

SYMMETRIZATION OF CONSERVATION LAWS WITH ENTROPY FOR HIGH-TEMPERATURE HYPERSONIC COMPUTATIONS⁽¹⁾

by

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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 *a priori* guarantees the stability of the discrete solution.

Citius, Altius, Fortius

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NOMENCLATURE

Roman Symbols

A_i	advective Jacobian matrices with respect to conservative variables
\tilde{A}_i	advective Jacobian matrices with respect to entropy variables
\tilde{A}_0	Riemannian metric tensor
a	speed of sound (m/s)
c	total number of moles per unit volume (mol/m ³)
c_p	specific heat at constant pressure (J/kg·K=m ² /s ² ·K)
c_{ps}	specific heat at constant pressure of species s (J/kg·K=m ² /s ² ·K)
c_s	mole concentration of species s (mol/m ³)
c_v	specific heat at constant volume (J/kg·K=m ² /s ² ·K)
c_v^{vib}	vibrational specific heat at constant volume (J/kg·K=m ² /s ² ·K)
\hat{c}_v^{vib}	vibrational specific heat at constant volume per mole (J/mol·K=kg·m ² /mol·s ² ·K)
c_{vs}	specific heat at constant volume of species s (J/kg·K=m ² /s ² ·K)
\hat{c}_{vs}	specific heat at constant volume per mole of species s (J/mol·K=kg·m ² /mol·s ² ·K)
c_{vs}^{vib}	vibrational specific heat at constant volume of species s (J/kg·K=m ² /s ² ·K)
$\hat{c}_{vs}^{\text{vib}}$	vibrational specific heat at constant volume per mole of species s (J/mol·K=kg·m ² /mol·s ² ·K)
D^T	multicomponent thermal diffusion coefficient vector
D_s^T	multicomponent thermal diffusion coefficient of species s (kg/m·s)
D_{sr}	multicomponent diffusion coefficient of species s into species r (m ² /s)
d_{si}	gradient of species s in direction i used for the computation of diffusion velocities (m ⁻¹)
E^{tot}	total energy per unit volume (J/m ³ =kg/m·s ²)

E^{vib}	vibrational energy per unit volume ($\text{J}/\text{m}^3=\text{kg}/\text{m}\cdot\text{s}^2$)
\mathcal{E}	internal energy ($\text{J}=\text{kg}\cdot\text{m}^2/\text{s}^2$)
\mathcal{E}^{vib}	vibrational energy ($\text{J}=\text{kg}\cdot\text{m}^2/\text{s}^2$)
e	specific internal energy ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e^{tot}	specific total energy ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e^{vib}	specific vibrational energy ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
\mathbf{e}^{vib}	specific vibrational energy vector
e_s	specific internal energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e_{s0}	reference specific internal energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
\hat{e}_s	specific internal energy per mole of species s ($\text{J}/\text{mol}=\text{kg}\cdot\text{m}^2/\text{mol}\cdot\text{s}^2$)
e_s^{rot}	specific rotational energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e_s^{tot}	specific total energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e_s^{trans}	specific translational energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e_s^{vib}	specific vibrational energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
\hat{e}_s^{vib}	specific vibrational energy per mole of species s ($\text{J}/\text{mol}=\text{kg}\cdot\text{m}^2/\text{mol}\cdot\text{s}^2$)
e_{s0}^{vib}	reference specific vibrational energy of species s ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e_0	reference specific internal energy ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
e_0^{vib}	reference specific vibrational energy ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)
$\mathbf{F}_i^{\text{adv}}$	advective flux vector in direction i
$\mathbf{F}_i^{\text{diff}}$	diffusive flux vector in direction i
$\mathbf{F}_i^{\text{heat}}$	heat flux vector in direction i
$\mathbf{F}_i^{\text{mass}}$	mass diffusion flux vector in direction i
$\mathbf{F}_i^{\text{visc}}$	viscous stress flux vector in direction i
\mathcal{F}	source vector in terms of conservative variables
$\tilde{\mathcal{F}}$	source vector in terms of entropy variables
\mathcal{G}	Gibbs free energy ($\text{J}=\text{kg}\cdot\text{m}^2/\text{s}^2$)
g	specific Gibbs free energy ($\text{J}/\text{kg}=\text{m}^2/\text{s}^2$)

g_s	specific Gibbs free energy of species s (J/kg= m^2/s^2)
\hat{g}_s	specific Gibbs free energy per mole of species s (J/mol= $\text{kg}\cdot\text{m}^2/\text{mol}\cdot\text{s}^2$)
\mathcal{H}	generalized entropy function (J/ $\text{m}^3\cdot\text{K}=\text{kg}/\text{m}\cdot\text{s}^2\cdot\text{K}$)
h	specific enthalpy (J/kg= m^2/s^2)
\mathbf{h}	specific enthalpy vector
h^{tot}	specific total enthalpy (J/kg= m^2/s^2)
h_s	specific enthalpy of species s (J/kg= m^2/s^2)
h_s^{tot}	specific total enthalpy of species s (J/kg= m^2/s^2)
h_s^0	specific heat of formation of species s (J/kg= m^2/s^2)
\hat{h}_s^0	specific heat of formation per mole of species s (J/mol= $\text{kg}\cdot\text{m}^2/\text{mol}\cdot\text{s}^2$)
h_0	reference specific enthalpy (J/kg= m^2/s^2)
\mathbf{J}_i	mass diffusion flux in direction i
J_{si}	mass diffusion flux of species s in direction i
\mathbf{K}	diffusivity matrix with respect to conservative variables
$\widetilde{\mathbf{K}}$	diffusivity matrix with respect to entropy variables
$\widetilde{\mathbf{K}}^{\text{heat}}$	heat conduction diffusivity matrix with respect to entropy variables
$\widetilde{\mathbf{K}}^{\text{mass}}$	mass-diffusion diffusivity matrix with respect to entropy variables
$\widetilde{\mathbf{K}}^{\text{mass-heat}}$	mass-diffusion/heat conduction diffusivity matrix with respect to entropy variables
$\widetilde{\mathbf{K}}^{\text{therm}}$	thermal diffusion matrix with respect to entropy variables
$\widetilde{\mathbf{K}}^{\text{visc}}$	viscous stress diffusivity matrix with respect to entropy variables
K_{cR}	equilibrium constant of reaction R
\mathbf{K}_{ij}	diffusivity coefficient matrix with respect to conservative variables
$\widetilde{\mathbf{K}}_{ij}$	diffusivity coefficient matrix with respect to entropy variables
$\widetilde{\mathbf{K}}_{ij}^{\text{heat}}$	heat conduction diffusivity coefficient-matrix with respect to entropy variables
$\widetilde{\mathbf{K}}_{ij}^{\text{mass}}$	mass-diffusion diffusivity coefficient-matrix with respect to entropy variables
$\widetilde{\mathbf{K}}_{ij}^{\text{mass-heat}}$	mass-diffusion/heat conduction diffusivity coefficient-matrix with respect to

	entropy variables
$\widetilde{\mathbf{K}}_{ij}^{\text{therm}}$	thermal diffusion coefficient-matrix with respect to entropy variables
$\widetilde{\mathbf{K}}_{ij}^{\text{visc}}$	viscous stress diffusivity coefficient-matrix with respect to entropy variables
\hat{M}	molar mass (kg/mol)
\hat{M}_s	molar mass of species s (kg/mol)
\mathcal{N}	total number of moles (mol)
\mathcal{N}_s	number of moles of species s (mol)
n	number of species
p	pressure (Pa=kg/m·s ²)
p_s	partial pressure of species s (Pa=kg/m·s ²)
p_{s0}	reference partial pressure of species s (Pa=kg/m·s ²)
p_0	reference pressure (Pa=kg/m·s ²)
$Q^{T-T^{\text{vib}}}$	translation-vibration energy transfer rate (W/m ³ =kg/m·s ³)
Q	heat received by the system (J=kg·m ² /s ²)
\mathbf{q}	heat flux
q_i	heat flux in direction i (W/m ² =kg/s ³)
q_i^{vib}	vibrational heat flux in direction i (W/m ² =kg/s ³)
R	specific gas constant (J/kg·K=m ² /s ² ·K)
\hat{R}	universal gas constant (= 8.3143 J/mol·K)
R_s	specific gas constant of species s (J/kg·K=m ² /s ² ·K)
S	entropy (J/K=kg·m ² /s ² ·K)
S^{ext}	entropy due to interactions with exterior (J/K=kg·m ² /s ² ·K)
S^{int}	entropy due to internal irreversibilities (J/K=kg·m ² /s ² ·K)
s	specific entropy (J/kg·K=m ² /s ² ·K)
s_s	specific entropy of species s (J/kg·K=m ² /s ² ·K)
\hat{s}_s	specific entropy per mole of species s (J/kg·K=m ² /s ² ·K)
s_0	reference specific entropy (J/kg·K=m ² /s ² ·K)

s_{s0}	reference specific entropy of species s ($\text{J}/\text{kg}\cdot\text{K}=\text{m}^2/\text{s}^2\cdot\text{K}$)
T	(translational-rotational) temperature (K)
T^{vib}	vibrational temperature (K)
T_0	reference temperature (K)
T_0^{vib}	reference vibrational temperature (K)
t	time (s)
\mathbf{U}	conservative variables vector
\mathbf{u}	velocity vector
u_i	velocity in direction i (m/s)
\mathbf{V}	entropy variable vector
\mathcal{V}	volume (m^3)
v	specific volume (m^3/kg)
\hat{v}_s	specific volume per mole of species s (m^3/kg)
v_{si}	diffusion velocity of species s in direction i (m/s)
x_s	mole fraction of species s
\mathbf{y}	mass fraction vector
y_s	mass fraction of species s

Greek Symbols

α	Onsager's phenomenological coefficient matrix for mass diffusion
$\bar{\alpha}$	Onsager's phenomenological coefficient matrix for mass diffusion and heat conduction
α_p	expansivity (K^{-1})
α_{sr}	Onsager's phenomenological coefficients for mass diffusion ($\text{kg s}/\text{m}^3$)
$\bar{\alpha}_{sr}$	Onsager's phenomenological coefficients for mass diffusion and heat conduction
β_T	isothermal compressibility ($\text{Pa}^{-1}=\text{m}\cdot\text{s}^2/\text{kg}$)
γ_s	ratio of specific heats of species s
δ_i	Kronecker delta vector

