the mixture internal energy e is indeed found in the close form

$$e = \sum_{i\in\mathfrak{S}} y_i e_i^{\rm PG} + \big(T\widetilde{\partial}_T a - a\big)\frac{1}{b}\ln\big(1+\frac{b}{v}\big), \tag{5.8}$$

where $e_i^{\rm PG} = e_i^{\rm PG}(T)$ denotes the perfect gas specific energy of the ith species. Similarly, the mixture entropy s reads

$$s = \sum_{i\in\mathfrak{S}} y_i s_i^{\rm PG\star} - \sum_{i\in\mathfrak{S}} \frac{y_i R}{m_i}\ln\Big(\frac{y_i RT}{m_i(v-b)p^{\rm st}}\Big) + \frac{\widetilde{\partial}_T a}{b}\ln\big(1+\frac{b}{v}\big), \tag{5.9}$$

where $s_i^{\rm PG\star} = s_i^{\rm PG\star}(T)$ denotes the perfect gas specific entropy of the ith species at pressure $p^{\rm st}$. The enthalpy h and Gibbs function g per unit mass are also easily evaluated in the form

$$h = \sum_{i\in\mathfrak{S}} y_i h_i^{\rm PG} + \big(T\widetilde{\partial}_T a - a\big)\frac{1}{b}\ln\big(1+\frac{b}{v}\big) + \sum_{i\in\mathfrak{S}} \frac{y_i}{m_i}\frac{RTb}{v-b} - \frac{a}{v+b}, \tag{5.10}$$

where $h_i^{\rm PG} = h_i^{\rm PG}(T)$ denotes the perfect gas specific enthalpy of the ith species, and the Gibbs function $g = f + pv$ is given by

$$\begin{aligned} g \;=\; & \sum_{i\in\mathfrak{S}} y_i\big(h_i^{\rm PG} - Ts_i^{\rm PG\star}\big) + \sum_{i\in\mathfrak{S}} \frac{y_i}{m_i} RT\ln\big(\frac{y_i RT}{m_i p^{\rm st}(v-b)}\big) \\ & + \sum_{i\in\mathfrak{S}} \frac{y_i}{m_i}\frac{RTb}{v-b} - \frac{a}{b}\ln\big(1+\frac{b}{v}\big) - \frac{a}{v+b}. \end{aligned} \tag{5.11}$$

5.3 SRK thermodynamic stability

We first establish that the thermal stability condition holds.

Proposition 5.6. *The heat par unit mass at constant volume of the mixture* $c_{\rm v} = \widetilde{\partial}_T e$ *is given by*

$$c_{\rm v} = c_{\rm v}^{\rm PG} + \frac{T\widetilde{\partial}^2_{TT} a}{b}\ln\big(1+\frac{b}{v}\big), \tag{5.12}$$

where $c_{\rm v}^{\rm PG} = \sum_{i\in\mathfrak{S}} y_i c_{{\rm v},i}^{\rm PG}$ *and* (SRK) *insures that thermal stability holds.*

Proof. We only have to derive (5.8) with respect to temperature in order to obtain (5.12). The inequality $\widetilde{\partial}^2_{TT} a \geqslant 0$ is then a direct consequence of Proposition 5.1. □

We now investigate the mechanical stability condition for the SRK cubic equation of state. In order to simplify notation, we define $r = R\sum_{i\in\mathfrak{S}} y_i/m_i$ so that the equation of state is written in the form

$$p = \frac{rT}{v-b} - \frac{a}{v(v+b)}. \tag{5.13}$$

Proposition 5.7. *For any* $y \in (0,\infty)^n$ *and* $v > b$, *there exists a unique temperature* $T^\star(v,y) > 0$ *such that* $\widetilde{\partial}_v p(T^\star, v, y) = 0$. *This temperature satisfies the nonlinear equation*

$$T^\star = \frac{a^\star}{r}\frac{(v-b)^2(2v+b)}{v^2(v+b)^2}, \tag{5.14}$$

where $a^\star = a(T^\star, y)$, $T^\star$ *is a* $C^\varkappa$ *function of* $v, y_1,\dots,y_n$ *and we have the relations*

$$\widetilde{\partial}^2_{Tv} p\, \widetilde{\partial}_v T^\star + \widetilde{\partial}^2_{vv} p = 0, \qquad \widetilde{\partial}^2_{Tv} p\, \widetilde{\partial}_{y_k} T^\star + \widetilde{\partial}^2_{v\,y_k} p = 0, \quad k \in \mathfrak{S}. \tag{5.15}$$

Finally, for any fixed y $(0,\infty)^n$, *we have*

$$\lim_{v\to b} T^\star = 0, \qquad \lim_{v\to\infty} T^\star = 0. \tag{5.16}$$

Proof. The partial derivative $\widetilde{\partial}_v p$ can be written

$$\widetilde{\partial}_v p = -\frac{rT}{(v-b)^2} + \frac{a(2v+b)}{v^2(v+b)^2}, \tag{5.17}$$

so that we have

$$\widetilde{\partial}^2_{Tv} p = -\frac{r}{(v-b)^2} + \frac{\widetilde{\partial}_T a(2v+b)}{v^2(v+b)^2}, \tag{5.18}$$

and since $\widetilde{\partial}_T a \leqslant 0$, we deduce that $\widetilde{\partial}_{Tv} p$ remains strictly negative. Moreover, we have for $T = 0$

$$\widetilde{\partial}_v p(0, v, y_1, \ldots, y_n) = \frac{a(0,y)\,(2v+b)}{v^2(v+b)^2} > 0,$$

since $a(0,y) = \sum_{i,j\in\mathfrak{S}} y_i y_j \alpha_i(0)\alpha_j(0) > 0$, and since $a(T,y)$ is bounded as a function of temperature we also get that

$$\lim_{T\to\infty} \widetilde{\partial}_v p(T, v, y_1, \ldots, y_n) = -\infty.$$

As a consequence, for any fixed $v, y_1, \ldots, y_n$ there exists a unique temperature $T^\star > 0$ such that $\widetilde{\partial}_v p(T^\star, v, y) = 0$, and this relation directly yields (5.14). From the implicit function theorem, the temperature $T^\star(v,y)$ is a $C^{\varkappa}$ function of $v, y_1, \ldots, y_n$ and we obtain the relations (5.15). Finally, since a is a bounded function of temperature, we deduce (5.16) from (5.14) and the proof is complete. ☐

