

SYMMETRIZATION OF CONSERVATION LAWS WITH ENTROPY FOR HIGH-TEMPERATURE HYPERSONIC COMPUTATIONS

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Abstract—Results of Hughes, Franca, and Mallet are generalized to conservation law systems taking into account high-temperature effects. Symmetric forms of different equation sets are derived in terms of entropy variables. First, the case of a general divariant gas is studied; it can be specialized to the usual Navier-Stokes equations, as well as to situations where the gas is vibrationally excited, and undergoes equilibrium chemical reactions. The case of a gas in thermochemical nonequilibrium is considered next. Transport phenomena, and in particular mass diffusion, are examined in the framework of symmetric advective-diffusive systems. Suitably defined finite element methods are shown to satisfy automatically the second law of thermodynamics, which guarantees *a priori* the stability of the discrete solution.

Citius, altius, fortius

NOMENCLATURE

A_j	advective Jacobian matrices with respect to conservative variables	e^{vib}	specific vibrational energy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\bar{A}_j	advective Jacobian matrices with respect to entropy variables	\mathbf{e}^{vib}	specific vibrational energy vector
\bar{A}_0	Riemannian metric tensor	e_s	specific internal energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
a	speed of sound (m s^{-1})	\dot{e}_s	specific internal energy per mole of species s ($\text{J mol}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2}$)
c	total number of moles per unit volume (mol m^{-3})	e_s^{rot}	specific rotational energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
c_p	specific heat at constant pressure ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	e_s^{tot}	specific total energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
c_{ps}	specific heat at constant pressure of species s ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	e_s^{trans}	specific translational energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
c_s	mole concentration of species s (mol m^{-3})	e_s^{vib}	specific vibrational energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
c_v	specific heat at constant volume ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	\dot{e}_s^{vib}	specific vibrational energy per mole of species s ($\text{J mol}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2}$)
\hat{c}_v^{vib}	vibrational specific heat at constant volume ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	e_{s0}	reference specific internal energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\hat{c}_v^{vib}	vibrational specific heat at constant volume per mole ($\text{J mol}^{-1} \text{K}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2} \text{K}^{-1}$)	e_{s0}^{vib}	reference specific vibrational energy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
c_{vs}	specific heat at constant volume of species s ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	e_0	reference specific internal energy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\dot{c}_{vs}	specific heat at constant volume per mole of species s ($\text{J mol}^{-1} \text{K}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2} \text{K}^{-1}$)	e_0^{vib}	reference specific vibrational energy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
c_{vs}^{vib}	vibrational specific heat at constant volume of species s ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	$\mathbf{F}_i^{\text{adv}}$	advective flux vector in direction i
$\hat{c}_{vs}^{\text{vib}}$	vibrational specific heat at constant volume per mole of species s ($\text{J mol}^{-1} \text{K}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2} \text{K}^{-1}$)	$\mathbf{F}_i^{\text{diff}}$	diffusive flux vector in direction i
$\mathbf{D}^{\text{therm}}$	multicomponent thermal diffusion coefficient vector	$\mathbf{F}_i^{\text{heat}}$	heat flux vector in direction i
D_s^{therm}	multicomponent thermal diffusion coefficient of species s ($\text{kg m}^{-1} \text{s}^{-1}$)	$\mathbf{F}_i^{\text{mass}}$	mass diffusion flux vector in direction i
D_{sr}	multicomponent diffusion coefficient of species s into species r ($\text{m}^2 \text{s}^{-1}$)	$\mathbf{F}_i^{\text{visc}}$	viscous stress flux vector in direction i
d_{oi}	gradient of species s in direction i used for the computation of diffusion velocities (m^{-1})	\mathcal{F}	source vector in terms of conservative variables
E^{tot}	total energy per unit volume ($\text{J m}^{-3} = \text{kg m}^{-1} \text{s}^{-2}$)	\mathcal{G}	source vector in terms of entropy variables
E^{vib}	vibrational energy per unit volume ($\text{J m}^{-3} = \text{kg m}^{-1} \text{s}^{-2}$)	g	Gibbs free energy ($\text{J} = \text{kg m}^2 \text{s}^{-2}$)
\mathcal{E}	internal energy ($\text{J} = \text{kg m}^2 \text{s}^{-2}$)	g_s	specific Gibbs free energy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\mathcal{E}^{vib}	vibrational energy ($\text{J} = \text{kg m}^2 \text{s}^{-2}$)	\dot{g}_s	specific Gibbs free energy per mole of species s ($\text{J mol}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2}$)
e	specific internal energy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)	\mathcal{H}	generalized entropy function ($\text{J m}^{-3} \text{K}^{-1} = \text{kg m}^{-1} \text{s}^{-2} \text{K}^{-1}$)
e^{tot}	specific total energy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)	h	specific enthalpy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
		\mathbf{h}	specific enthalpy vector
		h^{tot}	specific total enthalpy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
		h_s	specific enthalpy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
		h_s^{tot}	specific total enthalpy of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
		h_s^0	specific heat of formation of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)

\hat{h}_s^0	specific heat of formation per mole of species s ($\text{J mol}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2}$)	\mathbf{u}	velocity vector
h_0	reference specific enthalpy ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)	u_i	velocity in direction i (m s^{-1})
\mathbf{J}_i	mass diffusion flux in direction i	\mathbf{V}	entropy variable vector
J_{si}	mass diffusion flux of species s in direction i	\mathcal{V}	volume (m^3)
\mathbf{K}	diffusivity matrix with respect to conservative variables	v	specific volume ($\text{m}^3 \text{kg}^{-1}$)
$\hat{\mathbf{K}}$	diffusivity matrix with respect to entropy variables	\hat{v}_s	specific volume per mole of species s ($\text{m}^3 \text{mol}^{-1}$)
$\hat{\mathbf{K}}^{\text{heat}}$	heat conduction diffusivity matrix with respect to entropy variables	v_{si}	diffusion velocity of species s in direction i (m s^{-1})
$\hat{\mathbf{K}}^{\text{mass}}$	mass-diffusion diffusivity matrix with respect to entropy variables	x_s	mole fraction of species s
$\hat{\mathbf{K}}^{\text{mass-heat}}$	mass-diffusion/heat conduction matrix with respect to entropy variables	\mathbf{y}	mass fraction vector
$\hat{\mathbf{K}}^{\text{therm}}$	thermal diffusion matrix with respect to entropy variables	y_s	mass fraction of species s
$\hat{\mathbf{K}}^{\text{visc}}$	viscous stress diffusivity matrix with respect to entropy variables	<i>Greek symbols</i>	
$K_{c,R}$	equilibrium constant of reaction R	α	Onsager's phenomenological coefficient matrix for mass diffusion
\mathbf{K}_{ij}	diffusivity coefficient matrix with respect to conservative variables	$\tilde{\alpha}$	Onsager's phenomenological coefficient matrix for mass diffusion and heat conduction
$\hat{\mathbf{K}}_{ij}$	diffusivity coefficient matrix with respect to entropy variables	α_p	expansivity (K^{-1})
$\hat{\mathbf{K}}_{ij}^{\text{heat}}$	heat conduction diffusivity coefficient-matrix with respect to entropy variables	α_{sr}	Onsager's phenomenological coefficients for mass diffusion (kg s m^{-3})
$\hat{\mathbf{K}}_{ij}^{\text{mass}}$	mass-diffusion diffusivity coefficient-matrix with respect to entropy variables	$\tilde{\alpha}_{sr}$	Onsager's phenomenological coefficients for mass diffusion and heat conduction
$\hat{\mathbf{K}}_{ij}^{\text{mass-heat}}$	mass-diffusion/heat conduction diffusivity coefficient-matrix with respect to entropy variables	β_T	isothermal compressibility ($\text{Pa}^{-1} = \text{m}^2 \text{s}^2 \text{kg}^{-1}$)
$\hat{\mathbf{K}}_{ij}^{\text{therm}}$	thermal diffusion coefficient-matrix with respect to entropy variables	γ_s	ratio of specific heats of species of s
$\hat{\mathbf{K}}_{ij}^{\text{visc}}$	viscous stress diffusivity coefficient-matrix with respect to entropy variables	δ_i	Kronecker delta vector
\hat{M}	molar mass (kg mol^{-1})	δ_{ij}	Kronecker delta
\hat{M}_s	molar mass of species s (kg mol^{-1})	ε	strain tensor
\mathcal{N}	total number of moles (mol)	ε'	deviatoric part of the strain tensor
\mathcal{N}_s	number of moles of species s (mol)	ε''	dilatational part of the strain tensor
n	number of species	Θ_s^{vib}	characteristic vibrational temperature of species s (K)
p	pressure ($\text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$)	κ, κ'	coefficient of thermal conductivity ($\text{W m}^{-1} \text{K}^{-1} = \text{kg m s}^{-3} \text{K}^{-1}$)
p_s	partial pressure of species s ($\text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$)	κ^{vib}	coefficient of thermal conductivity of the vibrational energy ($\text{W m}^{-1} \text{K}^{-1} = \text{kg m s}^{-3} \text{K}^{-1}$)
p_{s0}	reference partial pressure of species s ($\text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$)	λ^{visc}	second viscosity coefficient ($\text{Pl} = \text{kg m}^{-1} \text{s}^{-1}$)
p_0	reference pressure ($\text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$)	μ^{visc}	first viscosity coefficient ($\text{Pl} = \text{kg m}^{-1} \text{s}^{-1}$)
$Q^{T-\text{vib}}$	translation-vibration energy transfer rate ($\text{W m}^{-3} = \text{kg m}^{-1} \text{s}^{-3}$)	μ_b^{vib}	bulk viscosity coefficient ($\text{Pl} = \text{kg m}^{-1} \text{s}^{-1}$)
\mathcal{Q}	heat received by the system ($\text{J} = \text{kg m}^2 \text{s}^{-2}$)	μ	specific chemical potential ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\mathbf{q}	heat flux	μ	specific chemical potential vector
q_i	heat flux in direction i ($\text{W m}^{-2} = \text{kg s}^{-3}$)	μ_s	specific chemical potential of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
q_i^{vib}	vibrational heat flux in direction i ($\text{W m}^{-2} = \text{kg s}^{-3}$)	$\hat{\mu}_s$	specific chemical potential per mole of species s ($\text{J mol}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2}$)
R	specific gas constant ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	μ_s^0	specific chemical potential of species s in the pure state, at unit pressure ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\hat{R}	universal gas constant ($= 8.3143 \text{ J mol}^{-1} \text{K}^{-1}$)	$\hat{\mu}_s^0$	specific chemical potential per mole of species s in the pure state, at unit pressure ($\text{J mol}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2}$)
R_s	specific gas constant of species s ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	μ_{s0}	reference specific chemical potential of species s ($\text{J kg}^{-1} = \text{m}^2 \text{s}^{-2}$)
\mathcal{S}	entropy ($\text{J K}^{-1} = \text{kg m}^2 \text{s}^{-2} \text{K}^{-1}$)	v_{sR}	stoichiometric coefficient of species s in reaction R
\mathcal{S}^{ext}	entropy due to interactions with exterior ($\text{J K}^{-1} = \text{kg m}^2 \text{s}^{-2} \text{K}^{-1}$)	ρ	density (kg m^{-3})
\mathcal{S}^{int}	entropy due to internal irreversibilities ($\text{J K}^{-1} = \text{kg m}^2 \text{s}^{-2} \text{K}^{-1}$)	ρ_s	density of species s (kg m^{-3})
s	specific entropy ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	ρ_{s0}	reference density of species s (kg m^{-3})
s_s	specific entropy of species s ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	σ_i	entropy flux in direction i ($\text{W m}^{-2} \text{K}^{-1} = \text{kg s}^{-3} \text{K}^{-1}$)
\hat{s}_s	specific entropy per mole of species s ($\text{J mol}^{-1} \text{K}^{-1} = \text{kg m}^2 \text{mol}^{-1} \text{s}^{-2} \text{K}^{-1}$)	τ	viscous stress tensor
s_{s0}	reference specific entropy of species s ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	τ_{ij}	viscous stress in direction i on a plane normal to direction j ($\text{Pa} = \text{kg m}^{-1} \text{s}^{-2}$)
s_s	reference specific entropy ($\text{J kg}^{-1} \text{K}^{-1} = \text{m}^2 \text{s}^{-2} \text{K}^{-1}$)	Ω	production rate vector
T	(translational-rotational) temperature (K)	Ω_s	production rate of species s ($\text{kg m}^{-3} \text{s}^{-1}$)
T^{vib}	vibrational temperature (K)	<i>Subscripts</i>	
T_0	reference temperature (K)	$()_{ijk}$	direction i, j , or k
T_0^{vib}	reference vibrational temperature (K)	$()_R$	reaction R
t	time (s)	$()_{s,r,t}$	species s , r , or t
\mathbf{U}	conservative variables vector	$()_0$	reference state
		<i>Superscripts</i>	
		$()^T$	transpose
		$()'_s$	all species, except species s
		$()^\wedge$	quantity per mole
		$()^\sim$	coefficient matrix with respect to entropy variables

1. INTRODUCTION

From the beginning, aeronautics and space flight have been driven by the urge to fly faster and higher. With current intense activity in the area of hypersonic transatmospheric vehicles, computational fluid dynamics has entered a new era. Until recently, the compressible Navier–Stokes equations were viewed by many as representing the state of the art. However, the combination of high speed and altitude results in very strong shock waves and the departure of air from a calorically perfect gas, due to the excitation of internal energy modes and chemical reactions. Over some of the flight regimes an assumption of thermochemical equilibrium is valid. However, regions of thermal and chemical nonequilibrium need to be accounted for in order to better predict aerothermal loads on the vehicles.

Although there is still much improvement needed in the accuracy and reliability of existing Navier–Stokes codes, the extension of numerical techniques to systems taking account of the mentioned phenomena is required. In particular, the symmetric form of the Navier–Stokes equations, a basis of certain methods, must be reconsidered in order to accommodate more general forms of the conservation equations.

An outline of this paper follows. In Sec. 2 we review the theory of symmetric advective–diffusive and hyperbolic systems. In Sec. 3 we consider the case of a general divariant gas, which we specialize to two kinds of frozen gases (the calorically and thermally perfect gases) and to a mixture of perfect gases in thermochemical equilibrium. In Sec. 4 we describe the more complex example of a multicomponent gas in thermochemical nonequilibrium. In Sec. 5 we summarize the advantages of the symmetric form. The detailed arrays for the so-called entropy-variables form of the equations and a simple equilibrium chemistry model are presented in the appendices.

2. SYMMETRIC ADVECTIVE–DIFFUSIVE SYSTEMS

We consider systems of conservation laws in the form

$$\mathbf{U}_{,t} + \mathbf{F}_{i,t}^{\text{adv}} = \mathbf{F}_{i,t}^{\text{diff}} + \mathcal{F}, \quad (1)$$

where \mathbf{U} is the vector of conservative variables; $\mathbf{F}_i^{\text{adv}}$ and $\mathbf{F}_i^{\text{diff}}$ are, respectively, the advective and the diffusive fluxes in the i th-direction; and \mathcal{F} is the source vector. In subsequent sections, we will present different systems and provide expressions for the corresponding vectors. Inferior commas denote partial differentiation and repeated indices indicate summation.

With reference to Eq. (1), we assume:

- (i) The diffusive fluxes can be written in the form

$$\mathbf{F}_i^{\text{diff}} = \mathbf{K}_{ij} \mathbf{U}_{,j}. \quad (2)$$

- (ii) The purely advective form of Eq. (1), namely

$$\mathbf{U}_{,t} + \mathbf{F}_{i,t}^{\text{adv}} = 0, \quad (3)$$

is hyperbolic, that is, any linear combination of the Jacobian matrices $\mathbf{A}_i = \mathbf{F}_{i,U}^{\text{adv}}$ possesses real eigenvalues and a complete set of eigenvectors.¹

It is useful to rewrite Eq. (1) in so-called quasi-linear form

$$\mathbf{U}_{,t} + \mathbf{A}_i \mathbf{U}_{,i} = (\mathbf{K}_{ij} \mathbf{U}_{,j})_{,i} + \mathcal{F}, \quad (4)$$

where $\mathbf{K} = [\mathbf{K}_{ij}]$ is the diffusivity matrix. The \mathbf{A}_i s and \mathbf{K} do not necessarily possess any particular properties of symmetry or positiveness and, in general, are functions of \mathbf{U} .

Under the change of variables $\mathbf{U} = \mathbf{U}(\mathbf{V})$, Eq. (1) becomes

$$\bar{\mathbf{A}}_0 \mathbf{V}_{,t} + \bar{\mathbf{A}}_i \mathbf{V}_{,i} = (\bar{\mathbf{K}}_{ij} \mathbf{V}_{,j})_{,i} + \bar{\mathcal{F}}, \quad (5)$$

where

$$\bar{\mathbf{A}}_0 = \mathbf{U}_{,\mathbf{V}} \quad (6)$$

$$\bar{\mathbf{A}}_i = \mathbf{A}_i \bar{\mathbf{A}}_0 \quad (7)$$

$$\bar{\mathbf{K}}_{ij} = \mathbf{K}_{ij} \bar{\mathbf{A}}_0 \quad (8)$$

$$\bar{\mathcal{F}} = \mathcal{F}(\mathbf{U}(\mathbf{V})). \quad (9)$$

We seek a particular change of variables satisfying the following conditions:

- (i) $\bar{\mathbf{A}}_0$ is symmetric, positive-definite.