δ_{ij}	Kronecker delta
ϵ	strain tensor
ϵ'	deviatoric part of the strain tensor
ϵ''	dilatational part of the strain tensor
Θ_s^{vib}	characteristic vibrational temperature of species s (K)
κ, κ'	coefficient of thermal conductivity ($\text{W/m}\cdot\text{K}=\text{kg}\cdot\text{m/s}^3\cdot\text{K}$)
κ^{vib}	coefficient of thermal conductivity of the vibrational energy ($\text{W/m}\cdot\text{K}=\text{kg}\cdot\text{m/s}^3\cdot\text{K}$)
λ^{visc}	second viscosity coefficient ($\text{Pl}=\text{kg/m}\cdot\text{s}$)
μ^{visc}	first viscosity coefficient ($\text{Pl}=\text{kg/m}\cdot\text{s}$)
μ_B^{visc}	bulk viscosity coefficient ($\text{Pl}=\text{kg/m}\cdot\text{s}$)
μ	specific chemical potential ($\text{J/kg}=\text{m}^2/\text{s}^2$)
$\boldsymbol{\mu}$	specific chemical potential vector
μ_s	specific chemical potential of species s ($\text{J/kg}=\text{m}^2/\text{s}^2$)
$\hat{\mu}_s$	specific chemical potential per mole of species s ($\text{J/mol}=\text{kg}\cdot\text{m}^2/\text{mol}\cdot\text{s}^2$)
μ_s^0	specific chemical potential of species s in the pure state, at unit pressure ($\text{J/kg}=\text{m}^2/\text{s}^2$)
$\hat{\mu}_s^0$	specific chemical potential per mole of species s in the pure state, at unit pressure ($\text{J/mol}=\text{kg}\cdot\text{m}^2/\text{mol}\cdot\text{s}^2$)
μ_{s0}	reference specific chemical potential of species s ($\text{J/kg}=\text{m}^2/\text{s}^2$)
ν_{sR}	stoichiometric coefficient of species s in reaction R
ρ	density (kg/m^3)
ρ_s	density of species s (kg/m^3)
ρ_{s0}	reference density of species s (kg/m^3)
σ_i	entropy flux in direction i ($\text{W/m}^2\cdot\text{K}=\text{kg/s}^3\cdot\text{K}$)
$\boldsymbol{\tau}$	viscous stress tensor
τ_{ij}	viscous stress in direction i on a plane normal to direction j ($\text{Pa}=\text{kg/m}\cdot\text{s}^2$)

Ω	production rate vector
Ω_s	production rate of species s (kg/m ³ ·s)

Subscripts

$()_{i;j;k}$	direction i , j , or k
$()_R$	reaction R
$()_{s;r;t}$	species s , r , or t
$()_0$	reference state

Superscripts

$()^T$	transpose
$()'_s$	all species, except species s

Overlines

$\hat{()}$	quantity per mole
$\widetilde{()}$	coefficient matrix with respect to entropy variables

I . 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. But 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 the 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 vehicle.

Although there is still much improvement needed in 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 Section 2, we review the theory of symmetric advective-diffusive and hyperbolic systems. In Section 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 Section 4 we describe the more complex example of a multicomponent gas in thermochemical nonequilibrium. In Section 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.

II . SYMMETRIC ADVECTIVE-DIFFUSIVE SYSTEMS.

We consider systems of conservation laws in the form

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

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 (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 (1), namely,

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

is hyperbolic, that is, any linear combination of the Jacobian matrices $\mathbf{A}_i = \mathbf{F}_{i,\mathbf{U}}^{\text{adv}}$ possesses real eigenvalues and a complete set of eigenvectors [36].

It is useful to rewrite (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 $\mathbf{U} = \mathbf{U}(\mathbf{V})$, (1) becomes:

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

where

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

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

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

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

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

- i) $\tilde{\mathbf{A}}_0$ is symmetric, positive-definite;
- ii) The $\tilde{\mathbf{A}}_i$'s are symmetric;
- iii) $\tilde{\mathbf{K}} = [\tilde{\mathbf{K}}_{ij}]$ is symmetric, positive-semidefinite.

When a change of variables $\mathbf{U} = \mathbf{U}(\mathbf{V})$ exists that engenders these properties, (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

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

Harten [8] and Tadmor [33] discuss the symmetrization of hyperbolic conservation laws and the satisfaction of generalized entropy inequalities. Harten presents two theorems first proved by Mock [22] 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. [12] 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.

III . 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., nonreacting, 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 equation (1), in the framework of the above assumptions.

3.1. Systems of Conservation Laws.

In three dimensions, the vectors of (1) read:

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

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

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

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

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

in Vincenti and Kruger [35], 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 [11, 1, 7, and 9]. 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 $\widetilde{\mathbf{K}}$. 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, (20) yields

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

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

To derive (21) we used Gibbs' relation,

$$ds = \frac{1}{T}(de + pdv) \quad (22)$$

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

$$\mathbf{Y} = \left\{ \begin{array}{c} v \\ \mathbf{u} \\ e \end{array} \right\} \quad (23)$$

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

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

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 $T = 0$ [37]. The positiveness of these determinants imply that $\tilde{\mathbf{A}}_0$ is positive definite [6], which in turn implies that \mathcal{H} is a strictly convex function of \mathbf{U} (viz., $\tilde{\mathbf{A}}_0^{-1} = \mathbf{V}_{,\mathbf{U}} = \mathcal{H}_{,\mathbf{U}\mathbf{U}}$).

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 (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 ($\approx 1,000$ 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 2,000 K, chemical reactions occur and air becomes a *chemically reacting mixture of perfect gases* [1]. After 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 (33):

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

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

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

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

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 $\hat{R} = 8.3143 \text{ J/mol.K}$ 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,

$$\mu = c_p T - c_p T \ln \frac{T}{T_0} + RT \ln \frac{p}{p_0} - T s_0 \quad (40)$$

where (p_0, T_0) defines the reference state of reference entropy s_0 . Then, (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

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

with

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

Therefore, in the case of a perfect gas,

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

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

$$\mu = \int_{T_0}^T c_p(\theta) d\theta + h_0 - T \int_{T_0}^T \frac{c_p(\theta)}{\theta} d\theta + RT \ln \frac{p}{p_0} - T s_0 \quad (51)$$

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:

$$\mu = e(T) + RT - T \left(\frac{e}{T} - \frac{e_0}{T_0} \right) - T \int_{T_0}^T \frac{e(\theta)}{\theta^2} d\theta - RT \ln \frac{T}{T_0} + RT \ln \frac{p}{p_0} - T s_0 \quad (58)$$

In deriving (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 [19]. 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% N₂ and 21% O₂ by volume). These molecules, as well as NO, can be assimilated to

rigid rotators, at least until 10,000 K [18]. 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 [26]:

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

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 of 2,500–3,500 K. Electronic excitation can be written in a form similar to (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 (60). Atoms do not have rotational or vibrational internal energy modes.

In the temperature range where air behaves as a thermally perfect gas (600–2,000 K roughly), it is chemically inert and its composition remains that of room temperature. Thus,

$$e(T) = y_{\text{N}_2} e_{\text{N}_2}(T) + y_{\text{O}_2} e_{\text{O}_2}(T) \quad (64)$$

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

$$y_{\text{N}_2} = \frac{\rho_{\text{N}_2}}{\rho} = .79 \frac{\hat{M}_{\text{N}_2}}{\hat{M}} = .7670 \quad (65)$$

$$y_{\text{O}_2} = \frac{\rho_{\text{O}_2}}{\rho} = .21 \frac{\hat{M}_{\text{O}_2}}{\hat{M}} = .2330 \quad (66)$$

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

$$\hat{M} = .79\hat{M}_{\text{N}_2} + .21\hat{M}_{\text{O}_2} = 28.84 \times 10^{-3} \text{ kg/mol} \quad (67)$$

with

$$\hat{M}_{\text{N}_2} = 28.0 \times 10^{-3} \text{ kg/mol} \quad (68)$$

$$\hat{M}_{\text{O}_2} = 32.0 \times 10^{-3} \text{ kg/mol} \quad (69)$$

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

$$\mu = e + RT - \frac{7}{2}RT \ln \frac{T}{T_0} + RT \ln \frac{p}{p_0} - T \left(\frac{e^{\text{vib}}}{T} - \frac{e_0^{\text{vib}}}{T_0} \right) + \sum_{s=\text{N}_2, \text{O}_2} y_s R_s T \ln \left[\frac{1 - \exp(-\Theta_s^{\text{vib}}/T)}{1 - \exp(-\Theta_s^{\text{vib}}/T_0)} \right] - T s_0 \quad (70)$$

where e is given by (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 (70) comes from the term $(e/T - e_0/T_0)$ in (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

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

(72) differs from the calorically perfect case (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

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

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 (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 will stress the importance of using the Newton-Raphson scheme to solve the resulting nonlinear 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 [19] 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.

IV . 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 nonequilibrium 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 [26], a multi-temperature model is crucial to compute accurately the aerothermal loads on the vehicle; models assuming thermal equilibrium tend indeed 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 involved [27] 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 (1) read:

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

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

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

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

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

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

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

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 [35], 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 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.,

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

but satisfy the relations [10]:

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

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

Equation (92), together with

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

implies that

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

As shown in Appendix C, the pressure term in (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 (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 [35, 10] and Wilke's mixing rule [26].

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:

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

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

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

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

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

$$e_s^{\text{rot}}(T) = \begin{cases} 0, & \text{for atoms} \\ 2 \times \frac{1}{2} R_s T, & \text{for diatomic molecules} \end{cases} \quad (103)$$

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

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 Prigogine [27]):

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

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, (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 entropy [35]:

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

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 (108), it is easy to derive the condition for chemical equilibrium (B.10), which is related to De Donder's notion of chemical affinity [27]. 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 (107) and (108), we get

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

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 (110) reads,

$$d\mathcal{G} = d\mathcal{E} + pd\mathcal{V} + \mathcal{V}dp - Td\mathcal{S} - \mathcal{S}dT \quad (111)$$

Substituting (109) into (111), we get

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

But,

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

Thus, (112) becomes

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

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

$$\mathcal{N} \hat{c}_v^{\text{vib}} = \sum_s \mathcal{N}_s \hat{c}_{v_s}^{\text{vib}} \quad (115)$$

and,

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

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

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

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:

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

Therefore,

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

Finally, (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,

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

(124) becomes

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

Converting into quantities per unit mass by dividing (126) by \hat{M}_s , and integrating from the state of reference entropy s_{s0} , we get:

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

where

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

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

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

4.5. Entropy Variables and Symmetrization.

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

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

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

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

yields the following vector of entropy variables:

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

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

The assumptions made in Section 4.3 concerning the form of the different energies are not necessary to derive (132). Knowing that e_s is the sum of a function of T and of a function of T^{vib} is sufficient. However, if (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:

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

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

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

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

where

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

and

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

ρ_{s0} and μ_{s0} being respectively the density and the chemical potential of species s in the state of reference entropy. The production rates of the different species, Ω_s , are given in terms of the ρ_s 's, T , and T^{vib} [26]. These quantities are readily available through (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 [2]. 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.

to:

		Primitive	Conservative	Entropy
from:	Primitive	=	explicit	explicit
	Conservative	numerical	=	numerical
	Entropy	explicit	explicit	=

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

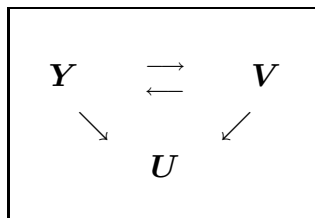


Figure 1. Explicit relations for rigid-rotator/harmonic-oscillator model.

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

V . ADVANTAGES OF SYMMETRIC CONSERVATION LAWS.

The advantages of the symmetry of (5) are practical as well as aesthetic. It can be shown that (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 (5). We will exemplify these properties with the system of Section 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 $\widetilde{\mathbf{K}}$.