Corollary 5.8. *We have the equivalence*

$$\widetilde{\partial}_v p(T, v, y) > 0 \Longleftrightarrow T < T^\star(v, y), \tag{5.19}$$

and since the derivative $\widetilde{\partial}_T p$ at fixed $v, y_1, \ldots, y_n$ is always positive, defining

$$p^\star(v, y) = p\big(T^\star(v, y), v, y\big), \tag{5.20}$$

we also have

$$\widetilde{\partial}_v p(T, v, y) > 0 \Longleftrightarrow p(T, v, y) < p^\star(v, y). \tag{5.21}$$

In other words, the mechanical stability condition $\widetilde{\partial}_v p(T, v, y) < 0$ is equivalent to $T < T^\star(v, y)$ or to $p(T, v, y) < p^\star(v, y)$ and we are now interested in the maximum value of $T^\star$ when v is varying. The corresponding point corresponds to the usual critical points *for fixed mass fractions* [36].

Proposition 5.9. *For any $y \in (0,\infty)^n$ there exists a unique maximum positive value of $T^\star$ for $v \in (b, \infty)$ and this maximum is reached for $v = \theta_{\mathrm{c}} b$, where $\theta_{\mathrm{c}} = 1/(\sqrt[3]{2} - 1)$.*

Proof. From (5.16) there exists a maximum positive value of $T^\star$ for $v \in (b, \infty)$ at fixed y. This maximum value of $T^\star$ is such that $\widetilde{\partial}_v T^\star = 0$ and thus $\widetilde{\partial}^2_{vv} p = 0$ from (5.15). The system of equations $\widetilde{\partial}_v p = 0$ and $\widetilde{\partial}^2_{vv} p = 0$ leads to the relations

$$-\frac{rT}{(v-b)^2} + \frac{a(2v+b)}{v^2(v+b)^2} = 0, \qquad \frac{rT}{(v-b)^3} - \frac{a(2v^2+3v+b)}{v^3(v+b)^3} = 0. \tag{5.22}$$

After some algebra, one may eliminate the temperature T and the coefficients r and a from one of the equations to obtain that $v^3 - 3v^2 b - 3vb^2 - b^3 = 0$. Upon rewriting this equation in the form $2v^3 = (v+b)^3$ we obtain the unique real solution $v_{\mathrm{c}} = \theta_{\mathrm{c}} b$ where $\theta_{\mathrm{c}} = 1/(\sqrt[3]{2} - 1)$ which is thus the unique solution within (b, ∞). Finally, we note that the corresponding $T^\star(\theta_{\mathrm{c}} b, y)$ satisfies the relation (5.14) evaluated for $v = \theta_{\mathrm{c}} b$. ☐

Corollary 5.10. *For any fixed $y \in (0,\infty)^n$, define the functions $T^{\star\star}(y)$ and $p^{\star\star}(y)$ with*

$$T^{\star\star}(y) = T^\star(\theta_{\mathrm{c}} b, y), \tag{5.23}$$

$$p^{\star\star}(y) = p^\star\big(\theta_{\mathrm{c}} b, y\big) = p\big(T^\star(\theta_{\mathrm{c}} b, y), \theta_{\mathrm{c}} b, y\big), \tag{5.24}$$

keeping in ming that $b = \sum_{i\in\mathfrak{S}} y_i b_i$. Then $T^{\star\star}(y)$ and $p^{\star\star}(y)$ correspond to the critical temperature and pressure of the frozen mixture with mass fractions y. Moreover, we always have the inequality

$$p^\star(v, y) \leqslant p^{\star\star}(y),$$

so that $\widetilde{\partial}_v p > 0$ implies $p(T, v, y) < p^{\star\star}(y)$. Finally, since the set $\overline{\Sigma} = \{y \in [0,\infty)^n;\ \langle y, u\rangle = 1\}$ is compact and $p\big(T^\star(\theta_{\mathrm{c}} v, y), \theta_{\mathrm{c}} v, y\big)$ is a smooth function of y, there exists a maximum pressure $\max_{y\in\overline{\Sigma}} p^{\star\star}(y)$ above which the fluid is supercritical for all mixtures.

Proof. Deriving $p^\star$ with respect to v we obtain that

$$\widetilde{\partial}_v p^\star = \widetilde{\partial}_T p\, \widetilde{\partial}_v T^\star + \widetilde{\partial}_v p = \widetilde{\partial}_T p\, \widetilde{\partial}_v T^\star.$$

Therefore, $\widetilde{\partial}_v p^\star$ has the sign of $\widetilde{\partial}_v T^\star$ which has the sign of $v - \theta_{\rm c} b$. This implies that $p^\star$ increases with v over $(b, \theta_{\rm c} b]$, decreases with v over $[\theta_{\rm c} b, \infty)$, and $p^\star\big(v, y\big) \leqslant p^\star\big(\theta_{\rm c} b, y\big) = p^{\star\star}(y)$. ☐

We incidentally investigate when the pressure given by the SRK equation of state is positive keeping in mind that pressure may be negative in a fluid [29].

Proposition 5.11. *For any $y \in (0,\infty)^n$ and any $v > b$, there exists a unique temperature $T^0(v, y) > 0$ such that $p(T^0, v, y) = 0$. This temperature satisfies the nonlinear equation*

$$T^0 = \frac{a^0}{r} \frac{v - b}{v(v + b)}, \tag{5.25}$$

where $a^0 = a(T^0, y)$, T^0 is a $C^\varkappa$ function of $v, y_1, \dots, y_n$ and we have the relations

$$\widetilde{\partial}_T p\, \widetilde{\partial}_v T^0 + \widetilde{\partial}_v p = 0, \qquad \widetilde{\partial}_T p\, \widetilde{\partial}_{y_k} T^0 + \widetilde{\partial}_{y_k} p = 0, \quad k \in \mathfrak{S}. \tag{5.26}$$

For any fixed y $(0, \infty)^n$, we also have

$$\lim_{v \to b} T^0 = 0, \qquad \lim_{v \to \infty} T^0 = 0. \tag{5.27}$$

Finally, we have $T^\star > T^0$ if and only if $v > (1 + \sqrt{2})b$.