- (ii) The $\bar{\mathbf{A}}_i$ s are symmetric.

(iii) $\bar{\mathbf{K}} = [\bar{\mathbf{K}}_{ij}]$ is symmetric, positive-semidefinite. When a change of variables $\mathbf{U} = \mathbf{U}(\mathbf{V})$ exists that engenders these properties, Eq. (5) is referred to as a *symmetric advective–diffusive system*. As we will see, symmetric systems and the notion of a generalized entropy function are intimately linked. A generalized entropy function is a scalar-valued function $\mathcal{H} = \mathcal{H}(\mathbf{U})$ that possesses the following properties:

- (i) \mathcal{H} is convex.

- (ii) There exist scalar-valued functions $\sigma_i = \sigma_i(\mathbf{U})$, called entropy fluxes, such that

$$\mathcal{H}_{,U} \mathbf{A}_i = \sigma_{i,U}. \quad (10)$$

Harten² and Tadmor³ discuss the symmetrization of hyperbolic conservation laws and the satisfaction of generalized entropy inequalities. Harten presents two theorems first proved by Mock⁴ and Godunov.⁵

Theorem (Mock)

A hyperbolic system of conservation laws possessing a generalized entropy function \mathcal{H} becomes symmetric hyperbolic under the change of variables

$$\mathbf{V}^T = \frac{\partial \mathcal{H}}{\partial \mathbf{U}}. \quad (11)$$

Theorem (Godunov)

If a hyperbolic system can be symmetrized by introducing a change of variables, then a generalized entropy function and corresponding entropy fluxes exist for this system.

Harten also considered the compressible Navier–Stokes equations, neglecting heat conduction, and proposed a family of admissible generalized entropy functions. Hughes *et al.*⁶ extended Harten's work to the full Navier–Stokes equations and showed that the only suitable members of Harten's family of generalized entropy functions are the ones that are at most trivially different from the physical entropy (up to an affine transformation).

Following along these lines, we derive herein symmetrized forms of conservation laws which apply to high-temperature hypersonic computations, beginning with the case of a general divariant gas.

3. GENERAL DIVARIANT GAS

The thermodynamic properties of a divariant gas, including its chemical composition in the case of a mixture of reacting gases, are completely defined in terms of two thermodynamic quantities, such as pressure p and temperature T . A hypersonic flow can be described as a divariant gas under the following assumptions:

- (i) The gas is in thermal equilibrium, i.e. the translational and internal energy modes are characterized by the same temperature T .
- (ii) The gas mixture is either frozen, i.e. non-reacting, or in chemical equilibrium.

In addition, we assume temperature levels low enough to preclude any ionization or radiative heat transfer.

In the next section, we give explicit forms for the different vectors of Eq. (1), in the framework of the above assumptions.

3.1. Systems of conservation laws

In three dimensions, the vectors of Eq. (1) read

$$\mathbf{U} = \begin{Bmatrix} U_1 \\ U_2 \\ U_3 \\ U_4 \\ U_5 \end{Bmatrix} = \rho \begin{Bmatrix} 1 \\ u_1 \\ u_2 \\ u_3 \\ e^{\text{tot}} \end{Bmatrix} \quad (12)$$

$$\mathbf{F}_i^{\text{adv}} = u_i \mathbf{U} + p \begin{Bmatrix} 0 \\ \delta_{1i} \\ \delta_{2i} \\ \delta_{3i} \\ u_i \end{Bmatrix} \quad (13)$$

$$\mathbf{F}_i^{\text{diff}} = \begin{Bmatrix} 0 \\ \tau_{1i} \\ \tau_{2i} \\ \tau_{3i} \\ \tau_{ij} u_j \end{Bmatrix} + \begin{Bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -q_i \end{Bmatrix} \quad (14)$$

$$\mathcal{F} = \mathbf{0}, \quad (15)$$

where ρ is the density; $\mathbf{u} = \{u_1, u_2, u_3\}^T$ is the velocity vector; e^{tot} is the total energy per unit mass, which is the sum of the internal energy per unit mass, e , and of the kinetic energy per unit mass, $|\mathbf{u}|^2/2$; p is the thermodynamic pressure; δ_{ij} is the Kronecker delta (viz. $\delta_{ii} = 1$, and $\delta_{ij} = 0$ for $i \neq j$); $\boldsymbol{\tau} = [\tau_{ij}]$ is the viscous stress tensor; $\mathbf{q} = \{q_1, q_2, q_3\}^T$ is the heat flux vector.

3.2. Constitutive relations

The system of partial differential equations of the previous section is supplemented with the following constitutive relations.

- (i) The viscous stress tensor $\boldsymbol{\tau}$ is given by

$$\tau_{ij} = \lambda^{\text{visc}} u_{k,k} \delta_{ij} + \mu^{\text{visc}} (u_{i,j} + u_{j,i}), \quad (16)$$

where λ^{visc} and μ^{visc} are the viscosity coefficients. λ^{visc} may be defined in terms of μ^{visc} and the bulk viscosity coefficient μ_B^{visc} by

$$\lambda^{\text{visc}} = \mu_B^{\text{visc}} - \frac{2}{3} \mu^{\text{visc}}. \quad (17)$$

For perfect monatomic gases, kinetic theory predicts that $\mu_B^{\text{visc}} = 0$. Stokes' hypothesis states that μ_B^{visc} can be taken equal to zero in the general case. However, as shown by Vincenti and Kruger,⁷ behaviors such as small departures from rotational equilibrium can be represented by means of bulk viscosity. In the present discussion, where thermal equilibrium is assumed, Stokes' hypothesis is valid.

- (ii) The heat flux is given by the usual Fourier law

$$q_i = -\kappa T_{,i}, \quad (18)$$

where κ is the coefficient of thermal conductivity.

All the parameters (λ^{visc} , μ^{visc} , μ_B^{visc} , κ) appearing in the preceding constitutive relations are assumed to be functions of the thermodynamic state of the gas.

In the present model, we have not considered any effect due to mass diffusion. Mass diffusion is indeed a phenomenon which by nature is not divariant, but depends on the actual chemical composition of the gas. In order to incorporate its effects into a model, one continuity equation is needed per species present in the mixture, which precludes a divariant description of the system. A few authors include the contribution of mass diffusion to the heat flux.^{8–11} Since the densities of the different species are only functions of

the thermodynamic state of the system (e.g. p and T), the heat flux due to mass diffusion can be written in terms of a pressure and a temperature gradient. However, one can show that this yields a nonsymmetric contribution to the diffusivity matrix \mathbf{K} . Moreover, correct entropy production is not guaranteed. Suitable modelization of mass diffusion will be presented in the next section, in which we deal with mixtures in chemical nonequilibrium.

3.3. Entropy variables and symmetrization

We consider the generalized entropy function \mathcal{H} ,

$$\mathcal{H} = \mathcal{H}(\mathbf{U}) = -\rho s, \quad (19)$$

where s is the thermodynamic entropy per unit mass. We will verify *a posteriori* that \mathcal{H} meets the requirements of a generalized entropy function and, in particular, we will check its convexity. We introduce a change of variables $\mathbf{U} \mapsto \mathbf{V}$ defined by

$$\mathbf{V}^T = \frac{\partial \mathcal{H}}{\partial \mathbf{U}}. \quad (20)$$

\mathbf{V} is referred to as the vector of (physical) entropy variables. For a divariant gas, Eq. (20) yields

$$\mathbf{V} = \frac{1}{T} \begin{Bmatrix} \mu - |\mathbf{u}|^2/2 \\ u_1 \\ u_2 \\ u_3 \\ -1 \end{Bmatrix}, \quad (21)$$

where $\mu = e + pv - Ts$ is the chemical potential per unit mass; $v = 1/\rho$ is the specific volume.

To derive Eq. (21) we used Gibbs' relation

$$ds = \frac{1}{T} (de + p dv). \quad (22)$$

The computation was made more manageable by the introduction of the auxiliary variables

$$\mathbf{Y} = \begin{Bmatrix} v \\ \mathbf{u} \\ e \end{Bmatrix} \quad (23)$$

and the application of the chain rule

$$\mathcal{H}_{,\mathbf{U}} = \mathcal{H}_{,\mathbf{Y}}(\mathbf{U}_{,\mathbf{Y}})^{-1}. \quad (24)$$

The Riemannian metric tensor $\tilde{\mathbf{A}}_0$ reads

$$\tilde{\mathbf{A}}_0 = \frac{\beta_T T}{v^2} \begin{bmatrix} 1 & u_1 & u_2 & u_3 & h + \frac{|\mathbf{u}|^2}{2} - \frac{v\alpha_p T}{\beta_T} \\ u_1^2 + \frac{v}{\beta_T} & u_1 u_2 & u_1 u_3 & u_1 \left(h + \frac{|\mathbf{u}|^2}{2} - \frac{v(\alpha_p T + 1)}{\beta_T} \right) \\ & u_2^2 + \frac{v}{\beta_T} & u_2 u_3 & u_2 \left(h + \frac{|\mathbf{u}|^2}{2} - \frac{v(\alpha_p T + 1)}{\beta_T} \right) \\ \text{Symm.} & & u_3^2 + \frac{v}{\beta_T} & u_3 \left(h + \frac{|\mathbf{u}|^2}{2} - \frac{v(\alpha_p T + 1)}{\beta_T} \right) \\ & & & a_{55} \end{bmatrix}, \quad (25)$$

where

$$a_{55} = \left(h + \frac{|\mathbf{u}|^2}{2} \right)^2 + \frac{v}{\beta_T} (c_p T - 2h\alpha_p T - |\mathbf{u}|^2(\alpha_p T - 1)) \quad (26)$$

and

$$h = e + pv = \mu - Ts \quad (\text{specific enthalpy}) \quad (27)$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p \quad (\text{expansivity}) \quad (28)$$

$$\beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T \quad (\text{isothermal compressibility}) \quad (29)$$

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p \quad (\text{specific heat at constant pressure}). \quad (30)$$

These coefficients are related to the specific heat at constant volume, namely

$$c_v = \left(\frac{\partial e}{\partial T} \right)_v, \quad (31)$$

by Mayer's relation

$$c_p - c_v = \frac{\alpha_p^2 v T}{\beta_T}. \quad (32)$$

The leading principal minors of $\tilde{\mathbf{A}}_0$ are positive provided that $T > 0$, $v > 0$, $c_v > 0$ and $\beta_T > 0$; these conditions are met for any thermally and mechanically stable fluid away from $T = 0$.¹² The positiveness of these determinants implies that $\tilde{\mathbf{A}}_0$ is positive definite,¹³ which in turn implies that \mathcal{H} is a strictly convex function of \mathbf{U} (viz. $\tilde{\mathbf{A}}_0^{-1} = \mathbf{V}_{,\mathbf{U}} = \mathcal{H}_{,\mathbf{UU}}$). Explicit definitions of the coefficient matrices are presented in Appendix A.

3.4. Equations of state

The system of equations presented in the previous sections must be closed by the addition of an equation of state, such as a relation giving the chemical potential in terms of the thermodynamical state, i.e.

$$\mu = \mu(p, T). \quad (33)$$

In general, there exists no explicit version of Eq. (33). However, for most aerodynamic applications the perfect gas assumption applies. Fortunately, the “real gas effects” of the aerodynamicist, such as vibrational excitation and dissociation, are unrelated to the “real gas” of the thermodynamicist. A true real gas is a gas for which intermolecular forces are important; this occurs either at very high pressures (≈ 1000 atm), or at low temperatures (< 30 K). At room temperature air is essentially a *calorically perfect gas*. It remains so until the temperature reaches approximately 600 K. Then, as the temperature increases further, vibrational excitation becomes important, and air behaves as a *thermally perfect gas*. Above 2000 K, chemical reactions occur and air becomes a *chemically reacting mixture of perfect gases*.⁹ Above 10,000 K ionization becomes significant. The description of the accompanying phenomena exceeds the scope of this paper.

All relevant thermodynamic quantities can be obtained from Eq. (33)

$$s = -\left(\frac{\partial \mu}{\partial T}\right)_p \quad v = \left(\frac{\partial \mu}{\partial p}\right)_T \quad (34)$$

$$h = \mu + Ts \quad e = h - pv \quad (35)$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{v} \left(\frac{\partial^2 \mu}{\partial p \partial T}\right) \quad (36)$$

$$\beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T = -\frac{1}{v} \left(\frac{\partial^2 \mu}{\partial p^2}\right)_T \quad (36)$$

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = -T \left(\frac{\partial^2 \mu}{\partial T^2}\right)_p \quad (37)$$

$$c_v = c_p - \frac{\alpha_p^2 v T}{\beta_T} \quad (37)$$

Relations (34)–(37) are sufficient to construct the flux vectors and the coefficient matrices. In the next sections, we review in greater detail the three categories of perfect gases mentioned above.

3.4.1. Calorically perfect gas. A calorically perfect gas satisfies the perfect gas law, viz.

$$pv = RT, \quad (38)$$

where R is the specific gas constant

$$R = \frac{\hat{R}}{\hat{M}}, \quad (39)$$

in which $\hat{R} = 8.3143 \text{ J mol}^{-1} \text{ K}^{-1}$ is the universal gas constant and \hat{M} is the molar mass of the gas. In addition, the specific heats c_p and c_v are constant. Such a gas is often simply referred to as a perfect gas.

A simple explicit expression is available for the chemical potential

$$\mu = c_p T - c_p T \ln \frac{T}{T_0} + RT \ln \frac{p}{p_0} - Ts_0, \quad (40)$$

where (p_0, T_0) defines the reference state for entropy. Then, Eqs (34)–(37) yield

$$s = c_p \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} + s_0 \quad (41)$$

$$h = c_p T \quad (42)$$

$$e = c_v T \quad (43)$$

$$\alpha_p = \frac{1}{T} \quad (44)$$

$$\beta_T = \frac{1}{p} \quad (45)$$

$$c_p - c_v = R. \quad (46)$$

3.4.2. Thermally perfect gas. A thermally perfect gas is only assumed to follow the perfect gas law (38). In general, the differential of internal energy per unit mass (with temperature and specific volume viewed as arguments) is given by

$$de = c_v dT + (l - p) dv \quad (47)$$

with

$$l = T \left(\frac{\partial p}{\partial T}\right)_v. \quad (48)$$

Therefore, in the case of a perfect gas

$$\left(\frac{\partial e}{\partial v}\right)_T = l - p = 0, \quad (49)$$

which implies that $e = e(T, v)$ does not depend on v . Consequently, c_v is a function of T only. In the same way, it can be shown that c_p depends solely on T

$$c_v = c_v(T) \quad c_p = c_p(T). \quad (50)$$

The chemical potential can be expressed as

$$\mu = \int_{T_0}^T c_p(\theta) d\theta + h_0 - T \int_{T_0}^T \frac{c_p(\theta)}{\theta} d\theta + RT \ln \frac{p}{p_0} - Ts_0 \quad (51)$$

and

$$s = \int_{T_0}^T \frac{c_p(\theta)}{\theta} d\theta - R \ln \frac{p}{p_0} + s_0 \quad (52)$$

$$h = \int_{T_0}^T c_p(\theta) d\theta + h_0 \quad (53)$$

$$e = h - RT = \int_{T_0}^T c_v(\theta) d\theta + e_0 \quad (54)$$

$$\alpha_p = \frac{1}{T} \quad (55)$$

$$\beta_T = \frac{1}{p} \quad (56)$$

$$c_p(T) - c_v(T) = R, \quad (57)$$

where e_0 and h_0 are, respectively, the values of e and h at the reference temperature T_0 .

The last piece of information that we need to complete the picture is an expression for the specific heat at constant pressure c_p . In fact, statistical and quantum mechanics usually provide direct information concerning the internal energy. In terms of $e(T)$, the chemical potential reads

$$\begin{aligned} \mu = e(T) + RT - T \left(\frac{e}{T} - \frac{e_0}{T_0} \right) - T \int_{T_0}^T \frac{e(\theta)}{\theta^2} d\theta \\ - RT \ln \frac{T}{T_0} + RT \ln \frac{p}{p_0} - Ts_0. \end{aligned} \quad (58)$$

In deriving Eq. (58), we have used the fact that

$$h_0 = e_0 + RT_0. \quad (59)$$

$e(T)$ is commonly obtained experimentally or theoretically through extensive computations. Results are available in the form of curve fits or look-up tables for fast computer access.¹⁴ However, under reasonable assumptions, a simple closed form expression can be derived for $e(T)$.