5.1. Positive Semidefiniteness of $\widetilde{\mathbf{K}}$.

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

5.1.1. The Mass-diffusion Diffusivity Matrix, $\widetilde{\mathbf{K}}^{\text{mass}}$.

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

if and only if $\boldsymbol{\alpha} = [\alpha_{sr}]$ 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 $\boldsymbol{\alpha}$ (see Onsager [24]).

5.1.2. The Viscous Stress Diffusivity Matrix, $\widetilde{\mathbf{K}}^{\text{visc}}$.

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

where $\boldsymbol{\epsilon}$ is the strain tensor:

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

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

$$\epsilon''_{ij} = \left(\frac{1}{3}\text{tr}\boldsymbol{\epsilon}\right)\delta_{ij} = \frac{1}{3}\epsilon_{kk}\delta_{ij} \quad (142)$$

$$\epsilon'_{ij} = \epsilon_{ij} - \epsilon''_{ij} \quad (143)$$

Then,

$$\nabla \mathbf{V} \cdot \widetilde{\mathbf{K}}^{\text{visc}} \nabla \mathbf{V} = \frac{1}{T} \left[(\lambda^{\text{visc}} + \frac{2}{3}\mu^{\text{visc}})(\text{tr}\boldsymbol{\epsilon})^2 + 2\mu^{\text{visc}}(\boldsymbol{\epsilon}' : \boldsymbol{\epsilon}') \right] \geq 0 \quad (144)$$

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, $\widetilde{\mathbf{K}}^{\text{heat}}$.

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

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

5.2. Clausius-Duhem Inequality.

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

$$\mathbf{V} \cdot \left[\widetilde{\mathbf{A}}_0 \mathbf{V}_{,t} + \widetilde{\mathbf{A}}_i \mathbf{V}_{,i} - (\widetilde{\mathbf{K}}_{ij} \mathbf{V}_{,j})_{,i} + \widetilde{\mathcal{F}} \right] \quad (146)$$

Integrating by parts the diffusivity term, and rearranging yield

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

From the preceding section, we know that the right-hand side in (147) is nonpositive.

Moreover, one can show that

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

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

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

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

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

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

Substituting (148)–(153) into (147), we get

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

An interpretation of (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 (5) (see Hughes, Franca and Mallet [12], Mallet [21], and Shakib [29]).

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

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

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 con-

vergence 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 [13, 14, 15]. 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 [16, 17], 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 [32]. For hyperbolic systems of conservation laws which possess a strictly convex entropy function and thus can be symmetrized via entropy variables, Johnson, Szepessy, and Hansbo [17] 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 of Galerkin/least-squares type methods sheds some rigor into an area of numerical analysis where it does not usually prevail.

VI . CONCLUSIONS.

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 no fundamental impediment was 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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REFERENCES

- [1] J.D. ANDERSON, JR., *Hypersonic and High Temperature Gas Dynamics*, McGraw-Hill, 1989.
- [2] G. CANDLER, “The Computation of Weakly Ionized Hypersonic Flows in Thermochemical Nonequilibrium”, *Ph.D. Thesis*, Department of Aeronautics and Astronautics, Stanford University, 1988.
- [3] G. CANDLER and R.W. MACCORMACK, “The Computation of Hypersonic Flows in Chemical and Thermal Nonequilibrium”, Third National Aerospace Plane Technology Symposium, June 2–4, 1987. Paper number 107.
- [4] S. CHAPMAN, and T.G. COWLING, *The Mathematical Theory of Non-uniform Gases*, Third Edition, Cambridge University Press, 1970.
- [5] S.K. GODUNOV, “The Problem of a Generalized Solution in the Theory of Quasilinear Equations and in Gas Dynamics”, *Russ. Math. Surveys*, Volume 17, pp 145–156, 1962.
- [6] G.H. GOLUB, and C.F. VAN LOAN, *Matrix Computations*, Second Edition, Johns Hopkins, 1989.
- [7] C.F. HANSEN, “Approximations for the Thermodynamic and Transport Properties of High-temperature Air”, NASA Technical Report TR-R-50, 1959.
- [8] A. HARTEN, “On the Symmetric Form of Systems of Conservation Laws with Entropy”, *Journal of Computational Physics*, Volume 49, pp 151–164, 1983.
- [9] J.O. HIRSCHFELDER, “Heat Transfer in Chemically Reacting Mixtures. I.”, *Journal of Chemical Physics*, Volume 26, Number 2, pp 274–281, 1957.
- [10] J.O. HIRSCHFELDER, C.F. CURTISS, and R.B. BIRD, *Molecular Theory of Gases and Liquids*, Second Printing, John Wiley, New York, 1954.
- [11] H. HOLLANDERS, L. MARRAFFA, J.-L. MONTAGNÉ, PH. MORICE, and H. VIVIAND, “Computational Methods for Hypersonic Flows: Special Techniques and Real Gas Effects”, Second Joint Europe/U.S. Short Course in Hypersonics, January 16–20, 1989, Colorado Springs, Colorado.
- [12] T.J.R. HUGHES, L.P. FRANCA and M. MALLET, “A New Finite Element Formulation for Computational Fluid Dynamics: I. Symmetric Forms of the Compressible Euler and Navier-Stokes Equations and the Second Law of Thermodynamics”, *Computer*

Methods in Applied Mechanics and Engineering, North-Holland, Volume 54, pp 223–234, 1986.

- [13] T.J.R. HUGHES, L.P. FRANCA, and M. MALLET, “A New Finite Element Formulation for Computational for Computational Fluid Dynamics: VI. Convergence Analysis of the Generalized SUPG Formulation for Linear Time-dependent Multidimensional Advective-diffusive Systems”, *Computer Methods in Applied Mechanics and Engineering*, Volume 63, pp 97–112, 1987.
- [14] T.J.R. HUGHES, L.P. FRANCA, and G. HULBERT, “A New Finite Element Formulation for Computational for Computational Fluid Dynamics: VIII. The Galerkin/Least-squares Method for Advective-diffusive Equations”, *Computer Methods in Applied Mechanics and Engineering*, Volume 73, pp 173–189, 1989.
- [15] T.J.R. HUGHES, F. CHALOT, and Z. JOHAN, *Finite Element Methods in Fluid Mechanics*, text in preparation.
- [16] C. JOHNSON, and A. SZEPESSY, “On the Convergence of a Finite Element Method for a Nonlinear Hyperbolic Conservation Law”, *Mathematics of Computation*, Volume 49, Number 180, pp 427–444, 1987.
- [17] C. JOHNSON, A. SZEPESSY, and P. HANSBO, “On the Convergence of Shock-capturing Streamline Diffusion Finite Element Methods for Hyperbolic Conservation Laws”, Preprint No 1987-21, Department of Mathematics, Chalmers University of Technology, Göteborg, Sweden.
- [18] Y. LIU, F. SHAKIB and M. VINOKUR, “A Comparison of Internal Energy Calculation Methods for Diatomic Molecules”, AIAA 28th Aerospace Sciences Meeting, January 8–11, 1990, Reno, Nevada. Paper AIAA-90-0351.
- [19] Y. LIU and M. VINOKUR, “Equilibrium Gas Flow Computations. I. Accurate and Efficient Calculations of Equilibrium Gas Properties”, AIAA 24th Thermophysics Conference, Buffalo, New York, June 12–14, 1989. Paper AIAA-89-1736.
- [20] Y. LIU and M. VINOKUR, “Equilibrium Gas Flow Computations. II. An Analysis of Numerical Formulations of Conservation Laws”, AIAA 26th Aerospace Sciences Meeting, January 11–14, 1988, Reno, Nevada. Paper AIAA-88-0127.
- [21] M. MALLET, “A Finite Element Method for Computational Fluid Dynamics”, *Ph.D. Thesis*, Division of Applied Mechanics, Stanford University, 1985.
- [22] MOCK, “Systems of Conservation Laws of Mixed Type”, *Journal of Differential Equations*, Volume 37, pp 70–88, 1980.
- [23] L. ONSAGER, “Reciprocal Relations in Irreversible Processes. I.”, *Physical Review*, Volume 37, pp 405–426, 1931.

-
- [24] L. ONSAGER, “Reciprocal Relations in Irreversible Processes. II.”, *Physical Review*, Volume 38, pp 2265–2279, 1931.
- [25] C. PARK, “On Convergence of Computation of Chemically Reacting Flows”, AIAA 23rd Aerospace Sciences Meeting, January 14–17, 1985, Reno, Nevada. Paper AIAA-85-0247.
- [26] C. PARK, *Nonequilibrium Hypersonic Aerothermodynamics*, Wiley-Interscience, 1990.
- [27] I. PRIGOGINE, *Introduction to Thermodynamics of Irreversible Processes*, Third Edition, Interscience, 1967.
- [28] J.V. RAKICH, H.E. BAILEY and C. PARK, “Computation of Nonequilibrium Three-dimensional Inviscid Flow over Blunt-nosed Bodies Flying at Supersonic Speeds”, AIAA 8th Fluid and Plasma Dynamics Conference, Hartford, Connecticut, June 16–18, 1975. Paper AIAA-75-835.
- [29] F. SHAKIB, “Finite Element Analysis of the Compressible Euler and Navier-Stokes Equations”, *Ph.D. Thesis*, Division of Applied Mechanics, Stanford University, 1989.
- [30] S. SRINIVASAN, J.C. TANNEHILL, and K.J. WEILMUNSTER, “Simplified Curve Fits for the Thermodynamic Properties of Equilibrium Air”, NASA Reference Publication RP-1181, 1987.
- [31] J.L. STEGER and R.F. WARMING, “Flux Vector Splitting of the Inviscid Gas Dynamics Equations with Applications to Finite Difference Methods”, NASA Technical Memorandum TM-78605, July 1979.
- [32] A. SZEPESSY, “Convergence of a Shock-capturing Streamline Diffusion Finite Element for Scalar Conservation Laws in Two Space Dimensions”, Preprint No 1988-07, Department of Mathematics, Chalmers University of Technology, Göteborg, Sweden.
- [33] E. TADMOR, “Skew-selfadjoint Form for Systems of Conservation Laws”, *Journal of Mathematical Analysis and Applications*, Volume 103, pp 428–442, 1984.
- [34] J.C. TANNEHILL, and P.H. MUGGE, “Improved Curve Fits for the Thermodynamic Properties of Equilibrium Air Suitable for Numerical Computation Using Time-dependent or Shock-capturing Methods”, NASA Contractor Report CR-2470, 1974.
- [35] W.G. VINCENTI and C.H. KRUGER, JR., *Introduction to Physical Gas Dynamics*, Krieger, 1965.
- [36] R.F. WARMING, R.M. BEAM and B.J. HYETT, “Diagonalization and Simultaneous Symmetrization of the Gas-dynamic Matrices”, *Mathematics of Computation*, Volume 29, Number 132, pp 1037–1045, 1975.
- [37] L.C. WOODS, *The Thermodynamics of Fluid Systems*, Oxford University Press, 1975.