Proof. The partial derivative $\widetilde{\partial}_T p$ can be written

$$\widetilde{\partial}_T p = \frac{r}{v - b} - \frac{\widetilde{\partial}_T a}{v(v + b)}, \tag{5.28}$$

and remains strictly positive. Moreover, we have for $T = 0$

$$p(0, v, y_1, \dots, y_n) = -\frac{a(0, y)}{v(v + b)} < 0,$$

since $a(0, y) > 0$, and since $a(T, y)$ is bounded as a function of temperature we also get that

$$\lim_{T \to \infty} p(T, v, y_1, \dots, y_n) = \infty.$$

As a consequence, for any fixed $v, y_1, \dots, y_n$ with $v > b$ there exists a unique temperature $T^0 > 0$ such that $p(T^0, v, y) = 0$, and this relation directly yields (5.25). From the implicit function theorem, the temperature $T^0(v, y)$ is a $C^\varkappa$ function of $v, y_1, \dots, y_n$ and we obtain the relations (5.26). Moreover, since a is a bounded function of temperature, we deduce (5.27) from (5.25).

In order to compare the temperatures $T^\star$ and T^0, we consider for y fixed the function of temperature $\mathcal{L}(T) = rT/a(T, y)$ which is only defined over the interval where $a(T, y)$ remains positive. This function $\mathcal{L}$ is a strictly increasing function of temperature as long as $a(T, y)$ is positive since

$$\mathcal{L}'(T) = \frac{r}{a} - \frac{rT}{a^2} \widetilde{\partial}_T a.$$

On the other hand, $a(T^0, y) > 0$ and $a(T^\star, y) > 0$ from (5.25) and (5.14), and we have

$$\mathcal{L}(T^\star) = \frac{(v - b)^2 (2v + b)}{v^2 (v + b)^2}, \qquad \mathcal{L}(T^0) = \frac{v - b}{v(v + b)}.$$

As a consequence, $T^\star - T^0$ has the sign of $(2v + b)(v - b) - v(v + b)$ which is easily rewritten into $v^2 - 2bv - b^2$ and the only positive zero of this expression is $v = (1 + \sqrt{2})b$ so that finally $T^\star > T^0$ if and only if $v > (1 + \sqrt{2})b$ and the proof is complete. ☐

Corollary 5.12. *For any $y \in \overline{\Sigma}$, the critical pressure $p^{\star\star}(y)$, is positive.*

Proof. This results from $\theta_{\rm c} = 1/(\sqrt[3]{2} - 1) > 1 + \sqrt{2}$ thanks to $1 + \sqrt{2} = 1/(\sqrt{2} - 1)$. ☐

Properties (P_0-P_2) have already been established in the framework of the SRK equation of state. From Section 3.3 we also know that Property (P_3) holds if v is large, or if we are close to a pure species state for which thermal and mechanical stability hold. We will investigate more closely (P_3) in Section 6 since *thermodynamic stability may not hold at high pressure and low temperature* and mixtures may split into several phases in agreement with experimental results. In the special situation of the SRK equation of state, the matrix Λ is given by the following proposition.

Proposition 5.13. *The coefficients of the matrix Λ are given by*

$$\begin{aligned}\Lambda_{ij} =& \frac{R\delta_{ij}}{m_i y_i} + \frac{R}{v-b}\Big(\frac{b_i}{m_j} + \frac{b_j}{m_i}\Big) + \sum_{k\in\mathfrak{S}} \frac{y_k}{m_k}\frac{R}{(v-b)^2} b_i b_j - \frac{2}{T}\frac{a_{ij}}{b}\ln\Big(1+\frac{b}{v}\Big) \\ &+ \frac{2}{T}\sum_{k\in\mathfrak{S}} y_k\big(a_{ik}b_j + a_{jk}b_i\big)\Big(\frac{1}{b^2}\ln\Big(1+\frac{b}{v}\Big) - \frac{1}{b(v+b)}\Big) \\ &+ \frac{1}{T} a b_i b_j\Big(-\frac{2}{b^3}\ln\Big(1+\frac{b}{v}\Big) + \frac{2}{b^2(v+b)} + \frac{1}{b(v+b)^2}\Big), \qquad i,j\in\mathfrak{S}. \qquad (5.29)\end{aligned}$$

Proof. This proposition is a direct consequence of (5.11). ☐

6 Numerical simulations for H_2-O_2-N_2 mixtures

We investigate in this section the thermodynamic stability of H_2-O_2-N_2 mixtures at low temperature and high pressure as well as the rôle of nonidealities in a typical transcritical hydrogen/air flame.

6.1 Thermodynamic stability of H_2-O_2-N_2 mixtures

The thermodynamic stability of ternary mixtures H_2-O_2-N_2 has been studied at pressure 200 atm. Thanks to the equivalent formulations of Proposition 3.4, we have located the first zero eigenvalue of the matrix $\widehat{\Lambda}^{\mathsf{r}}$ by investigating the first zero of its determinant. To this aim, we have used nonlinear solvers and continuation methods [51, 52] in order to generate the whole stability domain. Similar results have also been obtained at 100 atm or other pressures as long as they are above the critical pressures of H_2, O_2, and N_2 [17].

