

# FAST, POSITIVE AND CONSERVATIVE SCHEME FOR CHEMICALLY REACTIVE HYPERSONIC FLOW

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## ABSTRACT

A finite difference method for solving the quasi one-dimensional non-equilibrium hypersonic flow equations in a diverging nozzle is presented and discussed. In chemically reacting flows the system of equations to be solved is very stiff. Some reactions may be several orders of magnitude faster than others and generally, they are much faster than the convective process except for very high Ma numbers. For this reason the development of a numerical scheme whose stability is independent of the chemical reaction rates is of importance. The main advantage of this scheme is the conservation of each chemical component, the positivity of densities and vibrational energies, as well as its relative simplicity, which results in a fast computer code.

KEY WORDS Hypersonic flow Finite difference method

## THE GOVERNING EQUATIONS FOR QUASI 1-D INVISCID HYPERSONIC FLOW

In the present study we will discuss a numerical method for quasi one-dimensional hypersonic flows. For this purpose consider the following equations for hypersonic flow in a diverging nozzle:

$$\frac{\partial(SU)}{\partial t} + \frac{\partial(SF)}{\partial x} = SW + \frac{dS}{dx} P \tag{1}$$

where

$$U = \begin{pmatrix} \rho_1 \\ \rho_2 \\ \rho_3 \\ \rho_4 \\ \rho_5 \\ E_{v1} \\ E_{v2} \\ E_{v3} \\ m \\ E \end{pmatrix}, \quad F = \begin{pmatrix} \rho_1 u \\ \rho_2 u \\ \rho_3 u \\ \rho_4 u \\ \rho_5 u \\ E_{v1} u \\ E_{v2} u \\ E_{v3} u \\ \rho u^2 + p \\ (E + p)u \end{pmatrix}, \quad P = \begin{pmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ p \\ 0 \end{pmatrix}, \quad W = \begin{pmatrix} w_1 \\ w_2 \\ w_3 \\ w_4 \\ w_5 \\ \frac{E_{eq1} - E_{v1}}{\tau_1} + \frac{w_1^+}{\rho_1} E_{eq1} + \frac{w_1^-}{\rho_1} E_{v1} \\ \frac{E_{eq2} - E_{v2}}{\tau_2} + \frac{w_2^+}{\rho_2} E_{eq2} + \frac{w_2^-}{\rho_2} E_{v2} \\ \frac{E_{eq3} - E_{v3}}{\tau_3} + \frac{w_3^+}{\rho_3} E_{eq3} + \frac{w_3^-}{\rho_3} E_{v3} \\ 0 \\ 0 \end{pmatrix} \tag{2}$$

with  $\rho_1, \rho_2, \rho_3, \rho_4, \rho_5$  being the densities of the five species  $N_2, O_2, NO, N, O$  respectively,  $\rho = \rho_1 + \rho_2 + \rho_3 + \rho_4 + \rho_5$  is the total mass density,  $u$  is the velocity,  $m = \rho u$  is the momentum,  $p$  is the pressure,  $E_{v1}, E_{v2}, E_{v3}$  are the vibrational energies of  $N_2, O_2$  and  $NO$ , respectively, and  $E$  is the total energy.  $w_1, w_2, w_3, w_4, w_5$ , are the source terms arising from the chemical reactions.  $S(x)$  is the cross-sectional area of the nozzle along the  $x$ -axis. These equations are closed with the assumption of calorically perfect gas for each specie which yields the following equation of state:

$$p = \sum_{k=1}^5 \frac{\rho_k}{M_k} \mathcal{R} T \quad (3)$$

where  $\mathcal{R}$  is the universal gas constant,  $M_1, M_2, M_3, M_4, M_5$  are molecular masses, and the temperature  $T$  is determined from the following energy relation<sup>8</sup>:

$$E = \sum_{k=1}^5 \rho_k C_{vk} T + \sum_{k=1}^3 (\rho_k h_k^0 + E_{vk}) + \frac{mu}{2} \quad (4)$$

where  $C_{vk}$  is the specie specific heat and  $h_1^0, h_2^0$  and  $h_3^0$  are the heats of formations for the diatomic species  $N_2, O_2$  and  $NO$ , respectively, and are summarized in *Table 1*.

Equilibrium and vibrational energies are correlated by translational and vibrational temperatures as follows:

$$E_{eqk} = \rho_k \frac{\Theta_k}{\exp[(\Theta/T) - 1]} \frac{\mathcal{R}}{M_k}, \quad E_{vk} = \rho_k \frac{\Theta_k}{\exp[(\Theta/T_{vk}) - 1]} \frac{\mathcal{R}}{M_k} \quad (5)$$

In (5)  $T$  is the translational temperature and  $T_{vk}$  are the vibrational temperatures for the species  $k$ . The coefficients  $\Theta_k$  are obtained from spectroscopic data<sup>17</sup> and are summarized in *Table 1*. The vibrational-translational rate equation is derived in Anderson<sup>1</sup> and needs the Landau-Teller relaxation time:

$$\tau_i = \frac{101325 \sum_{j=1}^5 \frac{\rho_j}{M_j} \exp[A_i(T^{-1/3} - 0.015\mu_{ij}^{1/4}) - 18.42]}{p \sum_{j=1}^5 \frac{\rho_j}{M_j}}, \quad \mu_{ij} = \frac{M_i M_j}{M_i + M_j} \quad (6)$$

that are functions of pressure and temperature; these relations are presented as semi-empirical equations which are valid over a temperature range<sup>8,10</sup> from 300 to 9000 K.