At room temperature, air is essentially a mixture of diatomic oxygen and nitrogen (79% N_2 and 21% O_2 by volume). These molecules, as well as NO, can be assimilated to rigid rotators, at least up to 10,000 K.¹⁵ In these conditions, vibrational and rotational partition functions are separable, and vibrational modes can be considered as independent from rotational modes. In addition, in the same temperature range, molecular potential wells can be approximated by parabolas; consequently, vibrational excitation obeys the harmonic oscillator model. If the vibrational states are assumed to extend to infinity, the summation over them can be performed explicitly, leading to the following expression for the specific vibrational energy of a diatomic species s ¹⁶:

$$e_s^{\text{vib}} = \frac{R_s \Theta_s^{\text{vib}}}{\exp(\Theta_s^{\text{vib}}/T) - 1}, \quad (60)$$

where R_s is the specific gas constant for species s , and Θ_s^{vib} is its characteristic vibrational temperature. For the molecules of interest, Θ_s^{vib} is of the order 2500–3500 K. Electronic excitation can be written in a form similar to that of Eq. (60). However, we will neglect its contribution in the expression of internal energy. This is legitimate, since the lowest significant excited electronic state, one for O_2 , has a characteristic

temperature of nearly 11,400 K. Therefore, the specific internal energy of species s can be written as the sum of a translational, rotational, and vibrational contribution

$$e_s = e_s^{\text{trans}} + e_s^{\text{rot}} + e_s^{\text{vib}}, \quad (61)$$

where

$$e_s^{\text{trans}} = 3 \times \frac{1}{2} R_s T. \quad (62)$$

For diatomic molecules

$$e_s^{\text{rot}} = 2 \times \frac{1}{2} R_s T \quad (63)$$

and e_s^{vib} is given by Eq. (60). Atoms do not have rotational or vibrational internal energy modes.

In the temperature range where air behaves as a thermally perfect gas (600–2000 K roughly), it is chemically inert and its composition remains that of room temperature air. Thus

$$e(T) = y_{N_2} e_{N_2}(T) + y_{O_2} e_{O_2}(T), \quad (64)$$

where y_{N_2} and y_{O_2} are the constant mass fractions of N_2 and O_2 , given by

$$y_{N_2} = \frac{\rho_{N_2}}{\rho} = 0.79 \frac{\hat{M}_{N_2}}{\hat{M}} = 0.7670 \quad (65)$$

$$y_{O_2} = \frac{\rho_{O_2}}{\rho} = 0.21 \frac{\hat{M}_{O_2}}{\hat{M}} = 0.2330. \quad (66)$$

\hat{M} is the molar mass of the mixture

$$\hat{M} = 0.79 \hat{M}_{N_2} + 0.21 \hat{M}_{O_2} = 28.84 \times 10^{-3} \text{ kg/mol} \quad (67)$$

with

$$\hat{M}_{N_2} = 28.0 \times 10^{-3} \text{ kg/mol} \quad (68)$$

$$\hat{M}_{O_2} = 32.0 \times 10^{-3} \text{ kg/mol}. \quad (69)$$

Density is still related to pressure and temperature by the perfect gas law (38), where R is obtained using Eqs (39) and (67). Equation (58) can be integrated exactly, yielding the following expression for the chemical potential:

$$\begin{aligned} \mu = e + RT - \frac{7}{2} RT \ln \frac{T}{T_0} \\ + RT \ln \frac{p}{p_0} - T \left(\frac{e^{\text{vib}}}{T} - \frac{e_0^{\text{vib}}}{T_0} \right) \\ + \sum_{s=N_2, O_2} y_s R_s T \ln \left[\frac{1 - \exp(-\Theta_s^{\text{vib}}/T)}{1 - \exp(-\Theta_s^{\text{vib}}/T_0)} \right] - Ts_0, \end{aligned} \quad (70)$$

where e is given by Eqs (60)–(66); the summation concerns molecules of N_2 and O_2 ; the term

$(e^{\text{vib}}/T - e_0^{\text{vib}}/T_0)$ in Eq. (70) comes from the term $(e/T - e_0/T_0)$ in Eq. (58)

$$\begin{aligned} \frac{e}{T} - \frac{e_0}{T_0} &= \sum_s y_s \left[\frac{\frac{5}{2} R_s T + e_s^{\text{vib}}}{T} - \frac{\frac{5}{2} R_s T_0 + e_{s0}^{\text{vib}}}{T_0} \right] \\ &= \sum_s y_s \left[\frac{e_s^{\text{vib}}}{T} - \frac{e_{s0}^{\text{vib}}}{T_0} \right] \\ &= \frac{e^{\text{vib}}}{T} - \frac{e_0^{\text{vib}}}{T_0}. \end{aligned} \quad (71)$$

In turn, entropy can be written as

$$\begin{aligned} s &= \frac{7}{2} R \ln \frac{T}{T_0} - R \ln \frac{p}{p_0} + \frac{e^{\text{vib}}}{T} - \frac{e_0^{\text{vib}}}{T_0} \\ &\quad - \sum_s y_s R_s \ln \left[\frac{1 - \exp(-\Theta_s^{\text{vib}}/T)}{1 - \exp(-\Theta_s^{\text{vib}}/T_0)} \right] + s_0. \end{aligned} \quad (72)$$

Equation (72) differs from the calorically perfect case, Eq. (41), only by the terms induced by vibrational excitation.

3.4.3. Mixture of thermally perfect gases in chemical equilibrium. We now release the restriction imposed on the gas to be chemically inert. In order to be able to continue describing the mixture as a divariant gas, we must assume that it is in thermal and chemical equilibrium. In other words, a fluid element is supposed to respond instantaneously to any local change in pressure and temperature; this requires infinite chemical and vibrational rates.

We specialize our description to air. Before significant ionization, it can be considered as a mixture of N_2 , O_2 , NO , N , and O . Each of these species has a chemical potential given by

$$\begin{aligned} \mu_s &= e_s + R_s T - T \left(\frac{e_s}{T} - \frac{e_{s0}}{T_0} \right) - T \int_{T_0}^T \frac{e_s(\theta)}{\theta^2} d\theta \\ &\quad - R_s T \ln \frac{T}{T_0} + R_s T \ln \frac{p_s}{p_{s0}} - T s_{s0} \\ &= \mu_s^0(T) + R_s T \ln p_s \\ &= \mu_s^0(T) + R_s T (\ln p + \ln x_s), \end{aligned} \quad (73)$$

where the x_s s are the mole fractions of the different species; they are related to the concentrations, $c_s = \rho_s/\hat{M}_s$, and to the mass fractions by

$$x_s = \frac{c_s}{c} = \frac{\hat{M}}{\hat{M}_s} y_s. \quad (74)$$

c is the total number of moles per unit volume

$$c = \sum_s c_s. \quad (75)$$

\hat{M} is the molar mass of the mixture

$$\hat{M} = \sum_s x_s \hat{M}_s = \left(\sum_s \frac{y_s}{\hat{M}_s} \right)^{-1}. \quad (76)$$

According to the number of atoms in the particle, e_s takes the form of Eq. (61) to which the heat of formation has been added

$$e_s = e_s^{\text{trans}} + e_s^{\text{rot}} + e_s^{\text{vib}} + h_s^0. \quad (77)$$

h_s^0 is zero for the species present in the mixture at room temperature, i.e. N_2 and O_2 , and nonzero for NO , N , and O . p_s is the partial pressure of species s in the mixture

$$p_s = \rho_s R_s T. \quad (78)$$

The pressure p is obtained using Dalton's law

$$p = \sum_s p_s. \quad (79)$$

The chemical potential of the system can be written as

$$\mu(p, T) = \sum_s y_s(p, T) \mu_s(p, T), \quad (80)$$

where the mass fractions are no longer constants, but functions of the thermodynamic state. Unfortunately, there exist no explicit expressions for the y_s s, which thus must be evaluated numerically. Many computer programs are available for this purpose. They are essentially based on two equivalent methods: the equilibrium constant method and the free energy minimization method. The objective of this paper is not to describe equilibrium solvers in detail. However, we still stress the importance of using the Newton–Raphson scheme to solve the resulting non-linear systems: once convergence has been achieved, any thermodynamic derivative can be obtained directly from the linear system of the last iteration at essentially no extra cost (see Ref. 14 and Appendix B). Data can then be tabulated and interpolation formula designed to facilitate computer access. In Appendix B, we present a simple example of equilibrium chemistry calculations, where the strategy mentioned above is made clearer.

4. MIXTURE OF GASES IN THERMOCHEMICAL NONEQUILIBRIUM

Energy exchanges between translational and internal degrees of freedom, and chemical processes take place through molecular collisions. Equilibration between translational and rotational modes is fast and requires only a few collisions, say 20. Therefore, the assumption of equilibrium of the rotation with the translation is often justified, and both modes can be represented by the same temperature T . On the contrary, in response to drastic changes in the flow, such as through a shock wave, vibrational degrees of freedom demand many more collisions, typically on the order of 20,000, to reach their equilibrium level. Thus, if we assume that the oscillators have a Boltzmann distribution over their energy states, it will be expressed in terms of a

second temperature T^{vib} , different from the translational-rotational temperature T . An even larger number of collisions, on the order of 200,000, is needed to break apart molecules and trigger dissociation.

These collision processes take time. Consequently, before a fluid element reaches equilibrium, it has moved a certain distance, in a region where non-equilibrium prevails. The size of this nonequilibrium region depends on the dimensions and velocity of the vehicle. It is clear that, when the characteristic time for readjustment by collisions is of the same order as the characteristic time of the fluid flow, the equilibrium assumption breaks down, and nonequilibrium effects must be accounted for. According to Park,¹⁶ a multi-temperature model is crucial in order to compute accurately the aerothermal loads on the vehicle; models assuming thermal equilibrium indeed tend to predict that the flow is closer to equilibrium than it actually is, leading to incorrect values of pitching moment and trim angle.

Following the plan of the preceding section, we will present the symmetrization of a two-temperature model for non-ionized hypersonic flows in thermochemical nonequilibrium, and the corresponding entropy variables. In addition, since the thermodynamics of the irreversible processes involved¹⁷ is much less documented in the literature than Gibbs' classical thermodynamics, we will outline the derivations of entropy and of the chemical potentials of the different species present in the mixture.

4.1. Systems of conservation laws

In three dimensions, and for a mixture of n species, the vectors appearing in Eq. (1) read

$$\mathbf{U} = \begin{Bmatrix} U_1 \\ \vdots \\ U_n \\ \text{---} \\ U_{n+1} \\ U_{n+2} \\ U_{n+3} \\ \text{---} \\ U_{n+4} \\ U_{n+5} \end{Bmatrix} = \rho \begin{Bmatrix} \mathbf{y} \\ \mathbf{u} \\ \mathbf{e}^{\text{vib}} \\ \mathbf{e}^{\text{tot}} \end{Bmatrix} \quad (81)$$

$$\mathbf{F}_i^{\text{adv}} = u_i \mathbf{U} + p \begin{Bmatrix} \mathbf{0}_n \\ \boldsymbol{\delta}_i \\ 0 \\ u_i \end{Bmatrix} \quad (82)$$

$$\mathbf{F}_i^{\text{diff}} = \mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{visc}} + \mathbf{F}_i^{\text{heat}} \quad (83)$$

$$\mathbf{F}_i^{\text{mass}} = \begin{Bmatrix} -\mathbf{J}_i \\ \mathbf{0}_3 \\ -\mathbf{J}_i \cdot \mathbf{e}^{\text{vib}} \\ -\mathbf{J}_i \cdot \mathbf{h} \end{Bmatrix} \quad (84)$$

$$\mathbf{F}_i^{\text{visc}} = \begin{Bmatrix} \mathbf{0}_n \\ \tau_{ij} \boldsymbol{\delta}_j \\ 0 \\ \tau_{ij} u_j \end{Bmatrix} \quad (85)$$

$$\mathbf{F}_i^{\text{heat}} = \begin{Bmatrix} \mathbf{0}_n \\ \mathbf{0}_3 \\ -q_i^{\text{vib}} \\ -(q_i + q_i^{\text{vib}}) \end{Bmatrix} \quad (86)$$

$$\mathcal{F} = \begin{Bmatrix} \boldsymbol{\Omega} \\ \mathbf{0}_3 \\ \boldsymbol{\Omega} \cdot \mathbf{e}^{\text{vib}} + Q^{T-T^{\text{vib}}} \\ 0 \end{Bmatrix} \quad (87)$$

where $\mathbf{y} = \{y_s\}$ is the vector of mass fractions; $\boldsymbol{\delta}_i$ is a generalized Kronecker delta, $\boldsymbol{\delta}_i = \{\delta_{ij}\}$; $\mathbf{0}_n$ and $\mathbf{0}_3$ are respectively null vectors of length n and 3; the diffusive flux, due to translational nonequilibrium effects,⁷ splits up into three parts: a mass diffusion part, $\mathbf{F}_i^{\text{mass}}$, a viscous stress part, $\mathbf{F}_i^{\text{visc}}$, and a heat conduction part, $\mathbf{F}_i^{\text{heat}}$; \mathbf{J}_i is the mass diffusion flux in direction i , $\mathbf{J}_i = \{J_{si}\} = \{\rho_s v_{si}\}$, where v_{si} is the diffusion velocity of species s in direction i ; \mathbf{e}^{vib} and \mathbf{h} are, respectively, the vibrational energy and enthalpy vectors, $\mathbf{e}^{\text{vib}} = \{e_s^{\text{vib}}\}$ and $\mathbf{h} = \{h_s\}$; q_i and q_i^{vib} are the heat fluxes in direction i , respectively due to gradients in the translational-vibrational temperature T and the vibrational temperature T^{vib} ; $\boldsymbol{\Omega}$ is the vector of the production rates of the different species, $\boldsymbol{\Omega} = \{\Omega_s\}$; $Q^{T-T^{\text{vib}}}$ is the translation-vibration energy transfer rate; other notations are common with those of the preceding sections.

4.2. Constitutive relations

The following constitutive relations are needed to complete the definition of the diffusive flux.

- (i) Nonequilibrium kinetic theory provides the following expression for the diffusion velocities (neglecting the thermal diffusion effect or Soret effect):

$$J_{si} = \rho_s v_{si} = \sum_r \rho \frac{\hat{M}_s \hat{M}_r}{\hat{M}^2} D_{sr} d_{ri}, \quad (88)$$

where

$$d_{si} = x_{s,i} + (x_s - y_s)(\ln p)_{,i}. \quad (89)$$

The D_{sr} s are the multicomponent diffusion coefficients, which are intricate functions of temperature and of the chemical composition of the mixture. They are not symmetric, i.e.

$$D_{sr} \neq D_{rs}, \quad s \neq r, \quad (90)$$

but satisfy the relations¹⁸

$$D_{ss} = 0 \quad (91)$$

$$\sum_s (\hat{M}_s \hat{M}_r D_{sr} - \hat{M}_s \hat{M}_t D_{st}) = 0, \quad \forall r, t. \quad (92)$$

Equation (92), together with

$$\sum_s d_{st} = 0, \quad (93)$$

implies that

$$\sum_s \rho_s v_{si} = 0. \quad (94)$$

As shown in Appendix C, the pressure term in Eq. (89) is critical for obtaining a complete symmetrization of the system. However, the diffusion model presented here is apparently not widely used due to its ostensible complexity. Simpler models, which would retain symmetry, are currently under investigation.

(ii) The viscous stress tensor is given as before by

$$\tau_{ij} = \lambda^{\text{visc}} u_{k,k} \delta_{ij} + \mu^{\text{visc}} (u_{i,j} + u_{j,i}). \quad (95)$$

(iii) The heat fluxes are given by Fourier's law

$$q_i = -\kappa T_{,i} \quad (96)$$

$$q_i^{\text{vib}} = -\kappa^{\text{vib}} T_{,i}^{\text{vib}}. \quad (97)$$

In Eq. (96) we have neglected the diffusion thermo-effect or Dufour effect. For completeness, the coupling between mass diffusion and heat conduction resulting from the Soret and Dufour effects is considered in Appendix D.