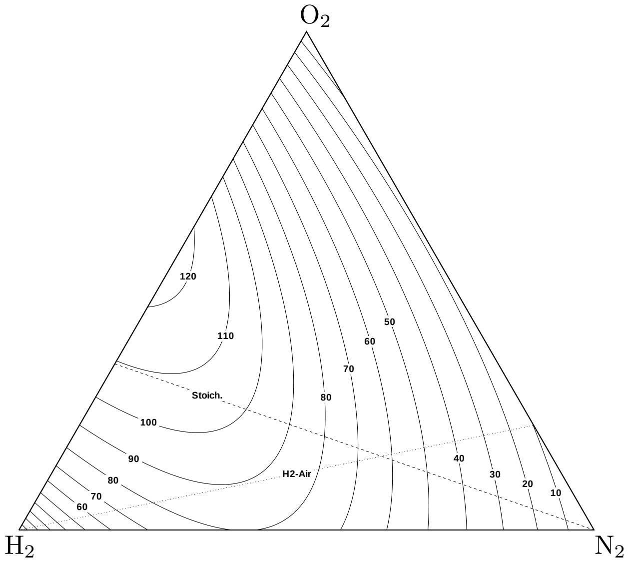

Figure 1: Thermodynamic stability limits isotherms for ternary H_2-O_2-N_2 mixture at 200 atm

The boundary of the stability domain for various temperatures at $p = 200$ atm is presented in Figure 1. The stable zones are easily identified since they include the corners associated with pure species states as established in Proposition 3.6. The critical pressures of H_2, O_2, and N_2, and indeed 12.8 atm, 49.8 atm, and 33.5 atm, respectively, and these pressures are below 200 atm. The unstable zone starts above 120 K between H_2 and O_2, increases as T decreases, and reach the H_2-N_2 boundary around 80 K. The binary O_2-N_2 mixture is predicted to be stable down to very low temperatures. The presence of H_2 thus has a destabilizing effect and rises the stability limit up to 120 K in H_2-O_2 binary mixtures and up to 80 K in H_2-N_2 binary mixtures.

Verschoyle [27] and Eubanks [28] have investigated binary mixtures of H_2 and N_2 at high pressure and low temperature. An important experimental result is that binary mixtures of H_2 and N_2 may not be thermodynamically stable at sufficiently high pressure and low temperature. In these situations, a mixture of H_2 and N_2 splits between a hydrogen-rich gaseous-like phase and a hydrogen-poor liquid-like phase [27, 28] in qualitative agreement with the theoretical results obtained from the SRK equation of state in Figure 1. Quantitative comparisons have been conducted with respect to the split phases and very good agreement has been obtained [17].

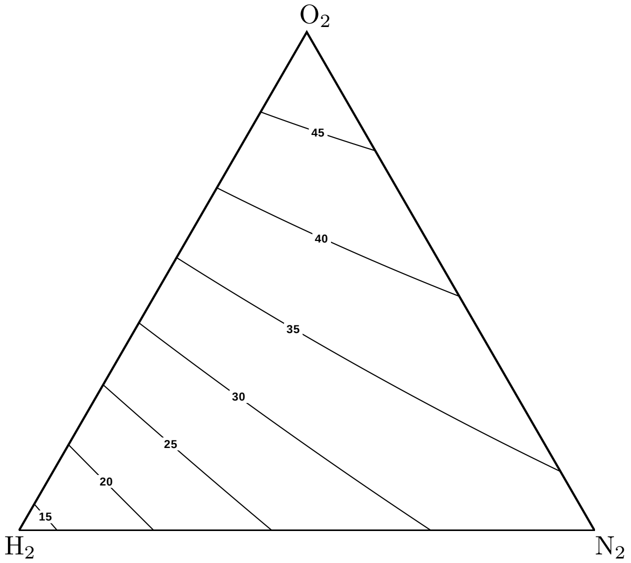

Figure 2: Critical pressure $p^{\star\star}$ for ternary H_2-O_2-N_2 mixtures

We next present in Figure 2 the critical pressure $p^{\star\star}(y)$ of H_2-O_2-N_2 mixtures for $y \in \overline{\Sigma}$. The critical pressure is typically between 12.8 and 49.8 atm which are the critical pressures of pure H_2 and O_2. In particular, above 49.8 atm, all H_2-O_2-N_2 mixtures are guaranteed to be in a supercritical state and the mechanical stability condition $\widetilde{\partial}_v p < 0$ is then fulfilled. This confirms that the thermodynamical unstable states presented in Figure 1 are associated with thermodynamical chemical instabilities and not thermodynamical mechanical instabilities.

6.2 Hydrogen-Air transcritical flames

We present in this section a typical transcritical planar flame structure computed with the help of the thermodynamics model of Section 5. The corresponding governing equations may be derived from the thermodynamics of irreversible processes [53, 54, 16], statistical mechanics, [55, 56, 57], statistical thermodynamics [25], as well as the kinetic theory of dense gases [58, 59]. For one-dimensional steady flames, the conservation equations express the conservation of mass and energy and, in the small Mach number limit, are in the form [17]

$$\mathrm{m}\, y_i' + \mathcal{F}_i' = m_i \omega_i, \qquad i \in \mathfrak{S}, \tag{6.1}$$

$$\mathrm{m}\, h' + q' = 0, \tag{6.2}$$

where $\mathrm{m} = \rho \mathrm{u}$ denotes the mass flow rate, ρ the mass density, u the fluid normal velocity, the superscript $'$ the derivative with respect to the spatial coordinate x, y_i the mass fraction of the ith species, $\mathcal{F}_i$ the diffusion flux of the ith species, m_i the molar mass of the ith species, ω_i the molar production rate of the ith species, $\mathfrak{S} = \{1, \dots, n\}$ the species indexing set, n the number of species, h the enthalpy per unit mass of the mixture, and q the heat flux. The momentum equation uncouples from (6.1)(6.2) and may only be used to evaluate a perturbed pressure. The unknowns are the temperature T, the species mass fractions y_i, $i \in \mathfrak{S}$, as well as the mass flow rate m which is a nonlinear eigenvalue [60].

The boundary conditions at the origin are naturally written in the form [61]

$$\mathrm{m}\big(y_i(0) - y_i^{\mathrm{fr}}\big) + \mathcal{F}_i(0) = 0, \quad i \in \mathfrak{S}, \qquad \mathrm{m}\big(h(0) - h^{\mathrm{fr}}\big) + q(0) = 0, \tag{6.3}$$

where the superscript $^{\mathrm{fr}}$ refers to the fresh mixture. The downstream boundary conditions are in the form

$$y_i'(+\infty) = 0, \quad i \in \mathfrak{S}, \qquad\qquad T'(+\infty) = 0, \tag{6.4}$$

and the translational invariance of the model is removed by imposing a given temperature T^{fx} at a given arbitrary point x^{fx} of $[0, \infty)$, $T(\mathrm{x}^{\mathrm{fx}}) - T^{\mathrm{fx}} = 0$. We have used a reaction mechanism involving $n = 9$ species and $n^{\mathrm{r}} = 19$ reactions mainly due to Warnatz [62] with forward rates in Arrhenius form $\kappa_j^{\mathrm{f}}(T) = \mathfrak{A}_j T^{\mathfrak{b}_j} \exp\big(-\mathfrak{E}_j/RT\big)$, $j \in \mathfrak{R}$, and with kinetic parameters $\mathfrak{A}_j$ $\mathfrak{b}_j$ and $\mathfrak{E}_j$, $j \in \mathfrak{R}$, as in Table 1.