The chemistry is modelled by a Dunn and Kang<sup>13</sup> air model, except that the ions and free electron, and the associated reaction steps are not included. This model comprises the five species  $N_2, O_2, NO, N, O$ , seventeen reactions and four temperatures. The chemical reactions to be

Table 1

	$\Theta$ (K)	$A$	$h^0$ (kJ/kg)
$N_2$	2270	220	-33786
$O_2$	3390	129	-15577
$NO$	2740	168	-21056

considered are:



where M represents any of the five species. The reaction rate for each species is determined from its forward and backward reaction rate coefficients. These coefficients are given by the following equations<sup>8,9,13</sup>:

$$\begin{aligned}
 R_1 &= \sum_{m=1}^5 \left( K_{f_{1,m}} \frac{\rho_1}{M_1} \frac{\rho_m}{M_m} - K_{b_{1,m}} \frac{\rho_4}{M_4} \frac{\rho_4}{M_4} \frac{\rho_m}{M_m} \right) = \Gamma_1 r_1 - \Omega_1 r_4^2 \\
 R_2 &= \sum_{m=1}^5 \left( K_{f_{2,m}} \frac{\rho_2}{M_2} \frac{\rho_m}{M_m} - K_{b_{2,m}} \frac{\rho_5}{M_5} \frac{\rho_5}{M_5} \frac{\rho_m}{M_m} \right) = \Gamma_2 r_2 - \Omega_2 r_5^2 \\
 R_3 &= \sum_{m=1}^5 \left( K_{f_{3,m}} \frac{\rho_3}{M_3} \frac{\rho_m}{M_m} - K_{b_{3,m}} \frac{\rho_4}{M_4} \frac{\rho_5}{M_5} \frac{\rho_m}{M_m} \right) = \Gamma_3 r_3 - \Omega_3 r_4 r_5 \\
 R_4 &= K_{f_4} \frac{\rho_1}{M_1} \frac{\rho_5}{M_5} - K_{b_4} \frac{\rho_3}{M_3} \frac{\rho_4}{M_4} = K_{f_4} r_1 r_5 - K_{b_4} r_3 r_4 \\
 R_5 &= K_{f_5} \frac{\rho_3}{M_3} \frac{\rho_5}{M_5} - K_{b_5} \frac{\rho_2}{M_2} \frac{\rho_4}{M_4} = K_{f_5} r_3 r_5 - K_{b_5} r_2 r_4
 \end{aligned}
 \tag{8}$$

where we have used the mass relations  $M_1 = 2a$ ,  $M_2 = 2b$ ,  $M_3 = a + b$ ,  $M_4 = a$ ,  $M_5 = b$  and the shortcut:

$$\begin{aligned}
 \alpha &= \frac{a}{a+b'}, & \beta &= \frac{b}{a+b}, & r_k &= \frac{\rho_k}{M_k}, & k &= 1, 2, 3, 4, 5 \\
 \Gamma_k &= \sum_{m=1}^5 K_{f_{k,m}} r_m, & \Omega_k &= \sum_{m=1}^5 K_{b_{k,m}} r_m, & k &= 1, 2, 3
 \end{aligned}
 \tag{9}$$

The parameters  $K_f$ ,  $K_b$  are modelled by the Arrhenius formula<sup>1,8,9</sup>. The source terms  $w_1 \dots w_5$  are obtained by combining all the reaction rates that correspond to the production or the consumption of species  $k$ :

$$\begin{aligned}
 w_1 &= M_1(-R_1 - R_4) \\
 w_2 &= M_2(-R_1 + R_5) \\
 w_3 &= M_3(-R_3 + R_4 - R_5) \\
 w_4 &= M_4(2R_1 + R_3 + R_4 + R_5) \\
 w_5 &= M_5(2R_2 + R_3 - R_4 - R_5)
 \end{aligned}
 \tag{10}$$

The total density of nitrogen is:

$$\rho_N = \rho_1 + \alpha \rho_3 + \rho_4
 \tag{11}$$

and similarly the total density of oxygen is:

$$\rho_O = \rho_2 + \beta \rho_3 + \rho_5
 \tag{12}$$

Then we have:

$$\begin{aligned}(\rho_N)_t + (u\rho_N)_x &= w_N \\ (\rho_O)_t + (u\rho_O)_x &= w_O\end{aligned}\quad (13)$$

where

$$\begin{aligned}w_N &= w_1 + \alpha w_3 + w_4 \\ w_O &= w_2 + \beta w_3 + w_5\end{aligned}\quad (14)$$

are the reaction rates of total nitrogen and oxygen. These conservations imply that  $w_N = w_O = 0$ . Consequently:

$$\sum_{i=1}^5 w_i = w_N + w_O = 0 \quad (15)$$

Thus the total mass is conserved as well. The production and consumption part of the source terms will be denoted with  $w^+$  and  $w^-$  respectively.