λ^{visc} , μ^{visc} , κ , and κ^{vib} can be computed from kinetic theory, but the corresponding formulae which involve temperatures, species densities and collision integrals are too complex for practical use. Reasonable approximations can be obtained using Eucken's relations^{7,18} and Wilke's mixing rule.¹⁶

4.3. Equation of state

We assume that the gas is a mixture of thermally perfect gases. In addition, we adopt the rigid-rotator and harmonic-oscillator model. In these conditions, simple closed form expressions exist for the different energies

$$e^{\text{tot}} = e + \frac{|\mathbf{u}|^2}{2} \quad (98)$$

$$e = \sum_s y_s e_s \quad (99)$$

$$e^{\text{vib}} = \sum_s y_s e_s^{\text{vib}} \quad (100)$$

$$e_s(T, T^{\text{vib}}) = e_s^{\text{trans}} + e_s^{\text{rot}} + e_s^{\text{vib}} + h_s^0 \quad (101)$$

$$e_s^{\text{trans}}(T) = 3 \times \frac{1}{2} R_s T \quad (102)$$

$$e_s^{\text{rot}}(T) = \begin{cases} 0, & \text{for atoms} \\ 2 \times \frac{1}{2} R_s T, & \text{for diatomic molecules} \end{cases}$$

$$e_s^{\text{vib}}(T^{\text{vib}}) = \begin{cases} 0, & \text{for atoms} \\ \frac{R_s \Theta_s^{\text{vib}}}{\exp(\Theta_s^{\text{vib}}/T^{\text{vib}}) - 1}, & \text{for diatomic molecules.} \end{cases} \quad (104)$$

4.4. Computation of entropy and chemical potentials

We consider a closed system, whose extensive properties are designated by script capital letters. Its change in entropy can be split into two parts (see Prigogine¹⁷):

$$d\mathcal{S} = d\mathcal{S}^{\text{ext}} + d\mathcal{S}^{\text{int}}, \quad (105)$$

where $d\mathcal{S}^{\text{ext}}$ is the flow of entropy into the system from its surroundings, and $d\mathcal{S}^{\text{int}}$ is the production of entropy by irreversible processes within the system itself. $d\mathcal{S}^{\text{ext}}$ is given by

$$d\mathcal{S}^{\text{ext}} = \frac{d\mathcal{Q}}{T}, \quad (106)$$

where $d\mathcal{Q}$ is the heat received by the system at the temperature T . Using the first law of thermodynamics, Eq. (106) can be rewritten as

$$d\mathcal{S}^{\text{ext}} = \frac{d\mathcal{E}}{T} + \frac{p}{T} d\mathcal{V}. \quad (107)$$

The internal irreversibilities inherent to the chemical and the vibrational nonequilibria produce the following entropy⁷:

$$d\mathcal{S}^{\text{int}} = -\frac{1}{T} \sum_s \hat{\mu}_s d\mathcal{N}_s + \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) d\mathcal{E}^{\text{vib}}, \quad (108)$$

where \mathcal{N}_s is the number of moles of species s in the system, and $\hat{\mu}_s$ the molar chemical potential of species s . In general, we indicate per mole quantities by the addition of a circumflex over the symbol.

The second law of thermodynamics states that $d\mathcal{S}^{\text{int}} = 0$ when the system undergoes reversible changes, and that $d\mathcal{S}^{\text{int}} > 0$ if the system is subject to irreversible processes. From Eq. (108), it is easy to derive the condition for chemical equilibrium [Eq. (B10)], which is related to De Donder's notion of chemical affinity.¹⁷ The production of entropy due to vibrational nonequilibrium can be seen as the result of an exchange of heat between two subsystems, one being in equilibrium at temperature T , the other at temperature T^{vib} . If we assume chemical equilibrium, the second law of thermodynamics dictates that, if $T > T^{\text{vib}}$, then the vibrational energy must increase; accordingly, if $T^{\text{vib}} > T$, then \mathcal{E}^{vib} will decrease. Combining Eqs (107) and (108), we obtain

$$d\mathcal{S} = \frac{d\mathcal{E}}{T} + \frac{p}{T} d\mathcal{V} - \frac{1}{T} \sum_s \hat{\mu}_s d\mathcal{N}_s + \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) d\mathcal{E}^{\text{vib}}. \quad (109)$$

$$(103)$$

In order to compute the entropy of the system, we need an expression for the chemical potentials $\hat{\mu}_s$. Let us introduce the Gibbs free energy, an extensive thermodynamic state variable defined by

$$\mathcal{G} = \mathcal{E} + p\mathcal{V} - T\mathcal{S}. \quad (110)$$

The differential of Eq. (110) reads

$$d\mathcal{G} = d\mathcal{E} + p d\mathcal{V} + \mathcal{V} dp - T d\mathcal{S} - \mathcal{S} dT. \quad (111)$$

Substituting Eq. (109) into Eq. (111), we obtain

$$d\mathcal{G} = \mathcal{V} dp - \mathcal{S} dT + \sum_s \hat{\mu}_s d\mathcal{N}_s - \left(\frac{T}{T^{\text{vib}}} - 1 \right) d\mathcal{E}^{\text{vib}}. \quad (112)$$

However,

$$\mathcal{E}^{\text{vib}} = \sum_s \mathcal{N}_s \hat{e}_s^{\text{vib}}. \quad (113)$$

Thus, Eq. (112) becomes

$$d\mathcal{G} = \mathcal{V} dp - \mathcal{S} dT - \left(\frac{T}{T^{\text{vib}}} - 1 \right) \mathcal{N} d\hat{e}_s^{\text{vib}} dT^{\text{vib}} + \sum_s \left[\hat{\mu}_s - \left(\frac{T}{T^{\text{vib}}} - 1 \right) \hat{e}_s^{\text{vib}} \right] d\mathcal{N}_s, \quad (114)$$

where $\mathcal{N} = \sum_s \mathcal{N}_s$ is the total number of moles in the system,

$$\mathcal{N} \hat{e}_s^{\text{vib}} = \sum_s \mathcal{N}_s \hat{e}_{rs}^{\text{vib}} \quad (115)$$

and

$$\hat{e}_{rs}^{\text{vib}} = \frac{\partial \hat{e}_s^{\text{vib}}(T^{\text{vib}})}{\partial T^{\text{vib}}}. \quad (116)$$

From Eq. (114), we deduce

$$\left(\frac{\partial \mathcal{G}}{\partial \mathcal{N}_s} \right)_{p,T,T^{\text{vib}},\mathcal{N}_s'} = \hat{\mu}_s - \left(\frac{T}{T^{\text{vib}}} - 1 \right) \hat{e}_s^{\text{vib}}. \quad (117)$$

\mathcal{G} is extensive, and as a function of p , T , T^{vib} , and \mathcal{N}_s , must therefore be homogeneous in \mathcal{N}_s

$$\mathcal{G} = \sum_s \left(\frac{\partial \mathcal{G}}{\partial \mathcal{N}_s} \right)_{p,T,T^{\text{vib}},\mathcal{N}_s'} \mathcal{N}_s = \sum_s \mathcal{N}_s \hat{g}_s. \quad (118)$$

From Eqs (117) and (118), we obtain

$$\hat{g}_s = \hat{\mu}_s - \left(\frac{T}{T^{\text{vib}}} - 1 \right) \hat{e}_s^{\text{vib}}. \quad (119)$$

We see that the well-known identity $\hat{g}_s = \hat{\mu}_s$ is satisfied only when vibrational degrees of freedom are at equilibrium with the translation, that is, when $T^{\text{vib}} = T$. Going back to the definition of \mathcal{G} , we can derive another expression for the \hat{g}_s s

$$\mathcal{G} = \mathcal{E} + p\mathcal{V} - T\mathcal{S}$$

$$\begin{aligned} &= \sum_s \mathcal{N}_s \left(\hat{e}_s + p_s \frac{\mathcal{V}}{\mathcal{N}_s} - T \hat{s}_s \right) \\ &= \sum_s \mathcal{N}_s (\hat{e}_s + p_s \hat{v}_s - T \hat{s}_s) = \sum_s \mathcal{N}_s \hat{g}_s. \end{aligned} \quad (120)$$

Therefore

$$\hat{g}_s = \hat{e}_s + p_s \hat{v}_s - T \hat{s}_s. \quad (121)$$

Finally, Eqs (119) and (121) lead to

$$\hat{\mu}_s = \hat{e}_s + p_s \hat{v}_s - T \hat{s}_s + \left(\frac{T}{T^{\text{vib}}} - 1 \right) \hat{e}_s^{\text{vib}}. \quad (122)$$

Then, substituting $\sum_s \mathcal{N}_s \hat{s}_s$ for \mathcal{S} into the expression for $d\mathcal{S}$ yields

$$\begin{aligned} &\sum_s \mathcal{N}_s d\hat{s}_s \\ &= \sum_s \left[\frac{d\hat{e}_s}{T} + \frac{p_s}{T} d\hat{v}_s + \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) d\hat{e}_s^{\text{vib}} \right] \mathcal{N}_s \\ &\quad + \sum_s \left[\hat{e}_s + p_s \hat{v}_s - \hat{\mu}_s + \left(\frac{T}{T^{\text{vib}}} - 1 \right) \hat{e}_s^{\text{vib}} - T \hat{s}_s \right] \frac{d\mathcal{N}_s}{T} \\ &= \sum_s \left[\frac{d\hat{e}_s}{T} + \frac{p_s}{T} d\hat{v}_s + \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) d\hat{e}_s^{\text{vib}} \right] \mathcal{N}_s. \end{aligned} \quad (123)$$

Thus

$$d\hat{s}_s = \frac{d\hat{e}_s}{T} + \frac{p_s}{T} d\hat{v}_s + \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) d\hat{e}_s^{\text{vib}}. \quad (124)$$

Writing \hat{e}_s in the form

$$\hat{e}_s = \hat{e}_{rs} T + \hat{e}_s^{\text{vib}}(T^{\text{vib}}) + \hat{h}_s^0, \quad (125)$$

Eq. (124) becomes

$$d\hat{s}_s = \hat{c}_{rs} \frac{dT}{T} + \hat{R} \frac{d\hat{v}_s}{\hat{v}_s} + \hat{e}_{rs}^{\text{vib}}(T^{\text{vib}}) \frac{dT^{\text{vib}}}{T^{\text{vib}}}. \quad (126)$$

Converting into quantities per unit mass by dividing Eq. (126) by \hat{M}_s , and integrating from the reference state of entropy, we obtain

$$\begin{aligned} s_s &= c_{ps} \ln \frac{T}{T_0} - R_s \ln \frac{p_s}{p_{s0}} + \frac{e_s^{\text{vib}}}{T^{\text{vib}}} - \frac{e_{s0}^{\text{vib}}}{T_0^{\text{vib}}} \\ &\quad - R_s \ln \left(\frac{1 - \exp(-\Theta_s^{\text{vib}}/T^{\text{vib}})}{1 - \exp(-\Theta_s^{\text{vib}}/T_0^{\text{vib}})} \right) + s_{s0}, \end{aligned} \quad (127)$$

where

$$c_{ps} = c_{vs} + R_s. \quad (128)$$

The specific entropy of the system is obtained from Eq. (127)

$$s = \sum_s y_s s_s. \quad (129)$$

4.5. Entropy variables and symmetrization

As in Sec. 3, we define the generalized entropy function \mathcal{H} as

$$\mathcal{H} = -\rho s, \quad (130)$$

where s is given by Eq. (129). The change of variables

$$\mathbf{V}^T = \frac{\partial \mathcal{H}}{\partial \mathbf{U}} \quad (131)$$

yields the following vector of entropy variables:

$$\mathbf{V} = \frac{1}{T} \begin{Bmatrix} \mu - \frac{|\mathbf{u}|^2}{2} \mathbf{1}_n \\ \mathbf{u} \\ \mathbf{I} - \frac{T}{T^{\text{vib}}} \\ -1 \end{Bmatrix}, \quad (132)$$

where $\mu = \{\mu_s\}$ and $\mathbf{1}_n^T = \{\underbrace{1 \dots 1}_{n \text{ terms}}\}$.

The assumptions made in Sec. 4.3 concerning the form of the different energies are not necessary to derive Eq. (132). Knowing that e_s is the sum of a function of T and of a function of T^{vib} is sufficient. However, if Eqs (101)–(104) are satisfied, we can express explicitly the primitive variables $\mathbf{Y}^T = \{\rho^T, \mathbf{u}^T, T^{\text{vib}}, T\}$ in terms of the entropy variables

$$u_i = -\frac{V_{n+i}}{V_{n+5}}, \quad i = 1, 2, 3 \quad (133)$$

$$T^{\text{vib}} = -\frac{1}{V_{n+4} + V_{n+5}} \quad (134)$$

$$T = -\frac{1}{V_{n+5}} \quad (135)$$

$$\rho_s = \rho_{s0} \left(\frac{T}{T_0} \right)^{1/(\gamma_s - 1)} \frac{1 - \exp(-\Theta_s^{\text{vib}}/T_0^{\text{vib}})}{1 - \exp(-\Theta_s^{\text{vib}}/T^{\text{vib}})} \\ \times \exp \left[\frac{\mu_s - h_s^0}{R_s T} - \frac{\mu_{s0} - h_s^0}{R_s T_0} \right], \quad (136)$$

where

$$\mu_s = T V_s + \frac{|\mathbf{u}|^2}{2} = -\frac{V_s}{V_{n+5}} \\ + \frac{1}{2V_{n+5}^2} (V_{n+1}^2 + V_{n+2}^2 + V_{n+3}^2) \quad (137)$$

$$\gamma_s = \frac{c_{ps}}{c_{vs}} \quad (138)$$

and ρ_{s0} and μ_{s0} are, respectively, the density and the chemical potential of species s in the state of reference entropy.

Table 1. Variable transformations for rigid-rotator/harmonic-oscillator model

to:

	Primitive	Conservative	Entropy
Primitive	=	explicit	explicit
Conservative	numerical	=	numerical
Entropy	explicit	explicit	=

The production rates of the different species, Ω_s , are given in terms of the ρ_s , T , and T^{vib} .¹⁶ These quantities are readily available through Eqs (133)–(136). In particular, there is no need to numerically solve for T^{vib} , as it would be the case with a strategy based on the conservative variables \mathbf{U} , unless one vibrational temperature is defined for each diatomic species.¹⁹ The characteristics of the different transformations between primitive, conservative, and entropy variables for the rigid-rotator/harmonic-oscillator model, are summarized in Table 1. Figure 1 also depicts the available explicit relations among the three sets of variables. While conservative variables appear clearly as a bottleneck, entropy variables are seen to bring in the ease of use of primitive variables, retaining the advantage of a conservation law form.

The Riemannian metric tensor $\tilde{\mathbf{A}}_0$ and the corresponding coefficient matrices are described in Appendix C.

5. ADVANTAGES OF SYMMETRIC CONSERVATION LAWS

The advantages of the symmetry of Eq. (5) are practical as well as aesthetic. It can be shown that Eq. (5) expresses intrinsically the mathematical and physical stability provided by the second law of thermodynamics. Moreover, strong mathematical foundations support the analysis of convergence of finite element methods applied to the numerical solution of Eq. (5). We will exemplify these properties with the system of Sec. 4, for which the sources of irreversibility are more numerous and richer. We will begin this section with the proof of the positive semidefiniteness of the diffusivity matrix $\tilde{\mathbf{K}}$.

5.1. Positive semidefiniteness of $\tilde{\mathbf{K}}$

As will be seen in the next section, when the dot product of Eq. (5) with \mathbf{V} is taken, the term $\mathbf{V}\mathbf{V} \cdot \tilde{\mathbf{K}}\mathbf{V}\mathbf{V} = \mathbf{V}_i \cdot \tilde{\mathbf{K}}_{ij} \mathbf{V}_j$ appears after an integration by parts. We will examine it for each of the three components of $\tilde{\mathbf{K}}$, namely $\tilde{\mathbf{K}}^{\text{mass}}$, $\tilde{\mathbf{K}}^{\text{visc}}$, and $\tilde{\mathbf{K}}^{\text{heat}}$.

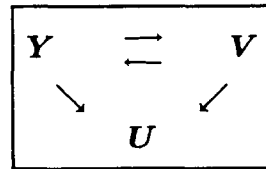


Fig. 1. Explicit relations for rigid-rotator/harmonic-oscillator model.

5.1.1. The mass-diffusion diffusivity matrix, \mathbf{K}^{mass}

$$\nabla \mathbf{V} \cdot \mathbf{K}^{\text{mass}} \nabla \mathbf{V}$$

$$\begin{aligned} &= \mathbf{V}_{,i} \cdot \mathbf{K}_{ij}^{\text{mass}} \mathbf{V}_{,j} = \mathbf{V}_{,i} \cdot \mathbf{F}_i^{\text{mass}} \\ &= \sum_i \sum_{s,r} \left[R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \alpha_{sr}) R_r \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) \right] \\ &= \sum_i \sum_{s,r} [R_s (\ln p_s)_{,i} (T \alpha_{sr}) R_r (\ln p_r)_{,i}] \geq 0 \end{aligned} \quad (139)$$

if and only if $\alpha = [\alpha_{sr}]$ is positive semidefinite. The α_{sr} s are Onsager's phenomenological coefficients for mass diffusion, as defined in Appendix C. The second law of thermodynamics requires the positiveness of α (see Ref. 20).