Table 1: Warnatz kinetics scheme for hydrogen combustion [62]

i	Reaction	$\mathfrak{A}_i$	$\mathfrak{b}_i$	$\mathfrak{E}_i$
1	$H + O_2 \leftrightarrows OH + O$	2.00E+14	0.00	16802.
2	$O + H_2 \leftrightarrows OH + H$	5.06E+04	2.67	6286.
3	$OH + H_2 \leftrightarrows H_2O + H$	1.00E+08	1.60	3298.
4	$2OH \leftrightarrows O + H_2O$	1.50E+09	1.14	100.
5	$H + H + M \leftrightarrows H_2 + M^a$	6.30E+17	-1.00	0.
6	$H + OH + M \leftrightarrows H_2O + M^a$	7.70E+21	-2.00	0.
7	$O + O + M \leftrightarrows O_2 + M^a$	1.00E+17	-1.00	0.
8	$H + O_2 + M \leftrightarrows HO_2 + M^a$	8.05E+17	-0.80	0.
9	$H + HO_2 \leftrightarrows 2OH$	1.50E+14	0.00	1004.
10	$H + HO_2 \leftrightarrows H_2 + O_2$	2.50E+13	0.00	693.
11	$H + HO_2 \leftrightarrows H_2O + O$	3.00E+13	0.00	1721.
12	$O + HO_2 \leftrightarrows O_2 + OH$	1.80E+13	0.00	-406.
13	$OH + HO_2 \leftrightarrows H_2O + O_2$	6.00E+13	0.00	0.
14	$HO_2 + HO_2 \leftrightarrows H_2O_2 + O_2$	2.50E+11	0.00	-1242.
15	$OH + OH + M \leftrightarrows H_2O_2 + M^a$	1.14E+22	-2.00	0.
16	$H_2O_2 + H \leftrightarrows HO_2 + H_2$	1.70E+12	0.00	3752.
17	$H_2O_2 + H \leftrightarrows H_2O + OH$	1.00E+13	0.00	3585.
18	$H_2O_2 + O \leftrightarrows HO_2 + OH$	2.80E+13	0.00	6405.
19	$H_2O_2 + OH \leftrightarrows H_2O + HO_2$	5.40E+12	0.00	1004.

[a] The third body M denotes any species of the mixture

[a] Third body efficiency $H_2 = 2.86$, $N_2 = 1.43$, $H_2O = 18.6$

Units are moles, centimeters, seconds, calories, and Kelvins

The thermodynamic built from the SRK equation of state in Section 5 and the chemistry with the nonideal rates of Section 4 have been used in the calculation. In a one dimensional framework, the mass and heat fluxes are in the form

$$\mathcal{F}_i = -\sum_{j \in \mathfrak{S}} L_{i,j} \Big(\frac{g_j}{T}\Big)' - L_{i,n+1} \Big(-\frac{1}{T}\Big)', \qquad i \in \mathfrak{S}, \tag{6.5}$$

$$q = -\sum_{j \in \mathfrak{S}} L_{n+1,j} \Big(\frac{g_j}{T}\Big)' - L_{n+1,n+1} \Big(-\frac{1}{T}\Big)', \tag{6.6}$$

where $L_{i,j}$, $i, j \in \mathfrak{S} \cup \{n+1\}$, are the transport coefficients. The transport matrix L with coefficients $L_{i,j}$, $1 \leqslant i, j \leqslant n+1$, is symmetric positive semi-definite and has nullspace $N(L) = \mathbb{R}\mathcal{U}$, with $\mathcal{U} \in \mathbb{R}^{n+1}$ and $\mathcal{U} = \big(1, \cdots, 1, 0\big)^t$. The evaluation of these coefficients is discussed in Giovangigli et al. [17] and is out of the scope of the present paper. Finally, it is remarkable that the chemical potentials μ_i, $i \in \mathfrak{S}$, are involved with thermodynamics, with the transport fluxes (6.5)(6.6) as well as the chemical production rates (4.3).

The determination of flame structures is based on adaptive flame solvers [63], adaptive continuation techniques [52], as well as optimized thermochemistry and transport libraries [64, 65, 66, 67, 68]. We present in Figure 3 the structure of a stoichiometric H_2-air flame with $T^{\mathrm{fr}} = 100$ K and $p = 200$ atm.

The temperature T, density ρ and mole fractions x_i, $i \in \mathfrak{S}$, are plotted in Figure 3 as function of the flame normal coordinate x. The flame front is roughly 40 μm wide and presents large density gradients due to the cold fresh gas temperature $T^{\mathrm{fr}} = 100$ K and to the combustion heat release.

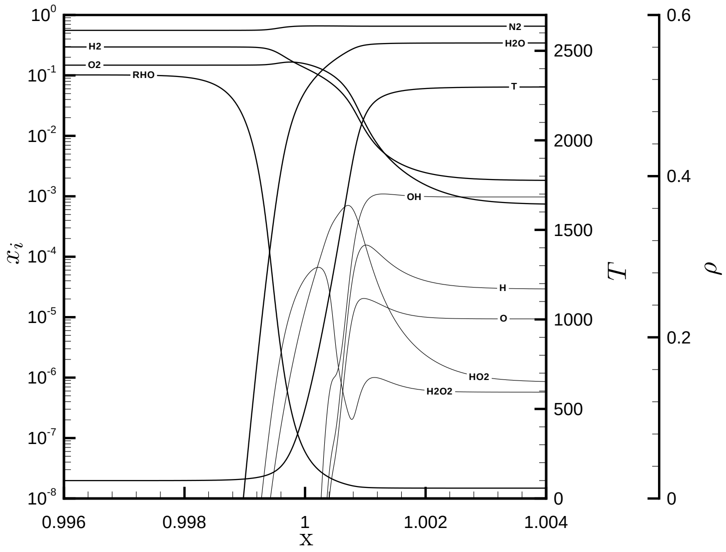

Figure 3: Structure of a transcritical stoichiometric H_2-air flame with $T^{\mathrm{fr}} = 100$ K and $p = 200$ atm. Density ($\mathrm{g\,cm^{-3}}$), temperature (K) and species mole fractions as functions of spatial coordinate (cm)