In order to simplify the construction of the upwind scheme a different form for the total energy equation is derived as follows. By setting:

$$\mathcal{E} = E - \sum_{k=1}^3 E_{vk} - \sum_{k=1}^3 \rho_k h_k^0 \quad (16)$$

the energy equation in (1) can also be written as:

$$(S\mathcal{E})_t + \left[ S \sum_{k=1}^3 (E_{vk} + \rho_k h_k^0) \right]_t + [Su(\mathcal{E} + p)]_x + \left[ Su \sum_{k=1}^3 (E_{vk} + \rho_k h_k^0) \right]_x = 0 \quad (17)$$

which, using the densities and vibrational energies relations becomes:

$$(S\mathcal{E})_t + [Su(\mathcal{E} + p)]_x = W_{\mathcal{E}} \quad (18)$$

where

$$W_{\mathcal{E}} = - \sum_{k=1}^3 \left( h_k^0 w_k + \frac{E_{eqk} - E_{vk}}{\tau_k} + \frac{w_k^+}{\rho_k} E_{eqk} + \frac{w_k^-}{\rho_k} E_{vk} \right) \quad (19)$$

The state equation now takes the form:

$$p = \beta \left( \mathcal{E} - \frac{\rho u^2}{2} \right) \quad \text{where} \quad \beta = \mathcal{R} \frac{\sum_{k=1}^5 \frac{\rho_k}{M_k}}{\sum_{k=1}^5 \rho_k C_{vk}} \quad (20)$$

From (20), one has:

$$\frac{\partial \beta}{\partial \rho_k} = \gamma_k \beta \quad \text{with} \quad \gamma_k = \left[ \frac{1}{M_k} - \frac{C_{vk}}{\sum_{j=1}^5 \frac{\rho_j}{M_j} \sum_{j=1}^5 \rho_j C_{vj}} \right] \quad (21)$$

and

$$\frac{\partial p}{\partial \rho_k} = \gamma_k p + \beta \frac{u^2}{2} \quad \frac{\partial p}{\partial m} = -\beta u \quad \frac{\partial p}{\partial E_{vk}} = 0 \quad \frac{\partial p}{\partial \mathcal{E}} = \beta \quad (22)$$

NUMERICAL SOLUTION TECHNIQUE

Consider a discretization of the one-dimensional physical domain into a set of elementary line segments of length  $\Delta x$ . Then consider the integral form of (1) over a line segment  $\Delta x$  yielding:

$$\begin{aligned} \frac{\partial}{\partial t} \int_{x_{i-1/2}}^{x_{i+1/2}} S(x)U(x, t) dx + S(x_{i+1/2})F(U(x_{i+1/2}, t)) - S(x_{i-1/2})F(U(x_{i-1/2}, t)) \\ = \int_{x_{i-1/2}}^{x_{i+1/2}} S(x)W(x, t) dx + \int_{x_{i-1/2}}^{x_{i+1/2}} \frac{dS}{dx}(x)P(U(x, t)) dx \end{aligned} \quad (23)$$

Now we use the mean value approximations:

$$\begin{aligned} S(x_i)U(x_i, t) &\approx \frac{1}{\Delta x} \int_{x_{i-1/2}}^{x_{i+1/2}} S(x)U(x, t) dx \\ S(x_i)W(x_i, t) &\approx \frac{1}{\Delta x} \int_{x_{i-1/2}}^{x_{i+1/2}} S(x)W(x, t) dx \\ \frac{dS}{dx}(x_i)P(x_i, t) &\approx \frac{1}{\Delta x} \int_{x_{i-1/2}}^{x_{i+1/2}} \frac{dS}{dx}(x)P(U(x, t)) dx \end{aligned} \quad (24)$$

so that a semi-discrete approximation of (23) is:

$$\frac{dU(x_i, t)}{dt} + \frac{S(x_{i+1/2})F(U(x_{i+1/2}, t)) - S(x_{i-1/2})F(U(x_{i-1/2}, t))}{S(x_i)\Delta x} = W(x_i, t) + \frac{dS}{dx}(x_i) \frac{P(U(x_i, t))}{S(x_i)} \quad (25)$$

In order to specify  $S(x_{i+1/2})F(U_{i+1/2}, t)$  we decompose the flux  $SF$  in two parts, which accounts for the flux from left to right and for the flux from right to left. From the homogeneity of  $F$  one has:

$$SF(U) = SA(U)U \quad (26)$$

where  $A(U)$  is the Jacobian of  $F(U)$  (see Table 2). Since  $A$  possesses a full set of linearly independent eigenvectors one can write:

$$A(U) = T^{-1}(U)\Lambda(U)T(U) \quad (27)$$

where  $\Lambda(U)$  is the eigenvalue diagonal matrix. Next we define:

$$A^\pm(U) = T^{-1}(U)\Lambda^\pm(U)T(U) \quad (28)$$

where  $\Lambda^\pm(U) = \text{diag}(\lambda_1^\pm(U), \lambda_2^\pm(U), \dots, \lambda_{l_0}^\pm(U))$  with:

$$\lambda_j^\pm(U) = \frac{\lambda_j(U) \pm |\lambda_j(U)|}{2} \quad (29)$$

so that  $A(U) = A^+(U) + A^-(U)$ . Assume now that the flux travelling across  $i + \frac{1}{2}$  in the positive  $x$ -direction originates at point  $i$  while the flux travelling in the negative  $x$ -direction originates at point  $i + 1$ . Specifically, by setting

$$F^\pm(U) = A^\pm(U)U \quad (30)$$

we define

$$S(x_{i+1/2})F(U(x_{i+1/2}, t)) \approx S_i F^+(U_i) + S_{i+1} F^-(U_{i+1}) \quad (31)$$