5.1.2. The viscous stress diffusivity matrix, \mathbf{K}^{visc}

$$\begin{aligned} \nabla \mathbf{V} \cdot \mathbf{K}^{\text{visc}} \nabla \mathbf{V} &= \mathbf{V}_{,i} \cdot \mathbf{K}_{ij}^{\text{visc}} \mathbf{V}_{,j} = \mathbf{V}_{,i} \cdot \mathbf{F}_i^{\text{visc}} \\ &= \frac{1}{T} [\lambda^{\text{visc}} (\nabla \cdot \mathbf{u})^2 + 2\mu^{\text{visc}} (\boldsymbol{\varepsilon} : \boldsymbol{\varepsilon})], \end{aligned} \quad (140)$$

where $\boldsymbol{\varepsilon}$ is the strain tensor

$$\varepsilon_{ij} = \frac{1}{2}(u_{i,j} + u_{j,i}). \quad (141)$$

$\boldsymbol{\varepsilon}$ can be split into a deviatoric part $\boldsymbol{\varepsilon}'$, and a dilatational part $\boldsymbol{\varepsilon}''$

$$\boldsymbol{\varepsilon}_{ij}'' = (\frac{1}{3} \text{tr } \boldsymbol{\varepsilon}) \delta_{ij} = \frac{1}{3} \varepsilon_{kk} \delta_{ij} \quad (142)$$

$$\boldsymbol{\varepsilon}_{ij}' = \varepsilon_{ij} - \varepsilon_{ij}''. \quad (143)$$

Then

$$\begin{aligned} \nabla \mathbf{V} \cdot \mathbf{K}^{\text{visc}} \nabla \mathbf{V} &= \frac{1}{T} [(\lambda^{\text{visc}} + \frac{2}{3}\mu^{\text{visc}})(\text{tr } \boldsymbol{\varepsilon})^2 \\ &+ 2\mu^{\text{visc}}(\boldsymbol{\varepsilon}' : \boldsymbol{\varepsilon}')] \geq 0 \end{aligned} \quad (144)$$

if and only if $\lambda^{\text{visc}} + \frac{2}{3}\mu^{\text{visc}} \geq 0$ and $\mu^{\text{visc}} \geq 0$.

5.1.3. The heat conduction diffusivity matrix, \mathbf{K}^{heat}

$$\begin{aligned} \nabla \mathbf{V} \cdot \mathbf{K}^{\text{heat}} \nabla \mathbf{V} &= \mathbf{V}_{,i} \cdot \mathbf{K}_{ij}^{\text{heat}} \mathbf{V}_{,j} = \mathbf{V}_{,i} \cdot \mathbf{F}_i^{\text{heat}} \\ &= \frac{\kappa}{T^2} (\nabla T)^2 + \frac{\kappa^{\text{vib}}}{T^{\text{vib}2}} (\nabla T^{\text{vib}})^2 \geq 0 \end{aligned} \quad (145)$$

if and only if $\kappa \geq 0$ and $\kappa^{\text{vib}} \geq 0$.

5.2. Clausius–Duhem inequality

The dot product of Eq. (5) with \mathbf{V} reads

$$\mathbf{V} \cdot [\tilde{\mathbf{A}}_0 \mathbf{V}_{,i} + \tilde{\mathbf{A}}_i \mathbf{V}_{,i} = (\tilde{\mathbf{K}}_{ij} \mathbf{V}_{,j})_{,i} + \tilde{\mathcal{F}}]. \quad (146)$$

Integrating by parts the diffusivity term, and rearranging, yields

$$\begin{aligned} \mathbf{V} \cdot \tilde{\mathbf{A}}_0 \mathbf{V}_{,i} + \mathbf{V} \cdot \mathbf{F}_{i,i}^{\text{adv}} - (\mathbf{V} \cdot \mathbf{F}_i^{\text{diff}})_{,i} - \mathbf{V} \cdot \tilde{\mathcal{F}} \\ = -\mathbf{V}_{,i} \cdot \tilde{\mathbf{K}}_{ij} \mathbf{V}_{,j}. \end{aligned} \quad (147)$$

From the preceding section, we know that the right-hand side in Eq. (147) is nonpositive. Moreover, one can show that

$$\mathbf{V} \cdot \tilde{\mathbf{A}}_0 \mathbf{V}_{,i} = \mathcal{H}_{,i} \quad (148)$$

$$\mathbf{V} \cdot \mathbf{F}_{i,i}^{\text{adv}} = (\mathcal{H} u_i)_{,i} \quad (149)$$

$$\mathbf{V} \cdot \mathbf{F}_i^{\text{mass}} = \sum_s \rho_s s_s v_{si} \quad (150)$$

$$\mathbf{V} \cdot \mathbf{F}_i^{\text{visc}} = 0 \quad (151)$$

$$\mathbf{V} \cdot \mathbf{F}_i^{\text{heat}} = \frac{q_i}{T} + \frac{q_i^{\text{vib}}}{T^{\text{vib}}} \quad (152)$$

$$\begin{aligned} \mathbf{V} \cdot \tilde{\mathcal{F}} &= \frac{1}{T} \sum_s g_s \Omega_s \\ &\quad - \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) Q^{T-T^{\text{vib}}}. \end{aligned} \quad (153)$$

Substituting Eqs (148)–(153) into Eq. (147), we obtain

$$\begin{aligned} \mathcal{H}_{,i} + (\mathcal{H} u_i)_{,i} - \left(\sum_s \rho_s s_s v_{si} \right)_{,i} - \left(\frac{q_i}{T} + \frac{q_i^{\text{vib}}}{T^{\text{vib}}} \right)_{,i} \\ - \frac{1}{T} \sum_s g_s \Omega_s + \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) Q^{T-T^{\text{vib}}} \leq 0. \end{aligned} \quad (154)$$

An interpretation of Eq. (154) is that the rate of growth of a convex function of the solution, $\mathcal{H}(\mathbf{U})$, is bounded from above. Appropriately defined finite element methods inherit the fundamental stability property possessed by solutions of Eq. (5) (see Refs 6, 21 and 22).

Setting $\mathcal{H} = -\rho s$ in Eq. (154) gives the local form of the Clausius–Duhem inequality, which governs entropy production of the system

$$\begin{aligned} (\rho s)_{,i} + (\rho s u_i)_{,i} + \left(\sum_s \rho_s s_s v_{si} \right)_{,i} + \left(\frac{q_i}{T} + \frac{q_i^{\text{vib}}}{T^{\text{vib}}} \right)_{,i} \\ + \frac{1}{T} \sum_s g_s \Omega_s - \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) Q^{T-T^{\text{vib}}} \geq 0. \end{aligned} \quad (155)$$

5.3. Mathematical foundations and elements of convergence proof

The finite element methods developed by Hughes *et al.*, variously referred to as Galerkin/least-squares, SUPG, and streamline diffusion, are the only ones for which convergence proofs and error estimates have been given for linear steady and unsteady multi-dimensional scalar advection–diffusion equations, over the full spectrum of advective–diffusive phenomena.^{23–25} Direct extensions of these results have also been established for linear *symmetric* advective–diffusive systems. Linear symmetric advective–diffusive systems are of interest in their own right, since they

serve as model equations for many nonlinear systems, such as those described in this paper.

Until fairly recently, there had been virtually no successful analyses for nonlinear problems. In a series of penetrating articles, Johnson *et al.* have proved a number of important mathematical convergence results for our techniques in the context of hyperbolic conservation laws: in Refs 26 and 27, they established a convergence proof for Burger's equation in one dimension. Szepessy extended this result to a general scalar conservation law in two dimensions.²⁸ For hyperbolic systems of conservation laws which possess a strictly convex entropy function and thus can be symmetrized via entropy variables, Johnson *et al.*²⁷ showed that limits of the finite element solutions are weak solutions of the original system and satisfy the entropy condition. Complete convergence proof appears as an extremely difficult, or even impossible task, since it is linked to the still unsolved problem of the existence of solutions to such systems. Nevertheless, the mathematical richness of symmetric advective-diffusive systems and Galerkin/least-squares type methods sheds some rigor into an area of numerical analysis where it does not usually prevail.

6. CONCLUSION

In this paper, we have presented different advective-diffusive systems to compute high-temperature hypersonic flows, and their symmetrization via entropy variables. In generalizing our techniques to higher Mach number flows, involving chemistry and high-temperature effects, entropy variables may have been expected to engender complications. In fact, not only was no fundamental impediment encountered, but also entropy variables appear as the "natural" variables to use. In addition, it is interesting to see how correct entropy production conditions the form of the constitutive relations, and in particular that of mass diffusion, while demonstrating the deficiencies of widely employed models such as Fick's law.

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APPENDIX A. COEFFICIENT MATRICES FOR A GENERAL DIVARIANT GAS

In this appendix, we present the flux vectors and the coefficient matrices of the conservation law system for a general divariant gas, expressed in terms of the (physical) entropy variables.

For convenience, U and V are repeated here

$$U = \frac{1}{v} \begin{Bmatrix} 1 \\ u_1 \\ u_2 \\ u_3 \\ e + |u|^2/2 \end{Bmatrix} \quad (A1)$$

$$V = \frac{1}{T} \begin{Bmatrix} \mu - |u|^2/2 \\ u_1 \\ u_2 \\ u_3 \\ -1 \end{Bmatrix}. \quad (A2)$$

Given p , T , and $\mu = \mu(p, T)$, we have the following relations:

$$s = - \left(\frac{\partial \mu}{\partial T} \right)_p$$

$$v = \left(\frac{\partial \mu}{\partial p} \right)_T \quad (A3)$$

$$h = \mu + Ts$$

$$e = h - pv \quad (A4)$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \left(\frac{\partial^2 \mu}{\partial p \partial T} \right)$$

$$\beta_T = - \frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = - \frac{1}{v} \left(\frac{\partial^2 \mu}{\partial p^2} \right)_T \quad (A5)$$

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p = -T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_p$$

$$c_v = c_p - \frac{\alpha_p^2 v T}{\beta_T}. \quad (A6)$$

We express the flux vectors and coefficient matrices with the help of the following variables:

$$k = \frac{|u|^2}{2} \quad d = \frac{v \alpha_p T}{\beta_T} \quad \bar{\gamma} = \frac{v \alpha_p}{\beta_T c_v} \quad (A7)$$

$$c_1 = u_1^2 + \frac{v}{\beta_T} \quad c_2 = u_2^2 + \frac{v}{\beta_T} \quad c_3 = u_3^2 + \frac{v}{\beta_T} \quad (A8)$$

$$\bar{c}_1 = u_1^2 + c_v T \quad \bar{c}_2 = u_2^2 + c_v T \quad \bar{c}_3 = u_3^2 + c_v T \quad (\text{A9})$$

$$e_1 = h + k \quad e_2 = e_1 - d \quad e_3 = e_2 + \frac{v}{\beta_T} \quad (\text{A10})$$

$$e_4 = e_2 + 2 \frac{v}{\beta_T} \quad (\text{A11})$$

$$\bar{e}_1 = h - k \quad \bar{e}_2 = \bar{e}_1 - d \quad \bar{e}_3 = \bar{e}_2 - c_v T \quad (\text{A12})$$

$$u_{12} = u_1 u_2 \quad u_{23} = u_2 u_3 \quad u_{31} = u_3 u_1 \quad (\text{A13})$$

$$u_{123} = u_1 u_2 u_3 \quad a^2 = \frac{v c_p}{c_v \beta_T} \quad (\text{A14})$$

$$e_5 = e_1^2 - 2e_1 d + \frac{v(2k + c_p T)}{\beta_T}$$

$$\bar{e}_5 = \bar{e}_1^2 - 2\bar{e}_1 d + 2k c_v T + \frac{v c_p T}{\beta_T}. \quad (\text{A15})$$

The Riemannian metric tensor $\bar{\mathbf{A}}_0 = \mathbf{U}_{,V}$ and its inverse $\bar{\mathbf{A}}_0^{-1} = \mathbf{V}_{,U}$ can be written as

$$\bar{\mathbf{A}}_0 = \frac{\beta_T T}{v^2} \begin{bmatrix} 1 & u_1 & u_2 & u_3 & e_2 \\ c_1 & u_{12} & u_{31} & u_1 e_3 \\ c_2 & u_{23} & u_2 e_3 \\ \text{Symm.} & c_3 & u_3 e_3 \\ e_5 \end{bmatrix} \quad (\text{A16})$$

and

$$\bar{\mathbf{A}}_0^{-1} = \frac{v}{c_v T^2} \begin{bmatrix} \bar{e}_5 & u_1 \bar{e}_3 & u_2 \bar{e}_3 & u_3 \bar{e}_3 & -\bar{e}_2 \\ & \bar{c}_1 & u_{12} & u_{31} & -u_1 \\ & & \bar{c}_2 & u_{23} & -u_2 \\ & & \text{Symm.} & \bar{c}_3 & -u_3 \\ & & & & 1 \end{bmatrix}. \quad (\text{A17})$$

The advective fluxes are

$$\mathbf{F}_i^{\text{adv}} = \rho u_i \begin{Bmatrix} 1 \\ u_1 \\ u_2 \\ u_3 \\ e + |\mathbf{u}|^2/2 \end{Bmatrix} + p \begin{Bmatrix} 0 \\ \delta_{1i} \\ \delta_{2i} \\ \delta_{3i} \\ u_i \end{Bmatrix}. \quad (\text{A18})$$

The advective Jacobians with respect to \mathbf{U} , $\mathbf{A}_i = \mathbf{F}_{i,U}^{\text{adv}}$, are given by

$$\mathbf{A}_1 = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ a^2 - u_1^2 - \bar{e}_1 \tilde{\gamma} & -u_1(\tilde{\gamma} - 2) & -u_2 \tilde{\gamma} & -u_3 \tilde{\gamma} & \tilde{\gamma} \\ -u_{12} & u_2 & u_1 & 0 & 0 \\ -u_{31} & u_3 & 0 & u_1 & 0 \\ -u_1(e_1 + \bar{e}_1 \tilde{\gamma} - a^2) & e_1 - u_1^2 \tilde{\gamma} & -u_{12} \tilde{\gamma} & -u_{31} \tilde{\gamma} & u_1(\tilde{\gamma} + 1) \end{bmatrix} \quad (\text{A19})$$

$$\mathbf{A}_2 = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ u_{12} & u_2 & u_1 & 0 & 0 \\ a^2 - u_2^2 - \bar{e}_1 \tilde{\gamma} & -u_1 \tilde{\gamma} & -u_2(\tilde{\gamma} - 2) & -u_3 \tilde{\gamma} & \tilde{\gamma} \\ -u_{23} & 0 & u_3 & u_2 & 0 \\ -u_2(e_1 + \bar{e}_1 \tilde{\gamma} - a^2) & -u_{12} \tilde{\gamma} & e_1 - u_2^2 \tilde{\gamma} & -u_{23} \tilde{\gamma} & u_2(\tilde{\gamma} + 1) \end{bmatrix} \quad (\text{A20})$$

$$\mathbf{A}_3 = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 \\ -u_{31} & u_3 & 0 & u_1 & 0 \\ -u_{23} & 0 & u_3 & u_2 & 0 \\ a^2 - u_3^2 - \bar{e}_1 \tilde{\gamma} & -u_1 \tilde{\gamma} & -u_2 \tilde{\gamma} & -u_3(\tilde{\gamma} - 2) & \tilde{\gamma} \\ -u_3(e_1 + \bar{e}_1 \tilde{\gamma} - a^2) & -u_{31} \tilde{\gamma} & -u_{23} \tilde{\gamma} & e_1 - u_3^2 \tilde{\gamma} & u_3(\tilde{\gamma} + 1) \end{bmatrix}. \quad (\text{A21})$$

Note that

$$\mathbf{A}_i \mathbf{U} = \rho u_i \begin{Bmatrix} 1 \\ u_1 \\ u_2 \\ u_3 \\ e + |\mathbf{u}|^2/2 \end{Bmatrix} + \left(\frac{c_p - v \alpha_p p}{\beta_T c_v p} \right) p \begin{Bmatrix} 0 \\ \delta_{1i} \\ \delta_{2i} \\ \delta_{3i} \\ u_i \end{Bmatrix}, \quad (\text{A22})$$

where $(c_p - v \alpha_p p)/\beta_T c_v p = 1$ only for a thermally perfect gas.