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, \mathbf{U} and \mathbf{V} are repeated here:

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

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

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

$$s = - \left(\frac{\partial \mu}{\partial T} \right)_p, \quad v = \left(\frac{\partial \mu}{\partial p} \right)_T \quad (\text{A.3})$$

$$h = \mu + Ts, \quad e = h - pv \quad (\text{A.4})$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T} \right)_p = \frac{1}{v} \left(\frac{\partial^2 \mu}{\partial p \partial T} \right), \quad \beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p} \right)_T = -\frac{1}{v} \left(\frac{\partial^2 \mu}{\partial p^2} \right)_T \quad (\text{A.5})$$

$$c_p = \left(\frac{\partial h}{\partial T} \right)_p = -T \left(\frac{\partial^2 \mu}{\partial T^2} \right)_p, \quad c_v = c_p - \frac{\alpha_p^2 v T}{\beta_T} \quad (\text{A.6})$$

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

$$k = \frac{|\mathbf{u}|^2}{2}, \quad d = \frac{v \alpha_p T}{\beta_T}, \quad \bar{\gamma} = \frac{v \alpha_p}{\beta_T c_v}, \quad (\text{A.7})$$

$$c_1 = u_1^2 + \frac{v}{\beta_T}, \quad c_2 = u_2^2 + \frac{v}{\beta_T}, \quad c_3 = u_3^2 + \frac{v}{\beta_T}, \quad (\text{A.8})$$

$$\bar{c}_1 = u_1^2 + c_v T, \quad \bar{c}_2 = u_2^2 + c_v T, \quad \bar{c}_3 = u_3^2 + c_v T, \quad (\text{A.9})$$

$$e_1 = h + k, \quad e_2 = e_1 - d, \quad e_3 = e_2 + \frac{v}{\beta_T}, \quad (\text{A.10})$$

$$e_4 = e_2 + 2\frac{v}{\beta_T}, \quad (\text{A.11})$$

$$\bar{e}_1 = h - k, \quad \bar{e}_2 = \bar{e}_1 - d, \quad \bar{e}_3 = \bar{e}_2 - c_v T, \quad (\text{A.12})$$

$$u_{12} = u_1 u_2, \quad u_{23} = u_2 u_3, \quad u_{31} = u_3 u_1, \quad (\text{A.13})$$

$$u_{123} = u_1 u_2 u_3, \quad a^2 = \frac{v c_p}{c_v \beta_T} \quad (\text{A.14})$$

$$e_5 = e_1^2 - 2e_1 d + \frac{v(2k + c_p T)}{\beta_T}, \quad \bar{e}_5 = \bar{e}_1^2 - 2\bar{e}_1 d + 2k c_v T + \frac{v c_p T}{\beta_T} \quad (\text{A.15})$$

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

$$\tilde{\mathbf{A}}_0 = \frac{\beta_T T}{v^2} \begin{bmatrix} 1 & u_1 & u_2 & u_3 & e_2 \\ & c_1 & u_{12} & u_{31} & u_1 e_3 \\ & & c_2 & u_{23} & u_2 e_3 \\ & & \text{symm.} & c_3 & u_3 e_3 \\ & & & & e_5 \end{bmatrix} \quad (\text{A.16})$$

and

$$\tilde{\mathbf{A}}_0^{-1} = \frac{v}{c_v T^2} \begin{bmatrix} \bar{e}_5 & u_1 \bar{e}_3 & u_2 \bar{e}_3 & u_3 \bar{e}_3 & -\bar{e}_2 \\ & \bar{c}_1 & u_{12} & u_{31} & -u_1 \\ & & \bar{c}_2 & u_{23} & -u_2 \\ & & \text{symm.} & \bar{c}_3 & -u_3 \\ & & & & 1 \end{bmatrix} \quad (\text{A.17})$$

The advective fluxes are

$$\mathbf{F}_i^{\text{adv}} = \rho u_i \begin{pmatrix} 1 \\ u_1 \\ u_2 \\ u_3 \\ e + |\mathbf{u}|^2/2 \end{pmatrix} + p \begin{pmatrix} 0 \\ \delta_{1i} \\ \delta_{2i} \\ \delta_{3i} \\ u_i \end{pmatrix} \quad (\text{A.18})$$

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

$$\mathbf{A}_1 = \begin{bmatrix} 0 & 1 & 0 & 0 & 0 \\ a^2 - u_1^2 - \bar{e}_1 \bar{\gamma} & -u_1(\bar{\gamma} - 2) & -u_2 \bar{\gamma} & -u_3 \bar{\gamma} & \bar{\gamma} \\ -u_{12} & u_2 & u_1 & 0 & 0 \\ -u_{31} & u_3 & 0 & u_1 & 0 \\ -u_1(e_1 + \bar{e}_1 \bar{\gamma} - a^2) & e_1 - u_1^2 \bar{\gamma} & -u_{12} \bar{\gamma} & -u_{31} \bar{\gamma} & u_1(\bar{\gamma} + 1) \end{bmatrix} \quad (\text{A.19})$$

$$\mathbf{A}_2 = \begin{bmatrix} 0 & 0 & 1 & 0 & 0 \\ u_{12} & u_2 & u_1 & 0 & 0 \\ a^2 - u_2^2 - \bar{e}_1 \bar{\gamma} & -u_1 \bar{\gamma} & -u_2(\bar{\gamma} - 2) & -u_3 \bar{\gamma} & \bar{\gamma} \\ -u_{23} & 0 & u_3 & u_2 & 0 \\ -u_2(e_1 + \bar{e}_1 \bar{\gamma} - a^2) & -u_{12} \bar{\gamma} & e_1 - u_2^2 \bar{\gamma} & -u_{23} \bar{\gamma} & u_2(\bar{\gamma} + 1) \end{bmatrix} \quad (\text{A.20})$$

$$\mathbf{A}_3 = \begin{bmatrix} 0 & 0 & 0 & 1 & 0 \\ -u_{31} & u_3 & 0 & u_1 & 0 \\ -u_{23} & 0 & u_3 & u_2 & 0 \\ a^2 - u_3^2 - \bar{e}_1 \bar{\gamma} & -u_1 \bar{\gamma} & -u_2 \bar{\gamma} & -u_3(\bar{\gamma} - 2) & \bar{\gamma} \\ -u_3(e_1 + \bar{e}_1 \bar{\gamma} - a^2) & -u_{31} \bar{\gamma} & -u_{23} \bar{\gamma} & e_1 - u_3^2 \bar{\gamma} & u_3(\bar{\gamma} + 1) \end{bmatrix} \quad (\text{A.21})$$

Note that

$$\mathbf{A}_i \mathbf{U} = \rho u_i \begin{Bmatrix} 1 \\ u_1 \\ u_2 \\ u_3 \\ e + |\mathbf{u}|^2/2 \end{Bmatrix} + \left(\frac{c_p - v \alpha_p p}{\beta_T c_v p} \right) p \begin{Bmatrix} 0 \\ \delta_{1i} \\ \delta_{2i} \\ \delta_{3i} \\ u_i \end{Bmatrix} \quad (\text{A.22})$$

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} , $\tilde{\mathbf{A}}_i = \mathbf{F}_{i,\mathbf{V}}^{\text{adv}} = \mathbf{A}_i \tilde{\mathbf{A}}_0$, are given by

$$\tilde{\mathbf{A}}_1 = \frac{\beta_T T}{v^2} \begin{bmatrix} u_1 & c_1 & u_{12} & u_{31} & u_1 e_3 \\ & u_1(u_1^2 + 3\frac{v}{\beta_T}) & u_2 c_1 & u_3 c_1 & e_1 \frac{v}{\beta_T} + u_1^2 e_4 \\ & & u_1 c_2 & u_{123} & u_{12} e_4 \\ & \text{symm.} & & u_1 c_3 & u_{31} e_4 \\ & & & & u_1(e_5 + 2e_1 \frac{v}{\beta_T}) \end{bmatrix} \quad (\text{A.23})$$

$$\tilde{\mathbf{A}}_2 = \frac{\beta_T T}{v^2} \begin{bmatrix} u_2 & u_{12} & c_2 & u_{23} & u_2 e_3 \\ & u_2 c_1 & u_1 c_2 & u_{123} & u_{12} e_4 \\ & & u_2(u_2^2 + 3\frac{v}{\beta_T}) & u_3 c_2 & e_1 \frac{v}{\beta_T} + u_2^2 e_4 \\ & \text{symm.} & & u_2 c_3 & u_{23} e_4 \\ & & & & u_2(e_5 + 2e_1 \frac{v}{\beta_T}) \end{bmatrix} \quad (\text{A.24})$$

$$\tilde{\mathbf{A}}_3 = \frac{\beta_T T}{v^2} \begin{bmatrix} u_3 & u_{31} & u_{23} & c_3 & u_3 e_3 \\ & u_3 c_1 & u_{123} & u_1 c_3 & u_{31} e_4 \\ & & u_3 c_2 & u_2 c_3 & u_{23} e_4 \\ & \text{symm.} & & u_3(u_3^2 + 3\frac{v}{\beta_T}) & e_1 \frac{v}{\beta_T} + u_3^2 e_4 \\ & & & & u_3(e_5 + 2e_1 \frac{v}{\beta_T}) \end{bmatrix} \quad (\text{A.25})$$

The diffusive fluxes are given as

$$\mathbf{F}_i^{\text{diff}} = \begin{pmatrix} 0 \\ \tau_{1i} \\ \tau_{2i} \\ \tau_{3i} \\ \tau_{ij} u_j \end{pmatrix} + \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ -q_i \end{pmatrix} \quad (\text{A.26})$$

where

$$\tau_{ij} = \lambda^{\text{visc}} u_{k,k} \delta_{ij} + \mu^{\text{visc}} (u_{i,j} + u_{j,i}) \quad (\text{A.27})$$

$$q_i = -\kappa T_{,i} \quad (\text{A.28})$$

The spatial gradients of the velocity components and temperature are

$$u_{i,j} = TV_{i+1,j} + Tu_i V_{5,j} \quad \text{for } i = 1, 2, 3 \quad (\text{A.29})$$

$$T_{,i} = T^2 V_{5,i} \quad (\text{A.30})$$

Let

$$\chi^{\text{visc}} = \lambda^{\text{visc}} + 2\mu^{\text{visc}} \quad (\text{A.31})$$