For an easy construction of  $A^\pm(U)$  we consider that the Jacobian  $A(U)$  has the eigenvalues

Table 2 Jacobian matrix  $A(U)$

$u \left(1 - \frac{\rho_1}{\rho}\right)$	...	$-\frac{u\rho_1}{\rho}$		$\frac{\rho_1}{\rho}$	
$\vdots$		$\vdots$	0	$\vdots$	0
$-\frac{u\rho_5}{\rho}$	...	$u \left(1 - \frac{\rho_5}{\rho}\right)$		$\frac{\rho_5}{\rho}$	
$-\frac{uE_{v1}}{\rho}$	...	$-\frac{uE_{v1}}{\rho}$	u	$\frac{E_{v1}}{\rho}$	0
$-\frac{uE_{v2}}{\rho}$	...	$-\frac{uE_{v2}}{\rho}$	u	$\frac{E_{v2}}{\rho}$	0
$-\frac{uE_{v3}}{\rho}$	...	$-\frac{uE_{v3}}{\rho}$	u	$\frac{E_{v3}}{\rho}$	0
$\frac{\partial p}{\partial \rho_1} - u^2$	...	$\frac{\partial p}{\partial \rho_5} - u^2$	0 0 0	$(2 - \beta)u$	$\beta$
$u \left(\frac{\partial p}{\partial \rho_1} - \frac{\mathcal{E} + p}{\rho}\right)$	...	$u \left(\frac{\partial p}{\partial \rho_5} - \frac{\mathcal{E} + p}{\rho}\right)$	0 0 0	$\frac{\mathcal{E} + p}{\rho} - \beta u^2$	$(1 + \beta)u$

given by:

$$\Lambda(U) = \text{diag}(u, u, u, u, u, u, u, u, u + c, u - c) \tag{32}$$

where  $c = \sqrt{(1 + \beta)p/\rho}$  is the frozen speed of sound. Using the matrix  $T$  of the corresponding eigenvectors we are able to rapidly construct the matrices  $A_u(U)$ ,  $A_{u+c}(U)$  and  $A_{u-c}(U)$  as:

$$\begin{aligned} A_u(U) &= T^{-1}(U)\Lambda_u T(U) \\ A_{u+c}(U) &= T^{-1}(U)\Lambda_{u+c} T(U) \\ A_{u-c}(U) &= T^{-1}(U)\Lambda_{u-c} T(U) \end{aligned} \tag{33}$$

with

$$\begin{aligned} \Lambda_u &= \text{diag}(1, 1, 1, 1, 1, 1, 1, 1, 0, 0) \\ \Lambda_{u+c} &= \text{diag}(0, 0, 0, 0, 0, 0, 0, 0, 1, 0) \\ \Lambda_{u-c} &= \text{diag}(0, 0, 0, 0, 0, 0, 0, 0, 0, 1) \end{aligned} \tag{34}$$

so that:

$$A^\pm(U) = u^\pm A_u(U) + (u+c)^\pm A_{u+c}(U) + (u-c)^\pm A_{u-c}(U) \tag{35}$$

The matrices  $A_u(U)$ ,  $A_{u+c}(U)$  and  $A_{u-c}(U)$  are shown in Tables 3, 4 and 5. We now define:

$$F_u(U) = A_u(U)U, \quad F_{u+c}(U) = A_{u+c}(U)U, \quad F_{u-c}(U) = A_{u-c}(U)U \tag{36}$$

so that

$$F^\pm(U) = u^\pm F_u(U) + (u+c)^\pm F_{u+c}(U) + (u-c)^\pm F_{u-c}(U) \tag{37}$$

If the fluxes are evaluated at time level  $n$  an explicit upwind scheme results. If the fluxes are evaluated at time level  $n + 1$  the resulting scheme is fully non-linear at each time step. Because