The mass flow rate is found to be $\mathrm{m} = 1.224\ \mathrm{g\,cm^{-2}\,s^{-1}}$ and the flame speed of $\mathrm{u_{ad}} = 2.079\ \mathrm{cm\,s^{-1}}$. The hydrogen and oxygen disappear in the flame front whereas water is formed and various active radicals are formed and partially recombined in the hot gases. In H_2-air flames, the HO_2 radical is generally formed early in the flame front by the reaction $H + O_2 + M \longrightarrow HO_2 + M$ until it is dominated by the reaction $H + O_2 \longrightarrow OH + O$ at sufficiently high temperatures. The HO_2 radical is then consumed through its reactions with more active radicals like H or OH. In high pressure flames, however, the reaction $H + O_2 + M \longrightarrow HO_2 + M$, which decreases the number of moles, dominates $H + O_2 \longrightarrow OH + O$ over a larger temperature domain thanks to the Le Chatellier effect. More specifically, the crossing temperature is around 1400 K for atmospheric flames and around 2100 K at $p = 100$ atm. A remarkable feature of high pressure H_2-air flames is thus the high concentrations of the HO_2 radical and large concentrations of the H_2O_2 radical are subsequently obtained mainly through the reactions $HO_2 + HO_2 \longrightarrow H_2O_2 + O_2$ and $H_2O + HO_2 \longrightarrow H_2O_2 + OH$.

6.3 Nonidealities in transcritical flames

The flame structure presented in the previous section is now used to illustrate the rôle of nonidealities both in the equation of state and in the chemical production rates.

We present in Figure 4 the relative magnitude of the attractive and repulsive contributions in the SRK equation of state as well as the relative magnitude of the volume per unit mass v with respect to the covolume b. Denoting by p_{a}, and p_{r} the attractive and repulsive contribution to the SRK equation of state

$$p_{\mathrm{r}} = \sum_{i\in\mathfrak{S}} \frac{y_i}{m_i}\frac{RT}{v-b}, \qquad p_{\mathrm{a}} = \frac{a}{v(v+b)},$$

the corresponding ratios p_{a}/p, p_{r}/p, and v/b are presented in Figure 4. The ratio v/b is approximately 1.68 in the fresh gases at $-\infty$ and around 77 in the hot combustion products. Nonidealities have therefore a dramatic effect in the fresh gases and a weak effect in the combustion products. This is confirmed by the ratios p_{a}/p and p_{r}/p which are respectively around 5 and 4 in the fresh gases at $-\infty$ and 1 and 0 in the hot gases at $+\infty$.

We present in Figure 5 the species activity coefficient $\widetilde{\mathsf{a}}_i$, $i \in \mathfrak{S}$, given by $\widetilde{\mathsf{a}}_i = \exp(\mu_i - \mu_i^{\mathrm{PG}})$. The species activities are then given $\mathsf{a}_i = \gamma_i^{\mathrm{PG}}\,\widetilde{\mathsf{a}}_i$, $i \in \mathfrak{S}$, in such a way that the species activity coefficients are a measure of nonidealities and should be unity in an ideal mixture. As for the nonidealities in the equation of state, the species activity coefficient differ from unity especially in the cold region. This is particularly the case for the species H_2O, O_2, N_2, HO_2 and H_2O_2, and to a less extend for H, O, OH, and H_2. More specifically, the limiting values as $\mathrm{x} \to -\infty$ of the species activity coefficients are $\widetilde{\mathsf{a}}_{H_2} \approx 2,35$, $\widetilde{\mathsf{a}}_{O_2} \approx 3.82\,10^{-2}$, $\widetilde{\mathsf{a}}_{H} \approx 1.61\,10^{-1}$, $\widetilde{\mathsf{a}}_{O} \approx 2.88\,10^{-1}$, $\widetilde{\mathsf{a}}_{OH} \approx 2.88\,10^{-1}$, $\widetilde{\mathsf{a}}_{HO_2} \approx 6.17\,10^{-2}$,

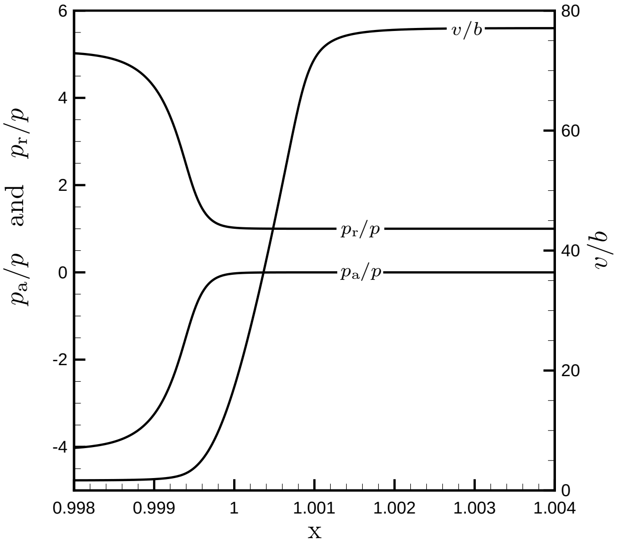

Figure 4: Thermodynamics of a transcritical stoichiometric H_2-air flame with $T^{\mathrm{fr}} = 100$ K and $p = 200$ atm.

$\widetilde{\mathsf{a}}_{H_2O_2} \approx 6.17\,10^{-2}$, $\widetilde{\mathsf{a}}_{H_2O} \approx 6.07\,10^{-8}$, $\widetilde{\mathsf{a}}_{N_2} \approx 8.57\,10^{-2}$. The catastrophic case of the H_2O species is associated with the instability of water at low temperatures. These activity coefficients deeply modify diffusive processes in the cold zone of the flame [17].