The advective Jacobian matrices with respect to \mathbf{V} , $\bar{\mathbf{A}}_i = \mathbf{F}_{i,\mathbf{V}}^{\text{adv}} = \mathbf{A}_i \bar{\mathbf{A}}_0$, are given by

$$\bar{\mathbf{A}}_1 = \frac{\beta_T T}{v^2} \begin{bmatrix} u_1 & c_1 & u_{12} & u_{31} & u_1 e_3 \\ & u_1 \left(u_1^2 + 3 \frac{v}{\beta_T} \right) & u_2 c_1 & u_3 c_1 & e_1 \frac{v}{\beta_T} + u_1^2 e_4 \\ & & u_1 c_2 & u_{123} & u_{12} e_4 \\ & & \text{Symm.} & u_1 c_3 & u_{31} e_4 \\ & & & & u_1 \left(e_5 + 2e_1 \frac{v}{\beta_T} \right) \end{bmatrix} \quad (\text{A23})$$

$$\bar{\mathbf{A}}_2 = \frac{\beta_T T}{v^2} \begin{bmatrix} u_2 & u_{12} & c_2 & u_{23} & u_2 e_3 \\ & u_2 c_1 & u_1 c_2 & u_{123} & u_{12} e_4 \\ & & u_2 \left(u_2^2 + 3 \frac{v}{\beta_T} \right) & u_3 c_2 & e_1 \frac{v}{\beta_T} + u_2^2 e_4 \\ & & \text{Symm.} & u_2 c_3 & u_{23} e_4 \\ & & & & u_2 \left(e_5 + 2e_1 \frac{v}{\beta_T} \right) \end{bmatrix} \quad (\text{A24})$$

$$\bar{\mathbf{A}}_3 = \frac{\beta_T T}{v^2} \begin{bmatrix} u_3 & u_{31} & u_{23} & c_3 & u_3 e_3 \\ & u_3 c_1 & u_{123} & u_1 c_3 & u_{31} e_4 \\ & & u_3 c_2 & u_2 c_3 & u_{23} e_4 \\ & & \text{Symm.} & u_3 \left(u_3^2 + 3 \frac{v}{\beta_T} \right) & e_1 \frac{v}{\beta_T} + u_3^2 e_4 \\ & & & & u_3 \left(e_5 + 2e_1 \frac{v}{\beta_T} \right) \end{bmatrix}. \quad (\text{A25})$$

The diffusive fluxes are given as

$$\mathbf{F}_i^{\text{diff}} = \begin{Bmatrix} 0 \\ \tau_{1i} \\ \tau_{2i} \\ \tau_{3i} \\ \tau_{ij} u_j \end{Bmatrix} + \begin{Bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -q_i \end{Bmatrix}, \quad (\text{A26})$$

where

$$\tau_{ij} = \lambda^{\text{visc}} u_{k,k} \delta_{ij} + \mu^{\text{visc}} (u_{ij} + u_{ji}) \quad (\text{A27})$$

$$q_i = -\kappa T_{,i}, \quad (\text{A28})$$

The spatial gradients of the velocity components and temperature are

$$u_{i,j} = TV_{i+1,j} + Tu_i T_{s,j} \quad \text{for } i = 1, 2, 3 \quad (\text{A29})$$

$$T_{,i} = T^2 V_{s,i}. \quad (\text{A30})$$

Let

$$\chi^{\text{visc}} = \lambda^{\text{visc}} + 2\mu^{\text{visc}}. \quad (\text{A31})$$

The diffusivity coefficient-matrices \mathbf{K}_{ij} , where $\mathbf{K}_{ij} \mathbf{V}_j = \mathbf{F}_i^{\text{diff}}$, are

$$\mathbf{K}_{11} = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ \chi^{\text{visc}} & 0 & 0 & 0 & \chi^{\text{visc}} u_1 \\ & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_2 \\ & \text{Symm.} & \mu^{\text{visc}} & 0 & \mu^{\text{visc}} u_3 \\ & & & \chi^{\text{visc}} u_1^2 + \mu^{\text{visc}}(u_2^2 + u_3^2) + \kappa T & \end{bmatrix} \quad (\text{A32})$$

$$\mathbf{K}_{22} = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ & \chi^{\text{visc}} & 0 & 0 & \chi^{\text{visc}} u_2 \\ & \text{Symm.} & \mu^{\text{visc}} & 0 & \mu^{\text{visc}} u_3 \\ & & & \chi^{\text{visc}} u_2^2 + \mu^{\text{visc}}(u_1^2 + u_3^2) + \kappa T & \end{bmatrix} \quad (\text{A33})$$

$$\mathbf{K}_{33} = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_2 \\ & \text{Symm.} & \chi^{\text{visc}} & 0 & \chi^{\text{visc}} u_3 \\ & & & \chi^{\text{visc}} u_3^2 + \mu^{\text{visc}}(u_1^2 + u_2^2) + \kappa T & \end{bmatrix} \quad (\text{A34})$$

$$\mathbf{K}_{12} = \mathbf{K}_{21}^T = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda^{\text{visc}} & 0 & \lambda^{\text{visc}} u_2 \\ 0 & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & \mu^{\text{visc}} u_2 & \lambda^{\text{visc}} u_1 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_{12} \end{bmatrix} \quad (\text{A35})$$

$$\mathbf{K}_{13} = \mathbf{K}_{31}^T = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda^{\text{visc}} & \lambda^{\text{visc}} u_3 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_1 \\ 0 & \mu^{\text{visc}} u_3 & 0 & \lambda^{\text{visc}} u_1 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_{31} \end{bmatrix} \quad (\text{A36})$$

$$\mathbf{K}_{23} = \mathbf{K}_{32}^T = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda^{\text{visc}} & \lambda^{\text{visc}} u_3 \\ 0 & 0 & \mu^{\text{visc}} & 0 & \mu^{\text{visc}} u_2 \\ 0 & 0 & \mu^{\text{visc}} u_3 & \lambda^{\text{visc}} u_2 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_{23} \end{bmatrix} \quad (\text{A37})$$

APPENDIX B.

A SIMPLE EQUILIBRIUM CHEMISTRY MODEL FOR AIR

In this appendix, air is considered as a thermally perfect mixture of N_2 , O_2 , NO , N , and O molecules (we number the species from 1 to 5 in this order). Given the thermodynamic state of the system (p , T), we propose to compute the equilibrium mass fraction of each component, and the quantities of Eqs (33)–(37). In order to solve for the five y_s s, we need five independent equations. By definition of the mass fractions, we have

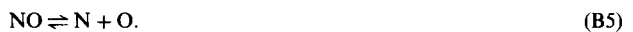
$$\sum_s y_s = 1. \quad (\text{B1})$$

In an inviscid flow, chemical reactions cannot change the elemental ratio between nitrogen and oxygen. Thus

$$\frac{2x_{\text{N}_2} + x_{\text{NO}} + x_{\text{N}}}{2x_{\text{O}_2} + x_{\text{NO}} + x_{\text{O}}} = \frac{79}{21}. \quad (\text{B2})$$

Even in the case of a viscous flow, Eq. (B2) holds approximately, since, nitrogen and oxygen atoms having nearly the same mass, the net diffusion velocities of the two elements are expected to be nearly identical.¹⁶

In addition to the mass conservation, Eq. (B1), and the element conservation, Eq. (B2), we need three more equations. These are provided by three independent chemical reactions, e.g.



For each of these reactions, we can write the law of mass action, viz.

$$\frac{c_N^2}{c_{N_2}} = K_{c1}(T) \quad (B6)$$

$$\frac{c_O^2}{c_{O_2}} = K_{c2}(T) \quad (B7)$$

$$\frac{c_N c_O}{c_{NO}} = K_{c3}(T), \quad (B8)$$

where the K_{cR} s, $R = 1, 2, 3$, are the equilibrium constants of the different reactions. Ideally, these functions of temperature should be computed from the molar chemical potentials¹⁴:

$$\hat{\mu}_s = \mu_s \hat{M}_s = \hat{\mu}_s^0(T) + \hat{R}T \ln p_s, \quad (B9)$$

where μ_s is given by Eq. (73). In terms of the $\hat{\mu}_s$ s, the condition for a reaction R to be at equilibrium reads

$$\sum_s \hat{\mu}_s \nu_{sR} = 0, \quad (B10)$$

where ν_{sR} is the stoichiometric coefficient of component s in reaction R . Equation (B10) can be written as the more familiar law of mass action

$$K_{cR}(T) = \prod_s c_s^{\nu_{sR}} = \frac{\exp\left(-\frac{\sum_s \hat{\mu}_s^0 \nu_{sR}}{\hat{R}T}\right)}{(\hat{R}T)^{\sum_s \nu_{sR}}}. \quad (B11)$$

For the sake of simplicity, we will use here curve fits for the K_{cR} s, similar to those proposed by Rakich or Park.^{16,29,30}

The resulting system of five nonlinear equations for the y_s s in terms of p and T [Eqs (B1), (B2), (B6)–(B8)] can formally be expressed as

$$\mathbf{f}(\mathbf{y}, p, T) = \mathbf{0}, \quad (B12)$$

where $\mathbf{y} = \{y_s\}$. Given an initial guess $\mathbf{y}^{(0)}$ for \mathbf{y} , we define the $(n+1)$ st Newton iterate by

$$\mathbf{y}^{(n+1)} = \mathbf{y}^{(n)} + \Delta \mathbf{y}^{(n)}, \quad (B13)$$

where

$$\Delta \mathbf{y}^{(n)} = -\mathbf{J}^{-1}(\mathbf{y}^{(n)}, p, T) \mathbf{f}(\mathbf{y}^{(n)}, p, T) \quad (B14)$$

and

$$\mathbf{J} = \left(\frac{\partial \mathbf{f}}{\partial \mathbf{y}} \right)_{p,T}. \quad (B15)$$

A good initial guess assures a quadratic convergence of the process.

The derivatives of \mathbf{y} with respect to p and T can easily be obtained from the Jacobian \mathbf{J} of the last Newton iteration. The differential of Eq. (B12) is

$$\mathbf{J} d\mathbf{y} + \left(\frac{\partial \mathbf{f}}{\partial p} \right)_{y,T} dp + \left(\frac{\partial \mathbf{f}}{\partial T} \right)_{y,p} dT = \mathbf{0}. \quad (B16)$$

Thus,

$$d\mathbf{y} = -\mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial p} \right)_{y,T} dp - \mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial T} \right)_{y,p} dT \quad (B17)$$

and

$$\left(\frac{\partial \mathbf{y}}{\partial p} \right)_T = -\mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial p} \right)_{y,T} \quad (B18)$$

$$\left(\frac{\partial \mathbf{y}}{\partial T} \right)_p = -\mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial T} \right)_{y,p} \quad (B19)$$

From these derivatives, one can for instance compute

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p = \sum_s y_s c_{ps} + \sum_s \left(\frac{\partial y_s}{\partial T} \right)_p h_s \quad (B20)$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{T} + \frac{1}{R} \sum_s \left(\frac{\partial y_s}{\partial T} \right)_p R_s \quad (B21)$$

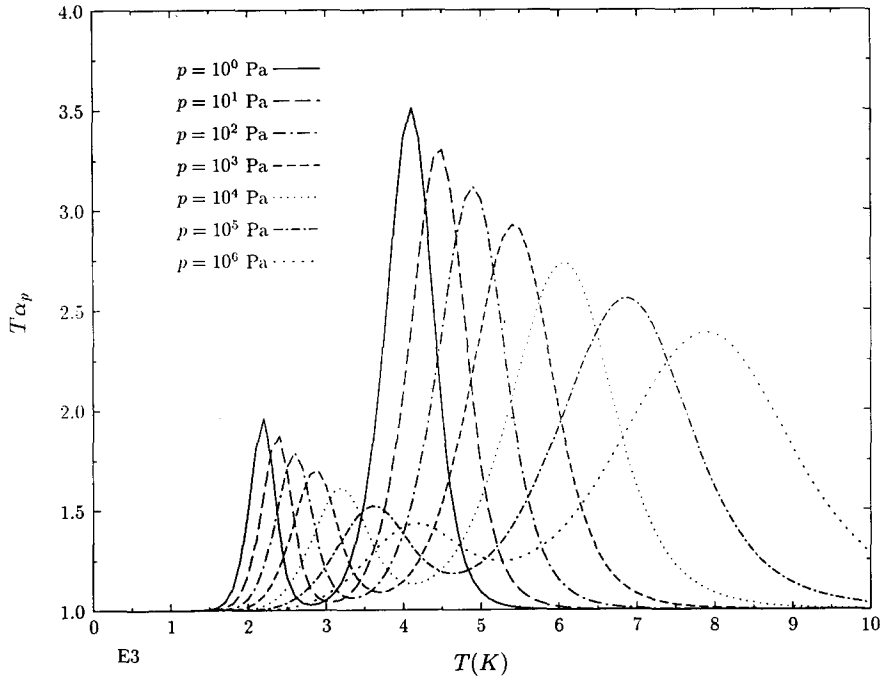


Fig. A1. Dimensionless expansivity.

$$\beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = \frac{1}{p} - \frac{1}{R} \sum_s \left(\frac{\partial y_s}{\partial p} \right)_T R_s \quad (\text{B22})$$

$$c_v = c_p - \frac{\alpha_p^2 v T}{\beta_T} \quad (\text{B23})$$

$$a^2 = \frac{v c_p}{c_v \beta_T}, \quad (\text{B24})$$

where c_{ps} is the specific heat at constant pressure of species s

$$c_{ps} = \left(\frac{\partial h_s}{\partial T} \right)_p \quad (\text{B25})$$

and a is the speed of sound. Nondimensionalized α_p , β_T , c_p , and a^2 are plotted respectively in Figs A1–A4, for the rigid-rotator/harmonic-oscillator model. α_p is nondimensionalized using R_0 , the specific gas constant of the mixture at room temperature, computed with a molar mass given by Eq. (67). In the range of temperatures where ionization can be neglected, they compare very well with classical computations,¹⁰ or with more recent curve fits.^{31,32}

APPENDIX C. COEFFICIENT MATRICES FOR A MIXTURE OF THERMALLY PERFECT GASES IN THERMOCHEMICAL NONEQUILIBRIUM

In this appendix, we present the flux vectors and the coefficient matrices of the conservation law system for a mixture of thermally perfect gases in thermochemical nonequilibrium, expressed in terms of the entropy variables. We assume that the internal energy modes obey the rigid-rotator and harmonic-oscillator model (see Sec. 4.3).

We first recall the expressions of \mathbf{U} and \mathbf{V}

$$\mathbf{U} = \frac{1}{v} \left\{ \begin{array}{c} \mathbf{y} \\ \mathbf{u} \\ e^{\text{vib}} \\ e + \frac{|\mathbf{u}|^2}{2} \end{array} \right\} \quad (\text{C1})$$

$$\mathbf{V} = \frac{1}{T} \left\{ \begin{array}{c} \mu - \frac{|\mathbf{u}|^2}{2} I_n \\ \mathbf{u} \\ 1 - \frac{T}{T^{\text{vib}}} \\ -1 \end{array} \right\}. \quad (\text{C2})$$

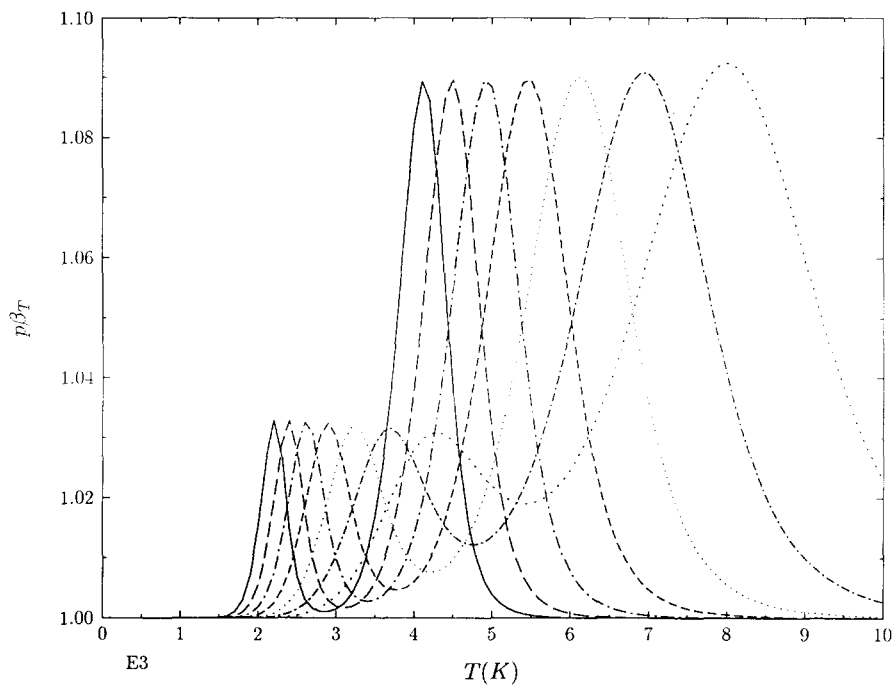


Fig. A2. Dimensionless isothermal compressibility.

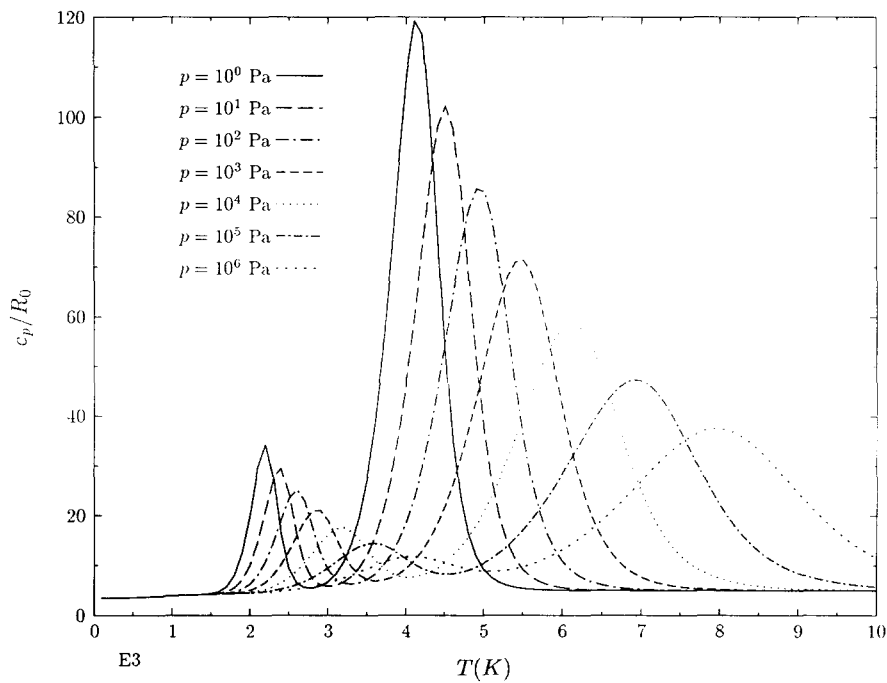


Fig. A3. Dimensionless specific heat at constant pressure.