Table 3 Matrix  $A_u(U)$

$1 - \frac{\rho_1}{\rho c^2} \frac{\partial p}{\partial \rho_1}$	...	$-\frac{\rho_1}{\rho c^2} \frac{\partial p}{\partial \rho_5}$		$\frac{\rho_1}{\rho c^2} \beta u$	$-\frac{\rho_1}{\rho c^2} \beta$
$\vdots$	$\ddots$	$\vdots$	0	$\vdots$	$\vdots$
$-\frac{\rho_5}{\rho c^2} \frac{\partial p}{\partial \rho_1}$	...	$1 - \frac{\rho_5}{\rho c^2} \frac{\partial p}{\partial \rho_5}$		$\frac{\rho_5}{\rho c^2} \beta u$	$-\frac{\rho_5}{\rho c^2} \beta$
$-\frac{E_{v1}}{\rho c^2} \frac{\partial p}{\partial \rho_1}$	...	$-\frac{E_{v1}}{\rho c^2} \frac{\partial p}{\partial \rho_5}$	1	$\frac{\beta u E_{v1}}{\rho c^2}$	$-\frac{\beta E_{v1}}{\rho c^2}$
$-\frac{E_{v2}}{\rho c^2} \frac{\partial p}{\partial \rho_1}$	...	$-\frac{E_{v2}}{\rho c^2} \frac{\partial p}{\partial \rho_5}$	1	$\frac{\beta u E_{v2}}{\rho c^2}$	$-\frac{\beta E_{v2}}{\rho c^2}$
$-\frac{E_{v3}}{\rho c^2} \frac{\partial p}{\partial \rho_1}$	...	$-\frac{E_{v3}}{\rho c^2} \frac{\partial p}{\partial \rho_5}$	1	$\frac{\beta u E_{v3}}{\rho c^2}$	$-\frac{\beta E_{v3}}{\rho c^2}$
$u \left(1 - \frac{1}{c^2} \frac{\partial p}{\partial \rho_1}\right)$	...	$u \left(1 - \frac{1}{c^2} \frac{\partial p}{\partial \rho_5}\right)$	0 0 0	$\beta \frac{u^2}{c^2}$	$-\beta \frac{u}{c^2}$
$u^2 \left(1 - \frac{1}{2c^2} \frac{\partial p}{\partial \rho_1}\right)$	...	$u^2 \left(1 - \frac{1}{2c^2} \frac{\partial p}{\partial \rho_5}\right)$	0 0 0	$\frac{\beta}{2} \frac{u^3}{c^2}$	$-\frac{\beta}{2} \frac{u^2}{c^2}$
$-\frac{1}{\beta} \frac{\partial p}{\partial \rho_1}$	...	$-\frac{1}{\beta} \frac{\partial p}{\partial \rho_5}$			

Table 4 Matrix  $A_{u+c}(U)$

$\frac{\rho_1}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_1} - u\right)$	...	$\frac{\rho_1}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_5} - u\right)$		$\frac{\rho_1}{2\rho c} \left(1 - \frac{\beta u}{c}\right)$	$\frac{\rho_1 \beta}{2\rho c^2}$
$\vdots$		$\vdots$	0	$\vdots$	$\vdots$
$\frac{\rho_5}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_1} - u\right)$	...	$\frac{\rho_5}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_5} - u\right)$		$\frac{\rho_5}{2\rho c} \left(1 - \frac{\beta u}{c}\right)$	$\frac{\rho_5 \beta}{2\rho c^2}$
$\frac{E_{v1}}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_1} - u\right)$	...	$\frac{E_{v1}}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_5} - u\right)$		$\frac{E_{v1}}{\rho c} \left(\frac{1}{2} - \frac{\beta u}{2c}\right)$	$\frac{\beta E_{v1}}{2\rho c^2}$
$\frac{E_{v2}}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_1} - u\right)$	...	$\frac{E_{v2}}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_5} - u\right)$	0	$\frac{E_{v2}}{\rho c} \left(\frac{1}{2} - \frac{\beta u}{2c}\right)$	$\frac{\beta E_{v2}}{2\rho c^2}$
$\frac{E_{v3}}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_1} - u\right)$	...	$\frac{E_{v3}}{2\rho c} \left(\frac{1}{c} \frac{\partial p}{\partial \rho_5} - u\right)$		$\frac{E_{v3}}{\rho c} \left(\frac{1}{2} - \frac{\beta u}{2c}\right)$	$\frac{\beta E_{v3}}{2\rho c^2}$
$\left(\frac{1+u}{c}\right)$	...	$\left(\frac{1+u}{c}\right)$	0 0 0	$\left(\frac{1+u}{c}\right)$	$\left(1 + \frac{u}{c}\right) \frac{\beta}{2c}$
$\left(-\frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_1}\right)$	...	$\left(-\frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_5}\right)$		$\left(\frac{1}{2} - \frac{\beta u}{2c}\right)$	
$\left(\frac{u^2}{2c} + \frac{c}{\beta} + u\right)$	...	$\left(\frac{u^2}{2c} + \frac{c}{\beta} + u\right)$	0 0 0	$\left(\frac{1}{2} - \frac{\beta u}{2c}\right)$	$\frac{\beta}{2c} \left(\frac{u^2}{2c} + \frac{c}{\beta} + u\right)$
$\left(-\frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_1}\right)$	...	$\left(-\frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_5}\right)$		$\left(\frac{u^2}{2c} + \frac{c}{\beta} + u\right)$	