We present in Figure 6 where the rates of progress of the Reaction $H + O_2 + M \leftrightarrows HO_2 + M$ for the four chemistry models described in Sections 4.1, 4.2, and 4.3. These rates correspond to the ideal rates τ_j^{PG}, $j \in \mathfrak{R}$, the nonideal rates deduced from statistical physics τ_j, $j \in \mathfrak{R}$, and the two intermediate forms $\tau_j^{\mathrm{HP-PG}}$ and τ_j^{HY}, $j \in \mathfrak{R}$. We found it more convenient to plot the various rates of progress for a given flame structure in order to avoid the small spatial translations obtained when the flame is recalculated for each rate. We have used Reaction 8 of the chemical mechanism since the corresponding rates are large. We observe that the influence of nonidealities is important $p = 200$ atm and it is interesting to note that the worse rates of progress are obtained with the chemistry models PG-HP and Hybrid. In other words, the perfect gas model is closer to the nonideal model than the 'intermediate' models.

7 Conclusion

We have investigated mathematically the construction of supercritical fluid thermodynamic from equations of states with a special emphasis on the SRK equation of state. Numerical simulation of H_2-O_2-N_2 chemical instabilities as well as H_2-O_2-N_2 transcritical flames have shown the applicability of the resulting thermodynamics and illustrated the rôle of nonidealities. Subsequent work should consider the mathematical structure of the resulting system of partial differential equations.

A Homogeneous flows and extensive variables

We briefly address in this section the thermodynamics of a homogeneous mixture. In this situation, there exists a natural set of extensive variables $\Xi = (E, V, M_1, \ldots, M_n)^t$, where E denotes the energy, V the volume, and M_i, $1 \leqslant i \leqslant n$, the species masses, and similarly a set of natural variables $Z = (T, V, M_1, \ldots, M_n)$. The thermodynamic functions then exactly coincide with the intensive one investigated in Section 2.1 but evaluated for Z. More specifically, denoting S the entropy of the homegeneous mixture, we have $S = s(T, V, M_1, \ldots, M_n)$, and similarly, denoting by E the energy of the gas in volume V, we have $E = e(T, V, M_1, \ldots, M_n)$ and analogous relations hold for all thermodynamic functions. Similarly, the thermodynamic functions of Ξ coincide with those of ζ of but evaluated for Ξ.

The two alternative intensive formulations discussed in Section 2 can then easily be understood by considering such a homogeneous mixtures. Considering indeed intensive *densities* per unit volume in-

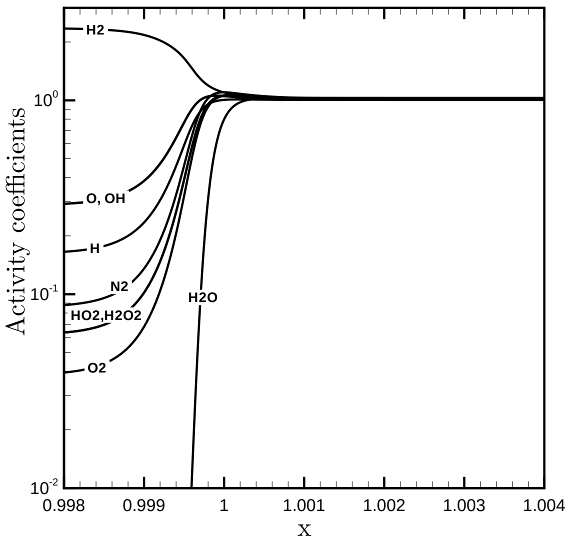

Figure 5: Activity coefficients in a transcritical stoichiometric H_2-air flame with $T^{\rm fr} = 100$ K and $p = 200$ atm.

stead of extensive quantities, the functions E, S, and $M_1, \dots, M_n$ have to be replaced by E/V, S/V, and $M_1/V, \dots, M_n/V$, that is, by $\mathcal{E}$, $\mathcal{S}$, and $\rho_1, \dots, \rho_n$. In this situation, the variables $(T, V, M_1, \dots, M_n)$ are transformed into $(T, 1, M_1/V, \dots, M_n/V)$, which are no longer independent. Similarly, starting from the variables $(T, p, M_1, \dots, M_n)$, we obtain—after dividing by the volume V—the reduced variables $(T, p, \rho_1, \dots, \rho_n)$, which again are not independent. This is consistent with the classical Gibbs–Duhem relation $s{\rm d}T - (1/\rho){\rm d}p + \sum_{k\in\mathfrak{S}} y_k {\rm d}g_k = 0$, which states that the natural set of $n+2$ *intensive* variables is a dependent set of variables. In summary, only $n+1$ intensive variables are independent, whereas $n+2$ independent variables were previously available by making use of extensivity. In non Gibbsian thermodynamics, we simply *eliminate* one of the dependent intensive variables. For instance, we either eliminate 1 from $(T, 1, M_1/V, \dots, M_n/V)$ or we eliminate the pressure from $(T, p, \rho_1, \dots, \rho_n)$ and we recover the variables $(T, \rho_1, \dots, \rho_n)$. Of course, we could have eliminated another variable instead of the pressure, but it would lead to the same type of formalism and be somewhat less elegant.

If we consider densities per unit mass instead of densities per unit volume, the quantities E, S, and $M_1, \dots, M_n$ have to be replaced by E/M, S/M, and $M_1/M, \dots, M_n/M$, that is, by e, s, and $y_1, \dots, y_n$, and the variables $(T, V, M_1, \dots, M_n)$ become $(T, v, M_1/M, \dots, M_n/M)$, that is to say, $(T, v, y_1, \dots, y_n)$. We again obtain a set of dependent variables since the mass fractions are supposed to satisfy a priori the constraint $\sum_{k\in\mathfrak{S}} y_k = 1$. By eliminating one of the mass fractions, we would obtain a formalism similar to the previous one. Instead of eliminating one of the mass fractions, however, we alternatively can consider the mass fractions as independent unknowns. In this situation, the a priori constraint between the mass fractions no longer exists, and the relation $\sum_{k\in\mathfrak{S}} y_k = 1$ must be a posteriori *deduced* from the governing equations. This yields the intensive Gibbsian thermodynamics formalism, which involves singular Hessians, but is formally identical to the classical Gibbs thermodynamics of homogeneous mixtures.