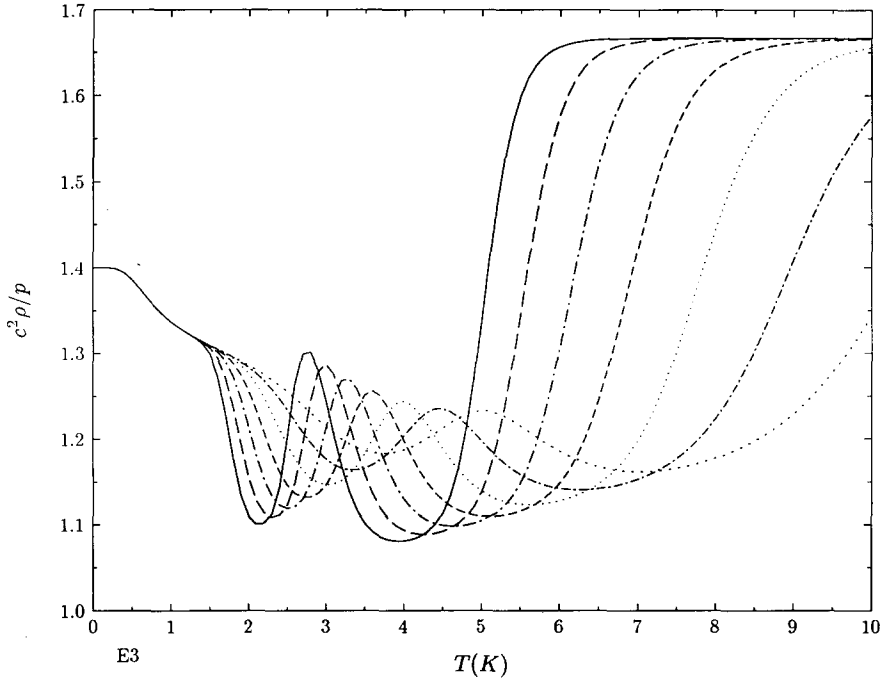


Fig. A4. Speed of sound parameter.

The Riemannian metric tensor $\bar{\mathbf{A}}_0 = \mathbf{U}_{,V}$ and its inverse $\bar{\mathbf{A}}_0^{-1} = \mathbf{V}_{,U}$ read

$$\bar{\mathbf{A}}_0 = \begin{bmatrix} \frac{\rho_1}{R_1} & 0 & \frac{\rho_1}{R_1} u_1 & \frac{\rho_1}{R_1} u_2 & \frac{\rho_1}{R_1} u_3 & \frac{\rho_1}{R_1} e_1^{\text{vib}} & \frac{\rho_1}{R_1} e_1^{\text{tot}} \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\rho_n}{R_n} & \frac{\rho_n}{R_n} u_1 & \frac{\rho_n}{R_n} u_2 & \frac{\rho_n}{R_n} u_3 & \frac{\rho_n}{R_n} e_n^{\text{vib}} & \frac{\rho_n}{R_n} e_n^{\text{tot}} \\ u_1^2 \frac{\rho_s}{R_s} + \rho T & u_1 u_2 \frac{\rho_s}{R_s} & u_1 u_3 \frac{\rho_s}{R_s} & u_1 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 \frac{\rho_s}{R_s} h_s^{\text{tot}} \\ u_2^2 \frac{\rho_s}{R_s} + \rho T & u_2 u_3 \frac{\rho_s}{R_s} & u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_2 \frac{\rho_s}{R_s} h_s^{\text{tot}} \\ u_3^2 \frac{\rho_s}{R_s} + \rho T & u_3 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_3 \frac{\rho_s}{R_s} h_s^{\text{tot}} \\ \text{Symm.} & \frac{\rho_s}{R_s} e_s^{\text{vib}^2} & \frac{\rho_s}{R_s} e_s^{\text{vib}} e_s^{\text{tot}} \\ & + \rho c_v^{\text{vib}} T^{\text{vib}^2} & + \rho c_v^{\text{vib}} T^{\text{vib}^2} \\ & & \frac{\rho_s}{R_s} e_s^{\text{tot}^2} + \rho u^2 T \\ & & + \rho(c_v T^2 + c_v^{\text{vib}} T^{\text{vib}^2}) \end{bmatrix} \quad (\text{C3})$$

$$\bar{\mathbf{A}}_0^{-1} = \frac{1}{\rho c_v T^2} \begin{bmatrix} \bar{a}_{11} & \dots & \bar{a}_{1n} & \bar{b}_1 u_1 & \bar{b}_1 u_2 & \bar{b}_1 u_3 & \bar{c}_1 & \bar{d}_1 \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \bar{a}_{nn} & \bar{b}_n u_1 & \bar{b}_n u_2 & \bar{b}_n u_3 & \bar{c}_n & \bar{d}_n \\ u_1^2 + c_v T & u_1 u_2 & u_1 u_3 & u_1 & -u_1 \\ u_2^2 + c_v T & u_2 u_3 & u_2 & -u_2 \\ \text{Symm.} & u_3^2 + c_v T & u_3 & -u_3 \\ & 1 + \frac{c_v T^2}{c_v^{\text{vib}} T^{\text{vib}^2}} & -1 \\ & & 1 \end{bmatrix}, \quad (\text{C4})$$

where

$$\bar{a}_{sr} = \left(c_{rs} T + h_s^0 - \frac{u^2}{2} \right) \left(c_{rs} T + h_r^0 - \frac{u^2}{2} \right) + e_s^{\text{vib}} e_r^{\text{vib}} \frac{c_v T^2}{c_v^{\text{vib}} T^{\text{vib}^2}} + c_v T u^2 + \rho c_v T^2 \frac{R_s}{\rho_s} \delta_{sr} \quad (\text{C5})$$

$$\bar{b}_s = c_{rs} T + h_s^0 - \frac{u^2}{2} - c_v T \quad (\text{C6})$$

$$\bar{c}_s = c_{rs} T + h_s^0 - \frac{u^2}{2} - e_s^{\text{vib}} \frac{c_v T^2}{c_v^{\text{vib}} T^{\text{vib}^2}} \quad (\text{C7})$$

$$\bar{d}_s = -\left(c_{rs}T + h_s^0 - \frac{u^2}{2}\right). \quad (C8)$$

$\bar{\mathbf{A}}_0$ is positive-definite, if $\rho_s > 0$, $c_r > 0$, $c_v^{\text{vib}} > 0$, $T > 0$, and $T^{\text{vib}} > 0$, where

$$c_v = \sum_s \gamma_s c_{rs} \quad (C9)$$

$$c_v^{\text{vib}} = \sum_s \gamma_s c_{rs}^{\text{vib}}. \quad (C10)$$

These conditions are satisfied in practice.

The advective fluxes are:

$$\mathbf{F}_i^{\text{adv}} = u_i \mathbf{U} + p \begin{Bmatrix} 0 \\ \delta_i \\ 0 \\ u_i \end{Bmatrix}. \quad (C11)$$

The advective Jacobians with respect to \mathbf{V} , $\bar{\mathbf{A}}_i = \mathbf{F}_{i,V}^{\text{adv}}$, are given by

$$\bar{\mathbf{A}}_1 = \begin{bmatrix} \frac{\rho_1}{R_1} u_1 & 0 & \frac{\rho_1}{R_1} (u_1^2 + R_1 T) & \frac{\rho_1}{R_1} u_1 u_2 & \frac{\rho_1}{R_1} u_1 u_3 & \frac{\rho_1}{R_1} e_1^{\text{vib}} u_1 & \frac{\rho_1}{R_1} h_1^{\text{tot}} u_1 \\ & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\ & & \frac{\rho_n}{R_n} u_1 & \frac{\rho_n}{R_n} (u_1^2 + R_n T) & \frac{\rho_n}{R_n} u_1 u_2 & \frac{\rho_n}{R_n} u_1 u_3 & \frac{\rho_n}{R_n} e_n^{\text{vib}} u_1 & \frac{\rho_n}{R_n} h_n^{\text{tot}} u_1 \\ & & & u_1^3 \frac{\rho_s}{R_s} & u_1^2 u_2 \frac{\rho_s}{R_s} & u_1^2 u_3 \frac{\rho_s}{R_s} & u_1^2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1^2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & + 3\rho T u_1 & + \rho T u_2 & + \rho T u_3 & + \rho T e^{\text{vib}} & + \rho T h^{\text{tot}} \\ & & & & u_1 u_2^2 \frac{\rho_s}{R_s} & u_1 u_2 u_3 \frac{\rho_s}{R_s} & u_1 u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 u_2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & & + \rho T u_1 & & & \\ & & & & & u_1 u_3 \frac{\rho_s}{R_s} & u_1 u_3 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 u_3 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & & & + \rho T u_1 & & \\ & & \text{Symm.} & & & & u_1 \frac{\rho_s}{R_s} e_s^{\text{vib}^2} & u_1 \frac{\rho_s}{R_s} e_s^{\text{vib}} h_s^{\text{tot}} \\ & & & & & & + \rho u_1 c_r^{\text{vib}} T^{\text{vib}^2} & + \rho u_1 c_r^{\text{vib}} T^{\text{vib}^2} \\ & & & & & & & u_1 \frac{\rho_s}{R_s} h_s^{\text{tot}^2} \\ & & & & & & & + \rho u_1 T (u^2 + c_p T) \\ & & & & & & & + \rho u_1 c_r^{\text{vib}} T^{\text{vib}^2} \end{bmatrix} \quad (C12)$$

$$\bar{\mathbf{A}}_2 = \begin{bmatrix} \frac{\rho_1}{R_1} u_2 & 0 & \frac{\rho_1}{R_1} u_1 u_2 & \frac{\rho_1}{R_1} (u_2^2 + R_1 T) & \frac{\rho_1}{R_1} u_2 u_3 & \frac{\rho_1}{R_1} e_1^{\text{vib}} u_2 & \frac{\rho_1}{R_1} h_1^{\text{tot}} u_2 \\ & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\ & & \frac{\rho_n}{R_n} u_2 & \frac{\rho_n}{R_n} u_1 u_2 & \frac{\rho_n}{R_n} (u_2^2 + R_n T) & \frac{\rho_n}{R_n} u_2 u_3 & \frac{\rho_n}{R_n} e_n^{\text{vib}} u_2 & \frac{\rho_n}{R_n} h_n^{\text{tot}} u_2 \\ & & & u_1^2 u_2 \frac{\rho_s}{R_s} & u_1 u_2^2 \frac{\rho_s}{R_s} & u_1 u_2 u_3 \frac{\rho_s}{R_s} & u_1 u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 u_2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & + \rho T u_2 & + \rho T u_1 & & & \\ & & & & u_2^3 \frac{\rho_s}{R_s} & u_2^2 u_3 \frac{\rho_s}{R_s} & u_2^2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_2^2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & & + 3\rho T u_2 & + \rho T u_3 & + \rho T e^{\text{vib}} & + \rho T h^{\text{tot}} \\ & & & & & u_2 u_3 \frac{\rho_s}{R_s} & u_2 u_3 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_2 u_3 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & & & + \rho T u_2 & & \\ & & \text{Symm.} & & & & u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}^2} & u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}} h_s^{\text{tot}} \\ & & & & & & + \rho u_2 c_r^{\text{vib}} T^{\text{vib}^2} & + \rho u_2 c_r^{\text{vib}} T^{\text{vib}^2} \\ & & & & & & & u_2 \frac{\rho_s}{R_s} h_s^{\text{tot}^2} \\ & & & & & & & + \rho u_2 T (u^2 + c_p T) \\ & & & & & & & + \rho u_2 c_r^{\text{vib}} T^{\text{vib}^2} \end{bmatrix} \quad (C13)$$

$$\bar{\mathbf{A}}_3 = \begin{bmatrix} \frac{\rho_1}{R_1} u_3 & 0 & \frac{\rho_1}{R_1} u_1 u_3 & \frac{\rho_1}{R_1} u_2 u_3 & \frac{\rho_1}{R_1} (u_3^2 + R_1 T) & \frac{\rho_1}{R_1} e^{\text{vib}} u_3 & \frac{\rho_1}{R_1} h_1^{\text{tot}} u_3 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\rho_n}{R_n} u_3 & \frac{\rho_n}{R_n} u_1 u_3 & \frac{\rho_n}{R_n} u_2 u_3 & \frac{\rho_n}{R_n} (u_3^2 + R_n T) & \frac{\rho_n}{R_n} e^{\text{vib}} u_3 & \frac{\rho_n}{R_n} h_n^{\text{tot}} u_3 & \frac{\rho_n}{R_n} h_n^{\text{tot}} u_3 \\ u_1^2 u_3 \frac{\rho_s}{R_s} + \rho T u_3 & u_1 u_2 u_3 \frac{\rho_s}{R_s} & u_1 u_3^2 \frac{\rho_s}{R_s} + \rho T u_1 & u_1 u_3 \frac{\rho_s}{R_s} e^{\text{vib}} & u_1 u_3 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) & & \\ & u_2^2 u_3 \frac{\rho_s}{R_s} + \rho T u_2 & u_2 u_3^2 \frac{\rho_s}{R_s} + \rho T u_2 & u_2 u_3 \frac{\rho_s}{R_s} e^{\text{vib}} & u_2 u_3 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) & & \\ & & u_3^2 \frac{\rho_s}{R_s} + 3\rho T u_3 & u_3^2 \frac{\rho_s}{R_s} e^{\text{vib}} & u_3^2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) & & \\ & & & + \rho T e^{\text{vib}} & + \rho T h^{\text{tot}} & & \\ & & & & u_3 \frac{\rho_s}{R_s} e^{\text{vib}^2} & u_3 \frac{\rho_s}{R_s} e^{\text{vib}} h_s^{\text{tot}} & \\ & & & & + \rho u_3 c_v^{\text{vib}} T^{\text{vib}^2} & + \rho u_3 c_v^{\text{vib}} T^{\text{vib}^2} & \\ & & & & & u_3 \frac{\rho_s}{R_s} h_s^{\text{tot}^2} & \\ & & & & & + \rho u_3 T (u^2 + c_p T) & \\ & & & & & + \rho u_3 c_v^{\text{vib}} T^{\text{vib}^2} & \end{bmatrix}. \quad (\text{C14})$$

Symm.

The diffusive fluxes are the sums of three contributions

$$\mathbf{F}_i^{\text{diff}} = \mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{visc}} + \mathbf{F}_i^{\text{heat}}, \quad (\text{C15})$$

where $\mathbf{F}_i^{\text{mass}}$, $\mathbf{F}_i^{\text{visc}}$, and $\mathbf{F}_i^{\text{heat}}$ are respectively the mass diffusion, the viscous stress, and the heat flux vectors.

The mass diffusion flux vectors are given by

$$\mathbf{F}_i^{\text{mass}} = \begin{Bmatrix} -\mathbf{J}_i \\ \mathbf{0}_3 \\ -\mathbf{J}_i \cdot \mathbf{e}^{\text{vib}} \\ -\mathbf{J}_i \cdot \mathbf{h} \end{Bmatrix}, \quad (\text{C16})$$

where

$$J_{si} = \rho_s v_{si} = \sum_r \rho \frac{\hat{M}_s \hat{M}_r}{\hat{M}^2} D_{sr} d_{ri} \quad (\text{C17})$$

and

$$d_{si} = x_{s,i} + (x_s - y_s)(\ln p)_i. \quad (\text{C18})$$

In terms of gradients of primitive variables, Eq. (C17) can be rewritten as

$$\rho_s v_{si} = - \sum_r \frac{\rho_r}{\rho_r} T \alpha_{sr} \rho_{r,i} - \beta_s T_{,i} \quad (\text{C19})$$

with

$$\beta_s = \sum_r \alpha_{sr} R_r. \quad (\text{C20})$$

The α_{sr} s are Onsager's phenomenological coefficients for mass diffusion.^{20,33} They are given in terms of the D_{sr} s by

$$\alpha_{sr} = \frac{\hat{M}_s}{\hat{M} T} \left(- \frac{\rho_r}{R_r} D_{sr} + \rho_r \sum_i \frac{y_i}{R_i} D_{si} \right). \quad (\text{C21})$$

The fundamental theorem of the thermodynamics of irreversible processes states that the α_{sr} s satisfy the reciprocal relations

$$\alpha_{sr} = \alpha_{rs}, \quad \forall s, r. \quad (\text{C22})$$

Moreover, one can also write

$$\sum_i \alpha_{si} = \sum_i \alpha_{ir} = 0, \quad \forall s, r. \quad (\text{C23})$$

Equation (C23) is equivalent to Eq. (92), and ensures that

$$\sum_i \rho_i v_{ji} = 0. \quad (C24)$$

The symmetry property of Eq. (C22) is checked for a mixture of three species by Hirschfelder *et al.*¹⁸ If the pressure term were omitted in the definition of the d_{ij} s, a nonsymmetric contribution would replace the α_{ij} s in Eq. (C19). In addition, the implicit pressure part of $-\mathbf{J}_i \cdot \mathbf{h}$ in $\mathbf{F}_i^{\text{mass}}$ would remain unbalanced in the diffusivity matrix.