Table 5 Matrix  $A_{v-i}(U)$

$\frac{\rho_1}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_1} \right) \dots \frac{\rho_1}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_5} \right)$		$-\frac{\rho_1}{2\rho c} \left( 1 + \frac{\beta u}{c} \right)$	$\frac{\rho_1 \beta}{2\rho c^2}$
$\vdots$	$0$	$\vdots$	$\vdots$
$\frac{\rho_5}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_1} \right) \dots \frac{\rho_5}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_5} \right)$		$-\frac{\rho_5}{2\rho c} \left( 1 + \frac{\beta u}{c} \right)$	$\frac{\rho_5 \beta}{2\rho c^2}$
$\frac{E_{v1}}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_1} \right) \dots \frac{E_{v1}}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_5} \right)$		$\frac{E_{v1}}{\rho c} \left( -\frac{1}{2} - \frac{\beta u}{2c} \right)$	$\frac{\beta E_{v1}}{2\rho c^2}$
$\frac{E_{v2}}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_1} \right) \dots \frac{E_{v2}}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_5} \right)$	$0$	$\frac{E_{v2}}{\rho c} \left( -\frac{1}{2} - \frac{\beta u}{2c} \right)$	$\frac{\beta E_{v1}}{2\rho c^2}$
$\frac{E_{v3}}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_1} \right) \dots \frac{E_{v3}}{2\rho c} \left( u + \frac{1}{c} \frac{\partial p}{\partial \rho_5} \right)$		$\frac{E_{v3}}{\rho c} \left( -\frac{1}{2} - \frac{\beta u}{2c} \right)$	$\frac{\beta E_{v3}}{2\rho c^2}$
$\begin{pmatrix} -1 + \frac{u}{c} \\ \left( \frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_1} \right) \end{pmatrix} \dots \begin{pmatrix} 1 + \frac{u}{c} \\ \left( -\frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_5} \right) \end{pmatrix}$	$0 \quad 0 \quad 0$	$\begin{pmatrix} \frac{u}{c} - 1 \\ \left( \frac{1}{2} + \frac{\beta u}{2c} \right) \end{pmatrix}$	$\left( -1 + \frac{u}{c} \right) \frac{\beta}{2c}$
$\begin{pmatrix} \frac{u^2}{2c} + \frac{c}{\beta} - u \\ \left( \frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_1} \right) \end{pmatrix} \dots \begin{pmatrix} \frac{u^2}{2c} + \frac{c}{\beta} - u \\ \left( \frac{u}{2} + \frac{1}{2c} \frac{\partial p}{\partial \rho_5} \right) \end{pmatrix}$	$0 \quad 0 \quad 0$	$-\begin{pmatrix} 1 + \frac{\beta u}{2c} \\ \left( \frac{u^2}{2c} + \frac{c}{\beta} - u \right) \end{pmatrix}$	$\frac{\beta}{2c} \left( \frac{u^2}{2c} + \frac{c}{\beta} - u \right)$

of the stiffness of the problem an explicit scheme is not convenient. However, the large non-linear system of equations arising from the implicit scheme cannot be easily solved. As a first approach fluxes are linearized as:

$$F(U^{n+1}) \approx F(U^n) + A(U^n)(U^{n+1} - U^n) = A(U^n)U^{n+1} \tag{38}$$

We can choose a semi-implicit discretization of (25) as:

$$S_i \frac{U_i^{n+1} - U_i^n}{\Delta t} + \frac{S_{i+1} A^-(U_{i+1}^n) U_{i+1}^{n+1} + S_i [A^+(U_i^n) - A^-(U_i^n)] U_i^{n+1} - S_{i-1} A^+(U_{i-1}^n) U_{i-1}^{n+1}}{\Delta x} = S_i W(U_i^{n+1}, U_i^n) + P(U_i^{n+1}, U_i^n) \tag{39}$$

where the source term  $W(U_i^{n+1}, U_i^n)$  is an approximation of the term  $W(U(x_i, t))$  and the term  $P(U_i^{n+1}, U_i^n)$  approximates:

$$P(U(x_i, t)) \frac{dS}{dx}(x_i) \tag{40}$$

Equation (39) constitutes a large block tridiagonal system whose blocks are full  $10 \times 10$  matrices. To simplify the computational algorithm even further, we reformulate flux (31) as:

$$S_i G^+(U_i) U_i + S_{i+1} G^-(U_{i+1}) U_{i+1} \tag{41}$$

with  $G^+$  and  $G^-$  being almost diagonal matrices satisfying:

$$G^+(U_i) U_i = A^+(U_i) U_i \quad \text{and} \quad G^-(U_i) U_i = A^-(U_i) U_i \tag{42}$$



By this approach the finite difference equation (39) is replaced by

$$S_i \frac{U_i^{n+1} - U_i^n}{\Delta t} + \frac{S_{i+1} G^-(U_{i+1}^n) U_{i+1}^{n+1} + S_i [G^+(U_i^n) - G^-(U_i^n)] U_i^{n+1} - S_{i-1} G^+(U_{i-1}^n) U_{i-1}^{n+1}}{\Delta x} = S_i W(U_i^{n+1}, U_i^n) + P(U_i^{n+1}, U_i^n) \tag{43}$$

Now we focus attention to the construction of the matrices  $G^+$  and  $G^-$ .