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

$$\widetilde{\mathbf{K}}_{11} = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ & \chi^{\text{visc}} & 0 & 0 & \chi^{\text{visc}}u_1 \\ & & \mu^{\text{visc}} & 0 & \mu^{\text{visc}}u_2 \\ & & \text{symm.} & \mu^{\text{visc}} & \mu^{\text{visc}}u_3 \\ & & & & \chi^{\text{visc}}u_1^2 + \mu^{\text{visc}}(u_2^2 + u_3^2) + \kappa T \end{bmatrix} \quad (\text{A.32})$$

$$\widetilde{\mathbf{K}}_{22} = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}}u_1 \\ & & \chi^{\text{visc}} & 0 & \chi^{\text{visc}}u_2 \\ & & \text{symm.} & \mu^{\text{visc}} & \mu^{\text{visc}}u_3 \\ & & & & \chi^{\text{visc}}u_2^2 + \mu^{\text{visc}}(u_1^2 + u_3^2) + \kappa T \end{bmatrix} \quad (\text{A.33})$$

$$\widetilde{\mathbf{K}}_{33} = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}}u_1 \\ & & \mu^{\text{visc}} & 0 & \mu^{\text{visc}}u_2 \\ & & \text{symm.} & \chi^{\text{visc}} & \chi^{\text{visc}}u_3 \\ & & & & \chi^{\text{visc}}u_3^2 + \mu^{\text{visc}}(u_1^2 + u_2^2) + \kappa T \end{bmatrix} \quad (\text{A.34})$$

$$\widetilde{\mathbf{K}}_{12} = \widetilde{\mathbf{K}}_{21}^T = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda^{\text{visc}} & 0 & \lambda^{\text{visc}}u_2 \\ 0 & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}}u_1 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & \mu^{\text{visc}}u_2 & \lambda^{\text{visc}}u_1 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}})u_{12} \end{bmatrix} \quad (\text{A.35})$$

$$\widetilde{\mathbf{K}}_{13} = \widetilde{\mathbf{K}}_{31}^T = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda^{\text{visc}} & \lambda^{\text{visc}}u_3 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}}u_1 \\ 0 & \mu^{\text{visc}}u_3 & 0 & \lambda^{\text{visc}}u_1 & (\lambda^{\text{visc}} + \mu^{\text{visc}})u_{31} \end{bmatrix} \quad (\text{A.36})$$

$$\widetilde{\mathbf{K}}_{23} = \widetilde{\mathbf{K}}_{32}^T = T \begin{bmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda^{\text{visc}} & \lambda^{\text{visc}}u_3 \\ 0 & 0 & \mu^{\text{visc}} & 0 & \mu^{\text{visc}}u_2 \\ 0 & 0 & \mu^{\text{visc}}u_3 & \lambda^{\text{visc}}u_2 & (\lambda^{\text{visc}} + \mu^{\text{visc}})u_{23} \end{bmatrix} \quad (\text{A.37})$$

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 (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

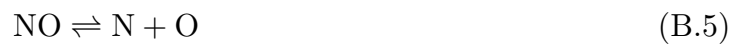
$$\sum_s y_s = 1 \quad (\text{B.1})$$

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

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

Even in the case of a viscous flow, (B.2) 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 [26].

In addition to the mass conservation (B.1), and the element conservation (B.2), 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.,

$$\frac{c_{\text{N}}^2}{c_{\text{N}_2}} = K_{c1}(T) \quad (\text{B.6})$$

$$\frac{c_{\text{O}}^2}{c_{\text{O}_2}} = K_{c2}(T) \quad (\text{B.7})$$

$$\frac{c_{\text{N}}c_{\text{O}}}{c_{\text{NO}}} = K_{c3}(T) \quad (\text{B.8})$$

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 potentials [19]:

$$\hat{\mu}_s = \mu_s \hat{M}_s = \hat{\mu}_s^0(T) + \hat{R}T \ln p_s \quad (\text{B.9})$$

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

$$\sum_s \hat{\mu}_s \nu_{sR} = 0 \quad (\text{B.10})$$

where ν_{sR} is the stoichiometric coefficient of component s in reaction R . Equations (B.10) can be rewritten as the more familiar law of mass action:

$$K_{cR}(T) = \prod_s c_s^{\nu_{sR}} = \frac{\exp\left(-\frac{\sum_s \hat{\mu}_s^0 \nu_{sR}}{\hat{R}T}\right)}{(\hat{R}T)^{\sum_s \nu_{sR}}} \quad (\text{B.11})$$

For the sake of simplicity, we will use here curve fits for the K_{cR} 's, similar to those proposed by Rakich or Park [28, 25, 26].

The resulting system of five nonlinear equations for the y_s 's in terms of p and T ((B.1), (B.2), (B.6)–(B.8)) can formally be expressed as

$$\mathbf{f}(\mathbf{y}, p, T) = \mathbf{0} \quad (\text{B.12})$$

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

$$\mathbf{y}^{(n+1)} = \mathbf{y}^{(n)} + \Delta \mathbf{y}^{(n)} \quad (\text{B.13})$$

where

$$\Delta \mathbf{y}^{(n)} = -\mathbf{J}^{-1}(\mathbf{y}^{(n)}, p, T) \mathbf{f}(\mathbf{y}^{(n)}, p, T) \quad (\text{B.14})$$

and

$$\mathbf{J} = \left(\frac{\partial \mathbf{f}}{\partial \mathbf{y}} \right)_{p, T} \quad (\text{B.15})$$

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 (B.12) is:

$$\mathbf{J}d\mathbf{y} + \left(\frac{\partial \mathbf{f}}{\partial p}\right)_{\mathbf{y},T} dp + \left(\frac{\partial \mathbf{f}}{\partial T}\right)_{\mathbf{y},p} dT = \mathbf{0} \quad (\text{B.16})$$

Thus,

$$d\mathbf{y} = -\mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial p}\right)_{\mathbf{y},T} dp - \mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial T}\right)_{\mathbf{y},p} dT \quad (\text{B.17})$$

and

$$\left(\frac{\partial \mathbf{y}}{\partial p}\right)_T = -\mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial p}\right)_{\mathbf{y},T} \quad (\text{B.18})$$

$$\left(\frac{\partial \mathbf{y}}{\partial T}\right)_p = -\mathbf{J}^{-1} \left(\frac{\partial \mathbf{f}}{\partial T}\right)_{\mathbf{y},p} \quad (\text{B.19})$$

From these derivatives, one can for instance compute

$$c_p = \left(\frac{\partial h}{\partial T}\right)_p = \sum_s y_s c_{ps} + \sum_s \left(\frac{\partial y_s}{\partial T}\right)_p h_s \quad (\text{B.20})$$

$$\alpha_p = \frac{1}{v} \left(\frac{\partial v}{\partial T}\right)_p = \frac{1}{T} + \frac{1}{R} \sum_s \left(\frac{\partial y_s}{\partial T}\right)_p R_s \quad (\text{B.21})$$

$$\beta_T = -\frac{1}{v} \left(\frac{\partial v}{\partial p}\right)_T = \frac{1}{p} - \frac{1}{R} \sum_s \left(\frac{\partial y_s}{\partial p}\right)_T R_s \quad (\text{B.22})$$

$$c_v = c_p - \frac{\alpha_p^2 v T}{\beta_T} \quad (\text{B.23})$$

$$a^2 = \frac{v c_p}{c_v \beta_T} \quad (\text{B.24})$$

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

$$c_{ps} = \left(\frac{\partial h_s}{\partial T}\right)_p \quad (\text{B.25})$$

and a is the speed of sound. Nondimensionalized α_p , β_T , c_p , and a^2 are plotted respectively in Figures 2–5, 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 [7], or with more recent curve fits [34, 30].

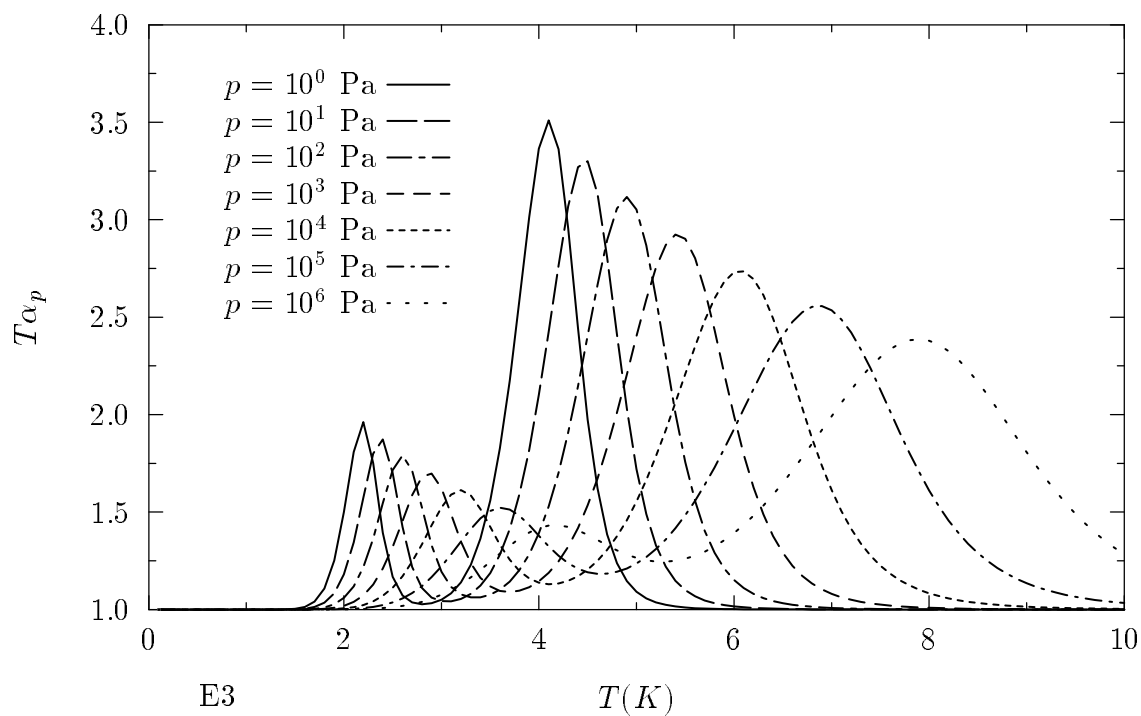


Figure 2. Dimensionless expansivity.

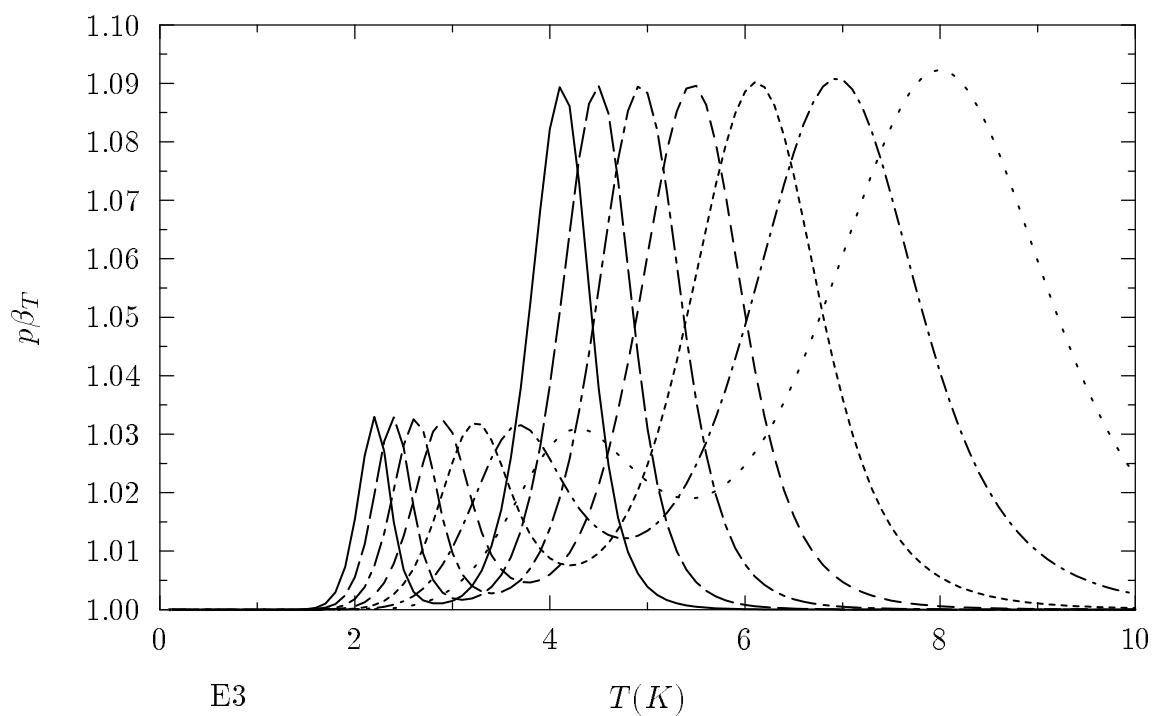


Figure 3. Dimensionless isothermal compressibility.