The mass-diffusion diffusivity coefficient matrices $\mathbf{K}_{ij}^{\text{mass}}$, where $\mathbf{K}_{ij}^{\text{mass}} \mathbf{V}_j = \mathbf{F}_i^{\text{mass}}$, are

$$\mathbf{K}_{ij}^{\text{mass}} = T \begin{bmatrix} \alpha & \mathbf{0}_{n \times 3} & \alpha \mathbf{e}^{\text{vib}} & \alpha \mathbf{h} \\ \mathbf{0}_{3 \times 3} & \mathbf{0}_3 & \mathbf{0}_3 & \mathbf{0}_3 \\ \text{Symm.} & \mathbf{e}^{\text{vib}} \cdot \alpha \mathbf{e}^{\text{vib}} & \mathbf{e}^{\text{vib}} \cdot \alpha \mathbf{h} & \mathbf{h} \cdot \alpha \mathbf{h} \end{bmatrix}, \quad i = 1, 2, 3 \quad (C25)$$

$$\mathbf{K}_{ij}^{\text{mass}} = \mathbf{0}, \quad i \neq j. \quad (C26)$$

The mass-diffusion diffusivity matrix $\mathbf{K}^{\text{mass}} = [\mathbf{K}_{ij}^{\text{mass}}]$ is positive semidefinite if and only if α is positive semidefinite (see Sec. 5).

The viscous stress flux vectors are given by

$$\mathbf{F}_i^{\text{visc}} = \begin{Bmatrix} \mathbf{0}_n \\ \tau_{ij} \delta_j \\ 0 \\ \tau_{ij} u_j \end{Bmatrix}, \quad (C27)$$

where

$$\tau_{ij} = \lambda^{\text{visc}} u_{k,k} \delta_{ij} + \mu^{\text{visc}} (u_{i,j} + u_{j,i}). \quad (C28)$$

Let

$$\chi^{\text{visc}} = \lambda^{\text{visc}} + 2\mu^{\text{visc}}. \quad (C29)$$

Then, the viscous stress diffusivity coefficient matrices $\mathbf{K}_{ij}^{\text{visc}}$, where $\mathbf{K}_{ij}^{\text{visc}} \mathbf{V}_j = \mathbf{F}_i^{\text{visc}}$, are

$$\mathbf{K}_{11}^{\text{visc}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ & \chi^{\text{visc}} & 0 & 0 & 0 & \chi^{\text{visc}} u_1 \\ & & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_2 \\ \text{Symm.} & & & \mu^{\text{visc}} & 0 & \mu^{\text{visc}} u_3 \\ & & & & 0 & 0 \\ & & & & & \chi^{\text{visc}} u_1^2 + \mu^{\text{visc}} (u_2^2 + u_3^2) \end{bmatrix} \quad (C30)$$

$$\mathbf{K}_{22}^{\text{visc}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ & & \chi^{\text{visc}} & 0 & 0 & \chi^{\text{visc}} u_2 \\ \text{Symm.} & & & \mu^{\text{visc}} & 0 & \mu^{\text{visc}} u_3 \\ & & & & 0 & 0 \\ & & & & & \chi^{\text{visc}} u_2^2 + \mu^{\text{visc}} (u_1^2 + u_3^2) \end{bmatrix} \quad (C31)$$

$$\mathbf{K}_{33}^{\text{visc}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ & & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_2 \\ \text{Symm.} & & & \chi^{\text{visc}} & 0 & \chi^{\text{visc}} u_3 \\ & & & & 0 & 0 \\ & & & & & \chi^{\text{visc}} u_3^2 + \mu^{\text{visc}} (u_1^2 + u_2^2) \end{bmatrix} \quad (C32)$$

$$\mathbf{K}_{12}^{\text{visc}} = \mathbf{K}_{21}^{\text{visc}T} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_n^T & 0 & \lambda^{\text{visc}} & 0 & 0 & \lambda^{\text{visc}} u_2 \\ \mathbf{0}_n^T & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & \mu^{\text{visc}} u_2 & \lambda^{\text{visc}} u_1 & 0 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_1 u_2 \end{bmatrix} \quad (C33)$$

$$\mathbf{K}_{13}^{\text{visc}} = \mathbf{K}_{31}^{\text{visc}T} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_n^T & 0 & 0 & \lambda^{\text{visc}} & 0 & \lambda^{\text{visc}} u_3 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & \mu^{\text{visc}} u_3 & 0 & \lambda^{\text{visc}} u_1 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_1 u_3 \end{bmatrix} \quad (\text{C34})$$

$$\mathbf{K}_{23}^{\text{visc}} = \mathbf{K}_{32}^{\text{visc}T} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_n^T & 0 & 0 & \lambda^{\text{visc}} & 0 & \lambda^{\text{visc}} u_3 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & 0 & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_2 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & 0 & \mu^{\text{visc}} u_3 & \lambda^{\text{visc}} u_2 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_2 u_3 \end{bmatrix} \quad (\text{C35})$$

The viscous stress diffusivity matrix $\mathbf{K}^{\text{visc}} = [\mathbf{K}_{ij}^{\text{visc}}]$ is positive, semidefinite if and only if $\mu^{\text{visc}} \geq 0$ and $(\lambda^{\text{visc}} + \frac{2}{3}\mu^{\text{visc}}) \geq 0$ (see Sec. 5).

The heat flux vectors are given by

$$\mathbf{F}_i^{\text{heat}} = \begin{Bmatrix} \mathbf{0}_n \\ \mathbf{0}_3 \\ -q_i^{\text{vib}} \\ -(q_i + q_i^{\text{vib}}) \end{Bmatrix}, \quad (\text{C36})$$

where

$$q_i = -\kappa T_{,i} \quad (\text{C37})$$

$$q_i^{\text{vib}} = -\kappa^{\text{vib}} T_{,i}^{\text{vib}}. \quad (\text{C38})$$

The heat conduction diffusivity coefficient matrices $\mathbf{K}_{ij}^{\text{heat}}$, where $\mathbf{K}_{ij}^{\text{heat}} \mathbf{V}_j = \mathbf{F}_i^{\text{heat}}$, are

$$\mathbf{K}_{ij}^{\text{heat}} = \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_{n \times 3} & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_{3 \times 3} & \mathbf{0}_3 & \mathbf{0}_3 & \mathbf{0}_3 \\ \text{Symm.} & \kappa^{\text{vib}} T^{\text{vib}2} & \kappa^{\text{vib}} T^{\text{vib}2} & \kappa T^2 + \kappa^{\text{vib}} T^{\text{vib}2} \end{bmatrix}, \quad i = 1, 2, 3 \quad (\text{C39})$$

$$\mathbf{K}_{ij}^{\text{heat}} = \mathbf{0}, \quad i \neq j. \quad (\text{C40})$$

The heat conduction diffusivity matrix $\mathbf{K}^{\text{heat}} = [\mathbf{K}_{ij}^{\text{heat}}]$ is positive, semidefinite if and only if $\kappa \geq 0$ and $\kappa^{\text{vib}} \geq 0$ (see Sec. 5).

Finally, the diffusivity matrix $\mathbf{K} = \mathbf{K}^{\text{mass}} + \mathbf{K}^{\text{visc}} + \mathbf{K}^{\text{heat}}$ is symmetric and positive, semidefinite, provided that

$$\alpha \geq 0 \quad (\text{C41})$$

$$\mu^{\text{visc}} \geq 0 \quad (\text{C42})$$

$$\lambda^{\text{visc}} + \frac{2}{3}\mu^{\text{visc}} \geq 0 \quad (\text{C43})$$

$$\kappa \geq 0 \quad (\text{C44})$$

$$\kappa^{\text{vib}} \geq 0. \quad (\text{C45})$$

APPENDIX D.

COUPLING OF MASS DIFFUSION AND HEAT CONDUCTION: THE Soret AND DUFOUR EFFECTS

According to elementary kinetic theory, mass diffusion results from a concentration gradient, the heat flux from a temperature gradient. The finer analysis provided by nonequilibrium kinetic theory indicates that, in addition to these phenomena, there exists a transport of mass due to a temperature gradient, and a transport of energy due to a concentration gradient. The thermal diffusion effect was not known theoretically, nor observed experimentally prior to the development of the Chapman–Enskog theory (see Ref. 34). Its existence was later to be confirmed by experiments conducted by Chapman and Dootson.¹⁸ This effect is an interaction phenomenon, which arises from the processing by collisions of the heat flow, a direct consequence of the temperature gradient. The reciprocal process to thermal diffusion, known as diffusion thermo-effect, is responsible for the heat flux in a gas mixture initially at uniform temperature, where an inhomogeneity of composition has triggered mass diffusion. These two phenomena, also referred to as respectively the Soret and Dufour effects, are frequently considered as “second-order” corrections, since they require the retention of at least two terms in the Sonine polynomial expansion of the distribution function, solution of the Boltzmann equation. In fact, in most aerospace applications, they can be neglected.¹⁶ However, as we will see, it is interesting to study them in the light of Onsager’s reciprocal relations, and to examine their impact on entropy production.

Appending the thermal diffusion effect to Eq. (88), the diffusion velocities are now given by

$$J_{si} = \rho_s v_{si} = \sum_r \rho \frac{\hat{M}_s \hat{M}_r}{\hat{M}^2} D_{sr} d_{ri} - D_s^{\text{therm}} (\ln T)_{,i}, \quad (\text{D1})$$

where the D_s^{therm} s are the multicomponent thermal diffusion coefficients; they satisfy

$$\sum_s D_s^{\text{therm}} = 0, \quad (\text{D2})$$

which is required together with Eq. (92) to ensure that the mass average of the diffusion velocities, Eq. (94), vanishes. In turn, the heat flux of Eq. (96) is augmented by a term describing the diffusion thermo-effect

$$q_i = -\kappa' T_{,i} - RT \sum_s \frac{D_s^{\text{therm}}}{y_s} d_{si}. \quad (\text{D3})$$

κ' is not the usual coefficient of thermal conductivity. It is conventional to eliminate the gradients d_{si} from the expression for q_i by means of the equation for the diffusion velocities, Eq. (D1). The heat flux is then given in terms of the diffusion velocities and the temperature gradients. Because of the thermal diffusion term in the expression for the diffusion velocities, a small term adds to κ' to result in the quantity κ , which is the usual coefficient of thermal conductivity. Details concerning the transformation, and the relation between κ and κ' , can be found in Ref. 18.

The Dufour effect part of Eq. (D3) can be written in terms of the primitive variables as

$$RT \sum_s \frac{D_s^{\text{therm}}}{y_s} d_{si} = \sum_s \frac{R_s}{\rho_s} TD_s^{\text{therm}} \rho_{s,i} + \sum_s R_s D_s^{\text{therm}} T_{,i}. \quad (\text{D4})$$

In order to account for the thermal diffusion and the diffusion thermo-effect, the diffusivity coefficient-matrices $\tilde{\mathbf{K}}_{ij}^{\text{mass}}$ and $\tilde{\mathbf{K}}_{ij}^{\text{heat}}$ of Appendix C must be supplemented by

$$\tilde{\mathbf{K}}_i^{\text{therm}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_{n \times 3} & \mathbf{0}_n & \mathbf{D}^{\text{therm}} \\ & \mathbf{0}_{3 \times 3} & \mathbf{0}_3 & \mathbf{0}_3 \\ \text{Symm.} & & 0 & \mathbf{e}^{\text{vib}} \cdot \mathbf{D}^{\text{therm}} \\ & & & 2\mathbf{h} \cdot \mathbf{D}^{\text{therm}} \end{bmatrix}, \quad i = 1, 2, 3 \quad (\text{D5})$$

$$\tilde{\mathbf{K}}_{ij}^{\text{therm}} = \mathbf{0}, \quad i \neq j. \quad (\text{D6})$$

Letting

$$\tilde{\mathbf{K}}^{\text{mass-heat}} = \tilde{\mathbf{K}}^{\text{mass}} + \tilde{\mathbf{K}}^{\text{heat}} + \tilde{\mathbf{K}}^{\text{therm}}, \quad (\text{D7})$$

where κ' replaces κ in $\tilde{\mathbf{K}}^{\text{heat}}$, we have

$$\tilde{\mathbf{K}}_{ij}^{\text{mass-heat}} \mathbf{V}_j = \mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{heat}}. \quad (\text{D8})$$

From Eq. (D8), one can see that mass diffusion and heat conduction are now linked together through the thermal diffusion matrix $\tilde{\mathbf{K}}^{\text{therm}}$. The coupling appears even more strongly from the standpoint of entropy production. As we will see shortly, the positive semidefiniteness of $\tilde{\mathbf{K}}^{\text{mass}}$ and $\tilde{\mathbf{K}}^{\text{heat}}$ are not enough to guarantee that of $\tilde{\mathbf{K}}^{\text{mass-heat}}$, the contribution from $\tilde{\mathbf{K}}^{\text{therm}}$ being nonpositive.

$$\begin{aligned} \mathbf{V} \mathbf{V} \cdot \tilde{\mathbf{K}}^{\text{mass-heat}} \mathbf{V} \mathbf{V} &= \mathbf{V}_j \cdot \tilde{\mathbf{K}}_{ij}^{\text{mass-heat}} \mathbf{V}_j = \mathbf{V}_j \cdot (\mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{heat}}) = \sum_i \left[\sum_{s,r} R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \tilde{\alpha}_{sr}) R_r \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) \right. \\ &\quad \left. + \sum_s R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (TD_s^{\text{therm}}) \frac{T_{,i}}{T^2} + \sum_r \frac{T_{,i}}{T^2} (TD_r^{\text{therm}}) \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) + \frac{T_{,i}}{T^2} (T^2 \kappa') \frac{T_{,i}}{T^2} \right]. \end{aligned} \quad (\text{D9})$$

We define the phenomenological coefficient-matrix for mass diffusion and heat conduction as follows:

$$\tilde{\boldsymbol{\alpha}} = \begin{bmatrix} \boldsymbol{\alpha} & \mathbf{D}^{\text{therm}} \\ \text{Symm.} & T \kappa' \end{bmatrix}. \quad (\text{D10})$$

Equation (D10) can be used to rewrite Eq. (D9), yielding

$$\begin{aligned} \mathbf{V} \mathbf{V} \cdot \tilde{\mathbf{K}}^{\text{mass-heat}} \mathbf{V} \mathbf{V} &= \sum_i \left[\sum_{s,r} R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \tilde{\alpha}_{sr}) R_r \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) + \sum_s R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \tilde{\alpha}_{s,n+1}) \frac{T_{,i}}{T^2} \right. \\ &\quad \left. + \sum_r \frac{T_{,i}}{T^2} (T \tilde{\alpha}_{n+1,r}) \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) + \frac{T_{,i}}{T^2} (T \tilde{\alpha}_{n+1,n+1}) \frac{T_{,i}}{T^2} \right] = \sum_i \sum_{s,r=1}^{n+1} [\mathbf{Z}_n (T \tilde{\alpha}_{sr}) \mathbf{Z}_n] \geq 0, \end{aligned} \quad (\text{D11})$$

where the vectors \mathbf{Z}_i are defined by

$$\mathbf{Z}_i = \begin{bmatrix} R_1 \left(\frac{\rho_{1,i}}{\rho_1} + \frac{T_{,i}}{T} \right) \\ \vdots \\ R_n \left(\frac{\rho_{n,i}}{\rho_n} + \frac{T_{,i}}{T} \right) \\ \frac{T_{,i}}{T^2} \end{bmatrix}. \quad (\text{D12})$$

The inequality in Eq. (D11) is satisfied if and only if $\tilde{\boldsymbol{\alpha}}$ is positive semidefinite, which is implied by the second law of thermodynamics. If the diffusion velocities are taken according to Eq. (D1), and the heat flux to Eq. (D3), the Clausius–Duhem inequality remains formally the same as Eq. (155)

$$(\rho s)_{,i} + (\rho s u_i)_{,i} + \left(\sum_s \rho_s s_s v_{si} \right)_{,i} + \left(\frac{q_i}{T} + \frac{q_i^{\text{vib}}}{T^{\text{vib}}} \right)_{,i} + \frac{1}{T} \sum_s g_s \Omega_s - \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) \mathcal{Q}^{T-T^{\text{vib}}} \geq 0. \quad (\text{D13})$$