EVALUATION OF  $G^\pm$

We can construct  $G^\pm$  by defining the matrices  $G_u$ ,  $G_{u+c}$  and  $G_{u-c}$  satisfying the relations:

$$G_u(U)U = F_u(U), \quad G_{u+c}(U)U = F_{u+c}(U), \quad G_{u-c}(U)U = F_{u-c}(U) \tag{44}$$

so that  $G^\pm$  can be taken to be:

$$G^\pm(U) = u^\pm(U) + (u+c)^\pm G_{u+c}(U) + (u-c)^\pm G_{u-c}(U) \tag{45}$$

After some manipulations one obtains:

$$F_u(U) = \begin{pmatrix} \frac{\beta \rho_1}{1+\beta} \\ \frac{\beta \rho_2}{1+\beta} \\ \frac{\beta \rho_3}{1+\beta} \\ \frac{\beta \rho_4}{1+\beta} \\ \frac{\beta \rho_5}{1+\beta} \\ \frac{\beta E_{v1}}{1+\beta} \\ \frac{\beta E_{v2}}{1+\beta} \\ \frac{\beta E_{v3}}{1+\beta} \\ m \frac{\beta}{1+\beta} \\ m \frac{\beta u}{2(1+\beta)} \end{pmatrix}, \quad F_{u+c}(U) = \begin{pmatrix} \frac{\rho_1}{2(1+\beta)} \\ \frac{\rho_2}{2(1+\beta)} \\ \frac{\rho_3}{2(1+\beta)} \\ \frac{\rho_4}{2(1+\beta)} \\ \frac{\rho_5}{2(1+\beta)} \\ \frac{E_{v1}}{2(1+\beta)} \\ \frac{E_{v2}}{2(1+\beta)} \\ \frac{E_{v3}}{2(1+\beta)} \\ \frac{m+\rho c}{2(1+\beta)} \\ c - \frac{\beta}{2} u \\ m \frac{c - \frac{\beta}{2} u}{2(1+\beta)} + \frac{\mathcal{E}}{2} \end{pmatrix}, \quad F_{u-c}(U) = \begin{pmatrix} \frac{\rho_1}{2(1+\beta)} \\ \frac{\rho_2}{2(1+\beta)} \\ \frac{\rho_3}{2(1+\beta)} \\ \frac{\rho_4}{2(1+\beta)} \\ \frac{\rho_5}{2(1+\beta)} \\ \frac{E_{v1}}{2(1+\beta)} \\ \frac{E_{v2}}{2(1+\beta)} \\ \frac{E_{v3}}{2(1+\beta)} \\ \frac{m-\rho c}{2(1+\beta)} \\ -c - \frac{\beta}{2} u \\ m \frac{-c - \frac{\beta}{2} u}{2(1+\beta)} + \frac{\mathcal{E}}{2} \end{pmatrix} \tag{46}$$

Thus, the matrices  $G_u$ ,  $G_{u+c}$  and  $G_{u-c}$  can be taken to be:

matrix $G_u$			
$\frac{\beta}{1+\beta}$	$0$		
$\ddots$		$0$	$0$
$0$	$\frac{\beta}{1+\beta}$		
		$\frac{\beta}{1+\beta}$	$0$
	$0$	$\frac{\beta}{1+\beta}$	$0$
			$\frac{\beta}{1+\beta}$
$0$		$0$	$0$
$0$		$0$	$\frac{u\beta}{2(1+\beta)}$

matrix $G_{u+c}$			
$\frac{1}{2(1+\beta)}$	$0$		
$\ddots$		$0$	$0$
$0$	$\frac{1}{2(1+\beta)}$		
		$\frac{1}{2(1+\beta)}$	$0$
	$0$	$\frac{1}{2(1+\beta)}$	$0$
			$\frac{1}{2(1+\beta)}$
$0$		$0$	$\frac{1}{2(1+\beta)} - \frac{\beta u}{4c}$
$0$		$0$	$\frac{c - \frac{\beta}{2}u}{2(1+\beta)}$
			$\frac{1}{2}$

Note then that the matrices  $G^\pm$  can be written in the form:

$$G^\pm = \begin{bmatrix} \mathcal{L}^\pm & 0 & 0 \\ 0 & \mathcal{M}^\pm & 0 \\ 0 & 0 & \mathcal{N}^\pm \end{bmatrix} \quad (47)$$

matrix $G_{u-c}$			
$\frac{1}{2(1+\beta)}$	$0$	$0$	$0$
$\ddots$	$0$	$0$	$0$
$0$	$\frac{1}{2(1+\beta)}$	$0$	$0$
$0$	$\frac{1}{2(1+\beta)}$	$0$	$0$
$0$	$\frac{1}{2(1+\beta)}$	$0$	$0$
$0$	$0$	$\frac{1}{2(1+\beta)} + \frac{\beta u}{4c}$	$-\frac{\beta}{2c}$
$0$	$0$	$-\frac{c - \frac{\beta}{2}u}{2(1+\beta)}$	$\frac{1}{2}$

where  $\mathcal{L}$  is a 5 by 5 diagonal matrix,  $\mathcal{M}$  is a 3 by 3 diagonal matrix, and  $\mathcal{N}$  is a 2 by 2 full matrix. Once the matrices  $G^\pm$  have been defined, the finite difference equation (39) can be replaced with the simpler equation (43).

### DISCRETIZATION OF CHEMICAL REACTION TERMS

In order to develop a stable and conservative numerical scheme for the first five components of the differential system we write the source terms  $(w_i)_{i=1}^5$  in the form  $\mathcal{C}(\rho)\rho$  where  $\mathcal{C}(\rho)$  is a 5 by 5 matrix with the properties:

- (a)  $c_{ii} < 0, c_{ij} \geq 0$  for  $i \neq j$
  - (b)  $\sum_{j=1}^5 c_{ji} = 0$  for  $i = 1, 2, 3, 4, 5$
- (48)

Matrix  $\mathcal{C}$  with properties (a) and (b) is not unique, in fact, terms like  $B\rho_i\rho_j$  can be written in either form:

$$(B\rho_i)\rho_j \text{ or } (B\rho_j)\rho_i \tag{49}$$

In this case we write:

$$\theta(B\rho_i)\rho_j + (1-\theta)(B\rho_j)\rho_i \tag{50}$$

with  $\theta$  being a weight parameter to be specified in such a way that properties (a) and (b) are both satisfied. Considering that we do not want positive terms on the main diagonal some choices are forced. Thus, a term  $B\rho_i\rho_j$  in  $w_i$  where  $B$  is negative must be expressed as  $(B\rho_j)\rho_i$ .