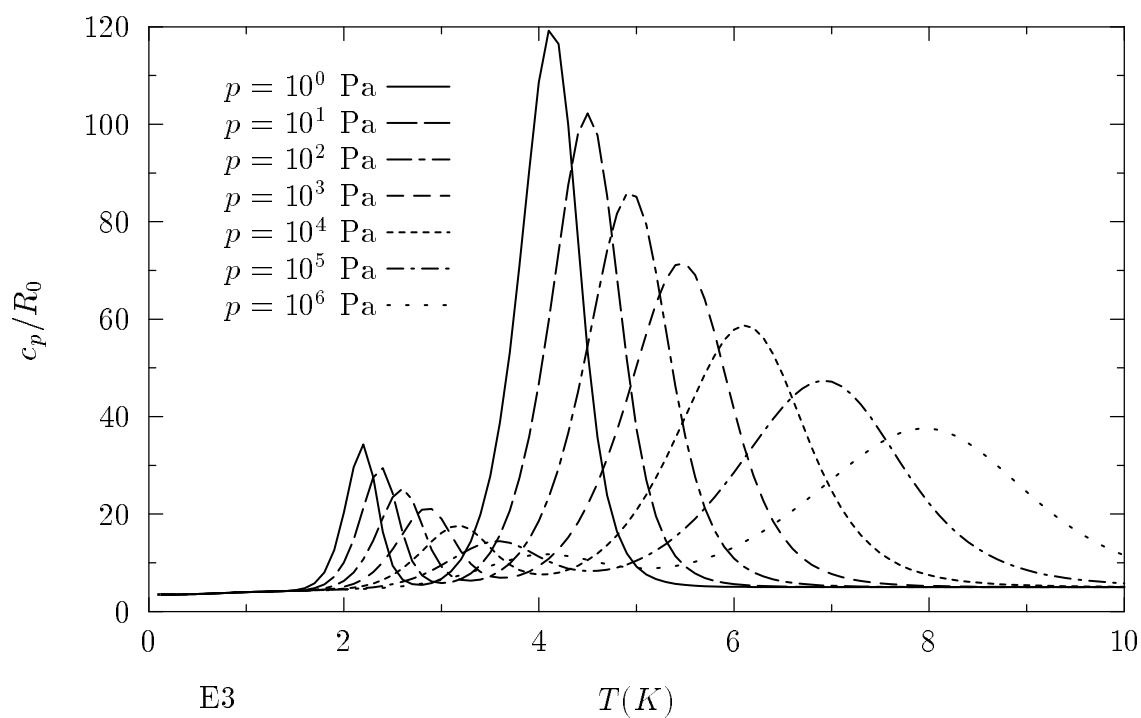


Figure 4. Dimensionless specific heat at constant pressure.

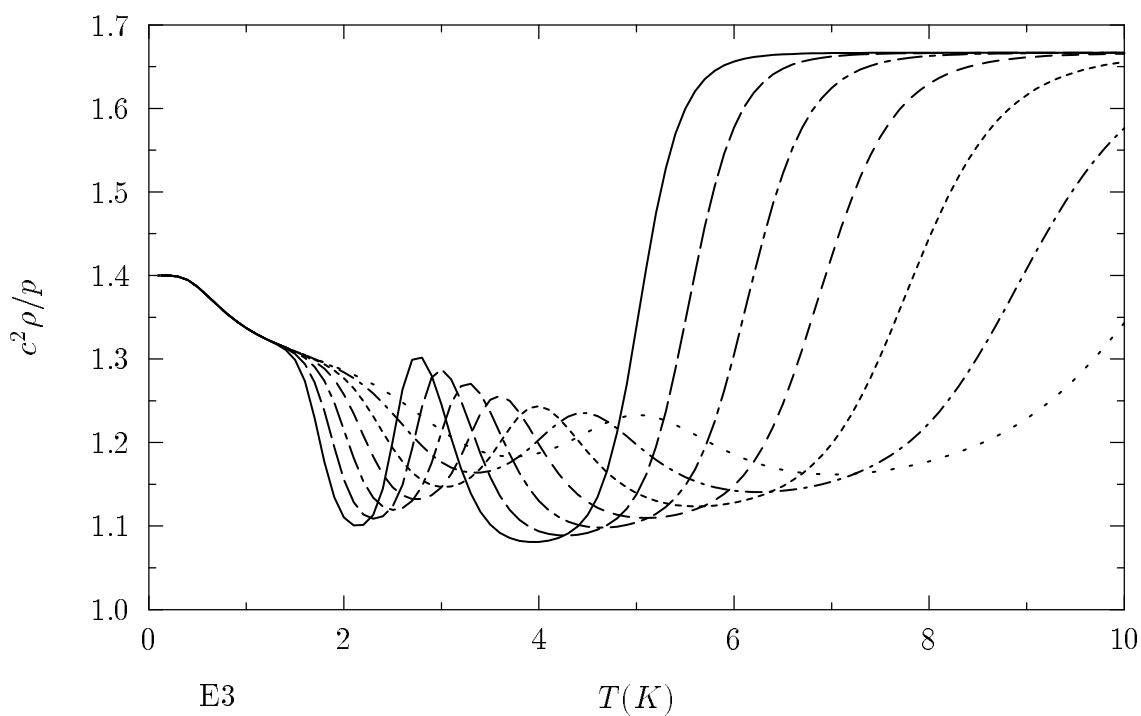


Figure 5. Speed of sound parameter.

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 Section 4.3).

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

$$\mathbf{U} = \frac{1}{v} \begin{Bmatrix} \mathbf{y} \\ \mathbf{u} \\ e^{\text{vib}} \\ e + \frac{|\mathbf{u}|^2}{2} \end{Bmatrix} \quad (\text{C.1})$$

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

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

$$\tilde{\mathbf{A}}_0 = \begin{bmatrix} \frac{\rho_1}{R_1} & 0 & \frac{\rho_1}{R_1} u_1 & \frac{\rho_1}{R_1} u_2 & \frac{\rho_1}{R_1} u_3 & \frac{\rho_1}{R_1} e_1^{\text{vib}} & \frac{\rho_1}{R_1} e_1^{\text{tot}} \\ \cdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ & \frac{\rho_n}{R_n} & \frac{\rho_n}{R_n} u_1 & \frac{\rho_n}{R_n} u_2 & \frac{\rho_n}{R_n} u_3 & \frac{\rho_n}{R_n} e_n^{\text{vib}} & \frac{\rho_n}{R_n} e_n^{\text{tot}} \\ & & u_1^2 \frac{\rho_s}{R_s} + \rho T & u_1 u_2 \frac{\rho_s}{R_s} & u_1 u_3 \frac{\rho_s}{R_s} & u_1 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 \frac{\rho_s}{R_s} h_s^{\text{tot}} \\ & & & u_2^2 \frac{\rho_s}{R_s} + \rho T & u_2 u_3 \frac{\rho_s}{R_s} & u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_2 \frac{\rho_s}{R_s} h_s^{\text{tot}} \\ & & & & u_3^2 \frac{\rho_s}{R_s} + \rho T & u_3 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_3 \frac{\rho_s}{R_s} h_s^{\text{tot}} \\ & & \text{symm.} & & & \frac{\rho_s}{R_s} e_s^{\text{vib}^2} & \frac{\rho_s}{R_s} e_s^{\text{vib}} e_s^{\text{tot}} \\ & & & & & + \rho c_v^{\text{vib}} T^{\text{vib}^2} & + \rho c_v^{\text{vib}} T^{\text{vib}^2} \\ & & & & & & \frac{\rho_s}{R_s} e_s^{\text{tot}^2} + \rho u^2 T \\ & & & & & & + \rho (c_v T^2 + c_v^{\text{vib}} T^{\text{vib}^2}) \end{bmatrix} \quad (\text{C.3})$$

$$\tilde{\mathbf{A}}_0^{-1} = \frac{1}{\rho c_v T^2} \begin{bmatrix} \bar{a}_{11} & \cdots & \bar{a}_{1n} & \bar{b}_1 u_1 & \bar{b}_1 u_2 & \bar{b}_1 u_3 & \bar{c}_1 & \bar{d}_1 \\ & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ & & \bar{a}_{nn} & \bar{b}_n u_1 & \bar{b}_n u_2 & \bar{b}_n u_3 & \bar{c}_n & \bar{d}_n \\ & & & u_1^2 + c_v T & u_1 u_2 & u_1 u_3 & u_1 & -u_1 \\ & & & & u_2^2 + c_v T & u_2 u_3 & u_2 & -u_2 \\ & & \text{symm.} & & & u_3^2 + c_v T & u_3 & -u_3 \\ & & & & & & 1 + \frac{c_v T^2}{c_v^{\text{vib}} T^{\text{vib}^2}} & -1 \\ & & & & & & & 1 \end{bmatrix} \quad (\text{C.4})$$

where

$$\begin{aligned} \bar{a}_{sr} &= (c_{vs}T + h_s^0 - \frac{u^2}{2})(c_{vr}T + h_r^0 - \frac{u^2}{2}) + e_s^{\text{vib}} e_r^{\text{vib}} \frac{c_v T^2}{c_v^{\text{vib}} T^{\text{vib}^2}} \\ &\quad + c_v T u^2 + \rho c_v T^2 \frac{R_s}{\rho_s} \delta_{sr} \end{aligned} \quad (\text{C.5})$$

$$\bar{b}_s = c_{vs}T + h_s^0 - \frac{u^2}{2} - c_v T \quad (\text{C.6})$$

$$\bar{c}_s = c_{vs}T + h_s^0 - \frac{u^2}{2} - e_s^{\text{vib}} \frac{c_v T^2}{c_v^{\text{vib}} T^{\text{vib}^2}} \quad (\text{C.7})$$

$$\bar{d}_s = -(c_{vs}T + h_s^0 - \frac{u^2}{2}) \quad (\text{C.8})$$

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

$$c_v = \sum_s y_s c_{vs} \quad (\text{C.9})$$

$$c_v^{\text{vib}} = \sum_s y_s c_{vs}^{\text{vib}} \quad (\text{C.10})$$

These conditions are satisfied in practice.