B Parameters for the SRK equation of state

The pure species attractive and repulsive parameters per unit mass $\alpha_i = \sqrt{a_i}$ and b_i, $i \in \mathfrak{S}$, associated with the SRK equation of state (5.1) may be obtained from the species critical points. More specifically, assuming that the ith species is chemically stable, the attractive and repulsive parameters may be evaluated in the form [69]

$$a_i\big(T_{{\rm c},i}\big) = 0.42748 \frac{R^2 T_{{\rm c},i}^2}{m_i^2 p_{{\rm c},i}}, \qquad b_i = 0.08664 \frac{R T_{{\rm c},i}}{m_i p_{{\rm c},i}}, \tag{B.1}$$

where $T_{{\rm c},i}$ and $p_{{\rm c},i}$ denote the corresponding critical temperature and pressure, respectively. A pure component fluid with the equation of state (5.1) and parameters (B.1) indeed displays a critical point

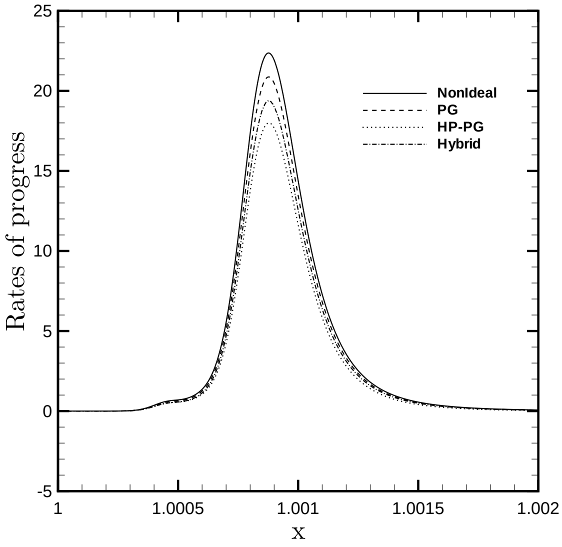

Figure 6: Chemical productions rates for reaction $H + O_2 + M \leftrightarrows HO_2 + M$ in a transcritical stoichiometric H_2-air flame with $T^{fr} = 100$ K and $p = 200$ atm.

located at temperature $T_{c,i}$ and pressure $p_{c,i}$. All the attractive and repulsive parameters of chemically stable species like H_2, O_2, N_2 or H_2O, or metastable species like H_2O_2, may thus be determined from critical states conditions.

This procedure, however, cannot be generalized in a straightforward way to chemically unstable species like radicals since critical states do not exist for such species [17]. More specifically, part of these molecules always recombine and prevent the existence of pure species states and the corresponding critical points. Assuming that the ith species is a Lennard-Jones gas, however, it is possible to estimate [47, 48] the critical volume per unit mass $v_{c,i}$ and the critical temperature $T_{c,i}i$ and to deduce that

$$a_i\big(T_{c,i}\big) = \big(5.55 \pm 0.12\big)\frac{\mathrm{N}^2 \epsilon_i \sigma_i^3}{m_i^2}, \qquad b_i = \big(0.855 \pm 0.018\big)\frac{\mathrm{N}\sigma_i^3}{m_i}, \tag{B.2}$$

where N is the Avogadro number, σ_i and ϵ_i the molecular diameter and Lennard-Jones potential well depth of the ith species. The relations (B.1) may thus be used for chemically stable species and the relations (B.2) for chemically unstable species like radicals with usual values for the Lennard-Jones parameters [17].

Once the attractive parameter $\alpha_i(T_{c,i}) = \sqrt{a_i(T_{c,i})}$ at temperature $T_{c,i}$ is evaluated, its temperature dependence $\alpha_i(T)$ may evaluated following Soave [42]

$$\alpha_i(T) = \alpha_i(T_{c,i})\widetilde{\alpha}_i(T_i^*), \tag{B.3}$$

where $T_i^* = T/T_{c,i}$ is the ith species reduced temperature, $\widetilde{\alpha}_i$ a nonnegative function of T_i^* given by $\widetilde{\alpha}_i = \big|1 + \mathrm{s}_i(1 - \sqrt{T_i^*})\big|$, $i \in \mathfrak{S}$, and the quantity s_i is expressed in the form $\mathrm{s}_i = 0.48508 + 1.5517\varpi_i - 0.151613\varpi_i^2$ where ϖ_i is the ith species acentric factor. From physical considerations the coefficient α_i should be a decreasing function of the reduced temperatures T_i^* as pointed out by Ozokwelu and Erbar [49] and Grabovski and Daubert [50], and should converge to zero as $T \to \infty$ in order to recover the perfect gas limit. Since the coefficient $\widetilde{\alpha}_i$ introduced by Soave does not satisfy such a property, it is first possible to truncate its temperature dependence in the form $\widetilde{\alpha}_i = \big(1 + \mathrm{s}_i(1 - \sqrt{T_i^*})\big)^+$ where $x^+ = \max(x, 0)$. However, these coefficients are not smooth enough, and they introduce small jumps in the temperature derivative of the attractive factor α_i and thereby of the attractive parameter $a = \sum_{i,j\in\mathfrak{S}} y_i y_j \alpha_i \alpha_j$ at the crossing temperatures $T_{c,i}(1 + 1/\mathrm{s}_i)^2$, $i \in \mathfrak{S}$, because of the coupling terms $i \neq j$. Even though such small jumps only arise in regions where the temperature is high and where nonidealities are negligible, it is recommanded—at least from a numerical point of view—to have smooth attractive factors. Numerical spurious behavior has indeed been observed due to these small discontinuities of the attractive factor temperature derivative. To this aim, we have preferred to use the new simple correlation $\widetilde{\alpha}_i = 1 + A\big(\mathrm{s}_i(1 - \sqrt{T_i^*})\big)$ where A is typically as in Proposition 5.2. The corresponding thermodynamic properties are inclose agreement with that of Soave or truncated Soave but are smoother [17].

Finally, the thermodynamic properties of perfect gases have been evaluated from the NIST/JANAF Thermochemical Tables as well as from the NASA coefficients [70, 71].

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