The advective fluxes are:

$$\mathbf{F}_i^{\text{adv}} = u_i \mathbf{U} + p \left\{ \begin{array}{c} \mathbf{0}_n \\ \boldsymbol{\delta}_i \\ 0 \\ u_i \end{array} \right\} \quad (\text{C.11})$$

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

$$\tilde{\mathbf{A}}_1 = \begin{bmatrix} \frac{\rho_1}{R_1} u_1 & 0 & \frac{\rho_1}{R_1} (u_1^2 + R_1 T) & \frac{\rho_1}{R_1} u_1 u_2 & \frac{\rho_1}{R_1} u_1 u_3 & \frac{\rho_1}{R_1} e_1^{\text{vib}} u_1 & \frac{\rho_1}{R_1} h_1^{\text{tot}} u_1 \\ \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\ \frac{\rho_n}{R_n} u_1 & \frac{\rho_n}{R_n} (u_1^2 + R_n T) & \frac{\rho_n}{R_n} u_1 u_2 & \frac{\rho_n}{R_n} u_1 u_3 & \frac{\rho_n}{R_n} e_n^{\text{vib}} u_1 & \frac{\rho_n}{R_n} h_n^{\text{tot}} u_1 \\ & u_1^3 \frac{\rho_s}{R_s} & u_1^2 u_2 \frac{\rho_s}{R_s} & u_1^2 u_3 \frac{\rho_s}{R_s} & u_1^2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1^2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & + 3\rho T u_1 & + \rho T u_2 & + \rho T u_3 & + \rho T e^{\text{vib}} & + \rho T h^{\text{tot}} \\ & & u_1 u_2^2 \frac{\rho_s}{R_s} & u_1 u_2 u_3 \frac{\rho_s}{R_s} & u_1 u_2 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 u_2 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & + \rho T u_1 & & & \\ & & & u_1 u_3^2 \frac{\rho_s}{R_s} & u_1 u_3 \frac{\rho_s}{R_s} e_s^{\text{vib}} & u_1 u_3 \left(\frac{\rho_s}{R_s} h_s^{\text{tot}} + \rho T \right) \\ & & & + \rho T u_1 & & \\ & & & & u_1 \frac{\rho_s}{R_s} e_s^{\text{vib}2} & u_1 \frac{\rho_s}{R_s} e_s^{\text{vib}} h_s^{\text{tot}} \\ & & & & + \rho u_1 c_v^{\text{vib}} T^{\text{vib}2} & + \rho u_1 c_v^{\text{vib}} T^{\text{vib}2} \\ & & & & & u_1 \frac{\rho_s}{R_s} h_s^{\text{tot}2} \\ & & & & & + \rho u_1 T (u^2 + c_p T) \\ & & & & & + \rho u_1 c_v^{\text{vib}} T^{\text{vib}2} \end{bmatrix} \quad (\text{C.12})$$

symm.

$$\tilde{\mathbf{A}}_3 = \begin{bmatrix}
\frac{\rho_1}{R_1}u_3 & 0 & \frac{\rho_1}{R_1}u_1u_3 & \frac{\rho_1}{R_1}u_2u_3 & \frac{\rho_1}{R_1}(u_3^2 + R_1T) & \frac{\rho_1}{R_1}e_1^{\text{vib}}u_3 & \frac{\rho_1}{R_1}h_1^{\text{tot}}u_3 \\
\vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\
\frac{\rho_n}{R_n}u_3 & \frac{\rho_n}{R_n}u_1u_3 & \frac{\rho_n}{R_n}u_2u_3 & \frac{\rho_n}{R_n}(u_3^2 + R_nT) & \frac{\rho_n}{R_n}e_n^{\text{vib}}u_3 & \frac{\rho_n}{R_n}h_n^{\text{tot}}u_3 \\
u_1^2u_3\frac{\rho_s}{R_s} & u_1u_2u_3\frac{\rho_s}{R_s} & u_1u_3^2\frac{\rho_s}{R_s} & u_1u_3^2\frac{\rho_s}{R_s} & u_1u_3\frac{\rho_s}{R_s}e_s^{\text{vib}} & u_1u_3(\frac{\rho_s}{R_s}h_s^{\text{tot}} + \rho T) \\
+ \rho T u_3 & & & + \rho T u_1 & & \\
u_2^2u_3\frac{\rho_s}{R_s} & u_2u_3^2\frac{\rho_s}{R_s} & u_2u_3^2\frac{\rho_s}{R_s} & u_2u_3^2\frac{\rho_s}{R_s} & u_2u_3\frac{\rho_s}{R_s}e_s^{\text{vib}} & u_2u_3(\frac{\rho_s}{R_s}h_s^{\text{tot}} + \rho T) \\
+ \rho T u_3 & & & + \rho T u_2 & & \\
u_3^3\frac{\rho_s}{R_s} & u_3^2\frac{\rho_s}{R_s}e_s^{\text{vib}} & u_3^2(\frac{\rho_s}{R_s}h_s^{\text{tot}} + \rho T) & u_3^3\frac{\rho_s}{R_s} & u_3^2\frac{\rho_s}{R_s}e_s^{\text{vib}} & u_3^2(\frac{\rho_s}{R_s}h_s^{\text{tot}} + \rho T) \\
+ 3\rho T u_3 & + \rho T e^{\text{vib}} & + \rho T h^{\text{tot}} & + 3\rho T u_3 & + \rho T e^{\text{vib}} & + \rho T h^{\text{tot}} \\
\text{symm.} & u_3\frac{\rho_s}{R_s}e_s^{\text{vib}2} & u_3\frac{\rho_s}{R_s}e_s^{\text{vib}}h_s^{\text{tot}} & & u_3\frac{\rho_s}{R_s}e_s^{\text{vib}2} & u_3\frac{\rho_s}{R_s}e_s^{\text{vib}}h_s^{\text{tot}} \\
& + \rho u_3c_v^{\text{vib}}T^{\text{vib}2} & + \rho u_3c_v^{\text{vib}}T^{\text{vib}2} & & + \rho u_3c_v^{\text{vib}}T^{\text{vib}2} & + \rho u_3c_v^{\text{vib}}T^{\text{vib}2} \\
& & & & & u_3\frac{\rho_s}{R_s}h_s^{\text{tot}2} \\
& & & & & + \rho u_3T(u^2 + c_pT) \\
& & & & & + \rho u_3c_v^{\text{vib}}T^{\text{vib}2}
\end{bmatrix} \tag{C.14}$$

The diffusive fluxes are the sums of three contributions:

$$\mathbf{F}_i^{\text{diff}} = \mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{visc}} + \mathbf{F}_i^{\text{heat}} \tag{C.15}$$

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:

$$\mathbf{F}_i^{\text{mass}} = \begin{pmatrix} -\mathbf{J}_i \\ \mathbf{0}_3 \\ -\mathbf{J}_i \cdot \mathbf{e}^{\text{vib}} \\ -\mathbf{J}_i \cdot \mathbf{h} \end{pmatrix} \tag{C.16}$$

where

$$J_{si} = \rho_s v_{si} = \sum_r \rho \frac{\hat{M}_s \hat{M}_r}{\hat{M}^2} D_{sr} d_{ri} \tag{C.17}$$

and

$$d_{si} = x_{s,i} + (x_s - y_s)(\ln p)_{,i} \quad (\text{C.18})$$

In terms of gradients of primitive variables, (C.17) can be rewritten as:

$$\rho_s v_{si} = - \sum_r \frac{R_r}{\rho_r} T \alpha_{sr} \rho_{r,i} - \beta_s T_{,i} \quad (\text{C.19})$$

with

$$\beta_s = \sum_r \alpha_{sr} R_r \quad (\text{C.20})$$

The α_{sr} 's are Onsager's phenomenological coefficients for mass diffusion [23, 24]. They are given in terms of the D_{sr} 's by

$$\alpha_{sr} = \frac{\hat{M}_s}{\hat{M}T} \left(-\frac{\rho_r}{R_r} D_{sr} + \rho_r \sum_t \frac{y_t}{R_t} D_{st} \right) \quad (\text{C.21})$$

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

$$\alpha_{sr} = \alpha_{rs} \quad , \quad \forall s, r \quad (\text{C.22})$$

Moreover, one can also write

$$\sum_t \alpha_{st} = \sum_t \alpha_{tr} = 0 \quad , \quad \forall s, r \quad (\text{C.23})$$

(C.23) is equivalent to (92), and ensures that

$$\sum_s \rho_s v_{si} = 0 \quad (\text{C.24})$$

The symmetry property (C.22) is checked for a mixture of three species in Hirschfelder, Curtiss, and Bird [10]. If the pressure term were omitted in the definition of the d_{si} 's, a nonsymmetric contribution would replace the α_{sr} 's in (C.19). 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 $\widetilde{\mathbf{K}}_{ij}^{\text{mass}}$, where $\widetilde{\mathbf{K}}_{ij}^{\text{mass}} \mathbf{V}_{,j} = \mathbf{F}_i^{\text{mass}}$, are

$$\widetilde{\mathbf{K}}_{ii}^{\text{mass}} = T \begin{bmatrix} \boldsymbol{\alpha} & \mathbf{0}_{n \times 3} & \boldsymbol{\alpha} \mathbf{e}^{\text{vib}} & \boldsymbol{\alpha} \mathbf{h} \\ & \mathbf{0}_{3 \times 3} & \mathbf{0}_3 & \mathbf{0}_3 \\ \text{symm.} & & \mathbf{e}^{\text{vib}} \cdot \boldsymbol{\alpha} \mathbf{e}^{\text{vib}} & \mathbf{e}^{\text{vib}} \cdot \boldsymbol{\alpha} \mathbf{h} \\ & & & \mathbf{h} \cdot \boldsymbol{\alpha} \mathbf{h} \end{bmatrix} \quad , \quad i = 1, 2, 3 \quad (\text{C.25})$$

$$\widetilde{\mathbf{K}}_{ij}^{\text{mass}} = \mathbf{0} \quad , \quad i \neq j \quad (\text{C.26})$$

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

The viscous stress flux vectors are given by:

$$\mathbf{F}_i^{\text{visc}} = \begin{pmatrix} \mathbf{0}_n \\ \tau_{ij}\boldsymbol{\delta}_j \\ 0 \\ \tau_{ij}u_j \end{pmatrix} \quad (\text{C.27})$$

where

$$\tau_{ij} = \lambda^{\text{visc}}u_{k,k}\delta_{ij} + \mu^{\text{visc}}(u_{i,j} + u_{j,i}) \quad (\text{C.28})$$

Let

$$\chi^{\text{visc}} = \lambda^{\text{visc}} + 2\mu^{\text{visc}} \quad (\text{C.29})$$

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

$$\widetilde{\mathbf{K}}_{11}^{\text{visc}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ & \chi^{\text{visc}} & 0 & 0 & 0 & \chi^{\text{visc}}u_1 \\ & & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}}u_2 \\ \text{symm.} & & & \mu^{\text{visc}} & 0 & \mu^{\text{visc}}u_3 \\ & & & & 0 & 0 \\ & & & & & \chi^{\text{visc}}u_1^2 + \mu^{\text{visc}}(u_2^2 + u_3^2) \end{bmatrix} \quad (\text{C.30})$$

$$\widetilde{\mathbf{K}}_{22}^{\text{visc}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}}u_1 \\ & & \chi^{\text{visc}} & 0 & 0 & \chi^{\text{visc}}u_2 \\ \text{symm.} & & & \mu^{\text{visc}} & 0 & \mu^{\text{visc}}u_3 \\ & & & & 0 & 0 \\ & & & & & \chi^{\text{visc}}u_2^2 + \mu^{\text{visc}}(u_1^2 + u_3^2) \end{bmatrix} \quad (\text{C.31})$$

$$\widetilde{\mathbf{K}}_{33}^{\text{visc}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}}u_1 \\ & & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}}u_2 \\ \text{symm.} & & & \chi^{\text{visc}} & 0 & \chi^{\text{visc}}u_3 \\ & & & & 0 & 0 \\ & & & & & \chi^{\text{visc}}u_3^2 + \mu^{\text{visc}}(u_1^2 + u_2^2) \end{bmatrix} \quad (\text{C.32})$$

$$\widetilde{\mathbf{K}}_{12}^{\text{visc}} = \widetilde{\mathbf{K}}_{21}^{\text{visc}T} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_n^T & 0 & \lambda^{\text{visc}} & 0 & 0 & \lambda^{\text{visc}} u_2 \\ \mathbf{0}_n^T & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & \mu^{\text{visc}} u_2 & \lambda^{\text{visc}} u_1 & 0 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_1 u_2 \end{bmatrix} \quad (\text{C.33})$$

$$\widetilde{\mathbf{K}}_{13}^{\text{visc}} = \widetilde{\mathbf{K}}_{31}^{\text{visc}T} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_n^T & 0 & 0 & \lambda^{\text{visc}} & 0 & \lambda^{\text{visc}} u_3 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & \mu^{\text{visc}} & 0 & 0 & 0 & \mu^{\text{visc}} u_1 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & \mu^{\text{visc}} u_3 & 0 & \lambda^{\text{visc}} u_1 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_1 u_3 \end{bmatrix} \quad (\text{C.34})$$

$$\widetilde{\mathbf{K}}_{23}^{\text{visc}} = \widetilde{\mathbf{K}}_{32}^{\text{visc}T} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n & \mathbf{0}_n \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & 0 & 0 & \lambda^{\text{visc}} & 0 & \lambda^{\text{visc}} u_3 \\ \mathbf{0}_n^T & 0 & \mu^{\text{visc}} & 0 & 0 & \mu^{\text{visc}} u_2 \\ \mathbf{0}_n^T & 0 & 0 & 0 & 0 & 0 \\ \mathbf{0}_n^T & 0 & \mu^{\text{visc}} u_3 & \lambda^{\text{visc}} u_2 & 0 & (\lambda^{\text{visc}} + \mu^{\text{visc}}) u_2 u_3 \end{bmatrix} \quad (\text{C.35})$$

The viscous stress diffusivity matrix $\widetilde{\mathbf{K}}^{\text{visc}} = [\widetilde{\mathbf{K}}_{ij}^{\text{visc}}]$ 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 Section 5).

The heat flux vectors are given by:

$$\mathbf{F}_i^{\text{heat}} = \begin{pmatrix} \mathbf{0}_n \\ \mathbf{0}_3 \\ -q_i^{\text{vib}} \\ -(q_i + q_i^{\text{vib}}) \end{pmatrix} \quad (\text{C.36})$$

where

$$q_i = -\kappa T_{,i} \quad (\text{C.37})$$

$$q_i^{\text{vib}} = -\kappa^{\text{vib}} T_{,i}^{\text{vib}} \quad (\text{C.38})$$

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

$$\widetilde{\mathbf{K}}_{ii}^{\text{heat}} = \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_{n \times 3} & \mathbf{0}_n & \mathbf{0}_n \\ & \mathbf{0}_{3 \times 3} & \mathbf{0}_3 & \mathbf{0}_3 \\ & \text{symm.} & \kappa^{\text{vib}} T^{\text{vib}^2} & \kappa^{\text{vib}} T^{\text{vib}^2} \\ & & & \kappa T^2 + \kappa^{\text{vib}} T^{\text{vib}^2} \end{bmatrix}, \quad i = 1, 2, 3 \quad (\text{C.39})$$

$$\widetilde{\mathbf{K}}_{ij}^{\text{heat}} = \mathbf{0}, \quad i \neq j \quad (\text{C.40})$$

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

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

$$\alpha \geq 0 \quad (\text{C.41})$$

$$\mu^{\text{visc}} \geq 0 \quad (\text{C.42})$$

$$\lambda^{\text{visc}} + \frac{2}{3} \mu^{\text{visc}} \geq 0 \quad (\text{C.43})$$

$$\kappa \geq 0 \quad (\text{C.44})$$

$$\kappa^{\text{vib}} \geq 0 \quad (\text{C.45})$$

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, and 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 Chapman & Cowling [4]). Its existence was later to be confirmed by experiments conducted by Chapman and Dootson [10]. 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 retaining 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 [26]. 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 (88), the diffusion velocities are now given by:

$$J_{si} = \rho_s v_{si} = \sum_r \rho \frac{\hat{M}_s \hat{M}_r}{\hat{M}^2} D_{sr} d_{ri} - D_s^T (\ln T)_{,i} \quad (\text{D.1})$$

where the D_s^T ’s are the multicomponent thermal diffusion coefficient; they satisfy

$$\sum_s D_s^T = 0 \quad (\text{D.2})$$

which is required together with (92) to ensure that the mass average of the diffusion

velocities (94) vanishes. In turn, the heat flux of (96) is augmented by a term describing the diffusion thermo-effect:

$$q_i = -\kappa' T_{,i} - RT \sum_s \frac{D_s^T}{y_s} d_{si} \quad (\text{D.3})$$

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 (D.1). 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 Hirschfelder et al. [10].

The Dufour effect part of (D.3) can be written in terms of the primitive variables as

$$RT \sum_s \frac{D_s^T}{y_s} d_{si} = \sum_s \frac{R_s}{\rho_s} T D_s^T \rho_{s,i} + \sum_s R_s D_s^T T_{,i} \quad (\text{D.4})$$

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

$$\widetilde{\mathbf{K}}_{ii}^{\text{therm}} = T \begin{bmatrix} \mathbf{0}_{n \times n} & \mathbf{0}_{n \times 3} & \mathbf{0}_n & \mathbf{D}^T \\ & \mathbf{0}_{3 \times 3} & \mathbf{0}_3 & \mathbf{0}_3 \\ \text{symm.} & & 0 & \mathbf{e}^{\text{vib}} \cdot \mathbf{D}^T \\ & & & 2\mathbf{h} \cdot \mathbf{D}^T \end{bmatrix}, \quad i = 1, 2, 3 \quad (\text{D.5})$$

$$\widetilde{\mathbf{K}}_{ij}^{\text{therm}} = \mathbf{0}, \quad i \neq j \quad (\text{D.6})$$

Letting

$$\widetilde{\mathbf{K}}^{\text{mass-heat}} = \widetilde{\mathbf{K}}^{\text{mass}} + \widetilde{\mathbf{K}}^{\text{heat}} + \widetilde{\mathbf{K}}^{\text{therm}} \quad (\text{D.7})$$

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

$$\widetilde{\mathbf{K}}_{ij}^{\text{mass-heat}} \mathbf{V}_{,j} = \mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{heat}} \quad (\text{D.8})$$

From (D.8), one can see that mass diffusion and heat conduction are now linked together through the thermal diffusion matrix $\widetilde{\mathbf{K}}^{\text{therm}}$. The coupling appears even more strongly

from the standpoint of entropy production. As we will see shortly, the positive semidefiniteness of $\widetilde{\mathbf{K}}^{\text{mass}}$ and $\widetilde{\mathbf{K}}^{\text{heat}}$ are not enough to guarantee that of $\widetilde{\mathbf{K}}^{\text{mass-heat}}$, the contribution from $\widetilde{\mathbf{K}}^{\text{therm}}$ being nonpositive.

$$\begin{aligned}
\nabla \mathbf{V} \cdot \widetilde{\mathbf{K}}^{\text{mass-heat}} \nabla \mathbf{V} &= \mathbf{V}_{,i} \cdot \widetilde{\mathbf{K}}_{ij}^{\text{mass-heat}} \mathbf{V}_{,j} = \mathbf{V}_{,i} \cdot (\mathbf{F}_i^{\text{mass}} + \mathbf{F}_i^{\text{heat}}) \\
&= \sum_i \left[\sum_{s,r} R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \alpha_{sr}) R_r \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) \right. \\
&\quad + \sum_s R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T D_s^T) \frac{T_{,i}}{T^2} \\
&\quad + \sum_r \frac{T_{,i}}{T^2} (T D_r^T) \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) \\
&\quad \left. + \frac{T_{,i}}{T^2} (T^2 \kappa') \frac{T_{,i}}{T^2} \right] \tag{D.9}
\end{aligned}$$

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

$$\bar{\alpha} = \begin{bmatrix} \boldsymbol{\alpha} & \mathbf{D}^T \\ \text{symm.} & T \kappa' \end{bmatrix} \tag{D.10}$$

(D.10) can be used to rewrite (D.9), yielding

$$\begin{aligned}
\nabla \mathbf{V} \cdot \widetilde{\mathbf{K}}^{\text{mass-heat}} \nabla \mathbf{V} &= \sum_i \left[\sum_{s,r} R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \bar{\alpha}_{sr}) R_r \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) \right. \\
&\quad + \sum_s R_s \left(\frac{\rho_{s,i}}{\rho_s} + \frac{T_{,i}}{T} \right) (T \bar{\alpha}_{s,n+1}) \frac{T_{,i}}{T^2} \\
&\quad + \sum_r \frac{T_{,i}}{T^2} (T \bar{\alpha}_{n+1,r}) \left(\frac{\rho_{r,i}}{\rho_r} + \frac{T_{,i}}{T} \right) \\
&\quad \left. + \frac{T_{,i}}{T^2} (T \bar{\alpha}_{n+1,n+1}) \frac{T_{,i}}{T^2} \right] \\
&= \sum_i \sum_{s,r=1}^{n+1} \left[Z_{si} (T \bar{\alpha}_{sr}) Z_{ri} \right] \geq 0 \tag{D.11}
\end{aligned}$$

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

$$\mathbf{Z}_i = \left\{ \begin{array}{c} R_1 \left(\frac{\rho_{1,i}}{\rho_1} + \frac{T_{,i}}{T} \right) \\ \vdots \\ R_n \left(\frac{\rho_{n,i}}{\rho_n} + \frac{T_{,i}}{T} \right) \\ \frac{T_{,i}}{T^2} \end{array} \right\} \quad (\text{D.12})$$

The inequality in (D.11) is satisfied if and only if $\bar{\alpha}$ is positive semidefinite, which is implied by the second law of thermodynamics. If the diffusion velocities are taken according to (D.1), and the heat flux to (D.3), the Clausius-Duhem inequality remains formally the same as (155):

$$\begin{aligned} (\rho s)_{,t} + (\rho s u_i)_{,i} + \left(\sum_s \rho_s s_s v_{si} \right)_{,i} + \left(\frac{q_i}{T} + \frac{q_i^{\text{vib}}}{T^{\text{vib}}} \right)_{,i} \\ + \frac{1}{T} \sum_s g_s \Omega_s - \left(\frac{1}{T^{\text{vib}}} - \frac{1}{T} \right) Q^{T-T^{\text{vib}}} \geq 0 \end{aligned} \quad (\text{D.13})$$