In summary, from (11) we have:

$$\begin{aligned}
 w_1 &= -(\Gamma_1 + K_{f_4}r_5)\rho_1 + (2\Omega_1r_4)\rho_4 + [1 - \theta_9](2K_{b_4}r_3)\rho_4 + \theta_9(2K_{b_4}\alpha r_4)\rho_3 \\
 w_2 &= -(\Gamma_2 + K_{b_5}r_4)\rho_2 + (2\Omega_2r_5)\rho_5 + [1 - \theta_8](2K_{f_5}r_3)\rho_5 + \theta_8(2K_{f_5}\beta r_5)\rho_3 \\
 w_3 &= -(\Gamma_3 + K_{b_4}r_4 + K_{f_5}r_5)\rho_3 + [1 - \theta_7]\left(\Omega_3\frac{r_4}{\beta}\right)\rho_5 + \theta_7\left(\Omega_3\frac{r_5}{\alpha}\right)\rho_4 + \\
 &\quad [1 - \theta_6]\left(K_{b_5}\frac{r_2}{\alpha}\right)\rho_4 + \theta_6\left(K_{b_5}\frac{r_4}{2\beta}\right)\rho_2 + [1 - \theta_5]\left(K_{f_4}\frac{r_1}{\beta}\right)\rho_5 + \theta_5\left(K_{f_4}\frac{r_5}{2\alpha}\right)\rho_1 \quad (51) \\
 w_4 &= -(2\Omega_1r_4 + \Omega_3r_5 + K_{b_4}r_3 + K_{b_5}r_2)\rho_4 + \Gamma_1\rho_1 + \Gamma_3\rho_3\alpha + \\
 &\quad [1 - \theta_1]\left(\frac{a}{b}K_{f_4}r_1\right)\rho_5 + \theta_1\left(\frac{1}{2}K_{f_4}r_5\right)\rho_1 + [1 - \theta_2]\left(\frac{a}{b}K_{f_5}r_3\right)\rho_5 + \theta_2(K_{f_5}\alpha r_5)\rho_3 \\
 w_5 &= -(2\Omega_2r_5 + \Omega_3r_4 + K_{f_4}r_1 + K_{f_5}r_3)\rho_5 + \Gamma_2\rho_2 + \Gamma_3\rho_3\beta + \\
 &\quad [1 - \theta_3]\left(\frac{b}{a}K_{b_4}r_3\right)\rho_4 + \theta_3(K_{b_4}\beta r_4)\rho_3 + [1 - \theta_4]\left(\frac{b}{a}K_{b_5}r_2\right)\rho_4 + \theta_4\left(\frac{1}{2}K_{b_5}r_4\right)\rho_2
 \end{aligned}$$

The conditions (a) and (b) are satisfied when  $\theta_1, \theta_2, \dots, \theta_9$  are given by:

$$\theta_5 = \alpha(2 - \theta_1), \quad \theta_6 = \beta(2 - \theta_4), \quad \theta_7 = \alpha, \quad \theta_8 = \frac{1}{2\beta}(1 - \alpha\theta_2), \quad \theta_9 = \frac{1}{2\alpha}(1 - \beta\theta_3) \quad (52)$$

where  $\theta_1, \theta_2, \theta_3, \theta_4$  are taken in the interval:

$$\theta_1, \theta_2 \in \left[1 - \frac{b}{a}, 1\right] \cap [0, 1], \quad \theta_3, \theta_4 \in \left[1 - \frac{a}{b}, 1\right] \cap [0, 1] \quad (53)$$

so that, finally,

Matrix of chemical reaction C				
$-\Gamma_1 - K_{f_4}r_5$	0	$(1 - \beta\theta_3)K_{b_4}r_4$	$+2\Omega_1r_4$ $\frac{a - b + b\theta_3}{a}K_{b_4}r_3$	0
0	$-\Gamma_2 - K_{b_5}r_4$	$(1 - \alpha\theta_2)K_{f_5}r_5$	0	$2\Omega_2r_5 +$ $\frac{b - a + a\theta_1}{b}K_{f_5}r_3$
$(1 - \frac{\theta_1}{2})K_{f_4}r_5$	$(1 - \frac{\theta_4}{2})K_{b_5}r_4$	$-\Gamma_3 - K_{f_5}r_5$ $-K_{b_4}r_4$	$\Omega_3r_5 +$ $\frac{a - b + b\theta_4}{a}K_{b_5}r_2$	$\Omega_3r_4 +$ $\frac{b - a + a\theta_1}{b}K_{f_4}r_1$
$\Gamma_1 + \frac{\theta_1}{2}K_{f_4}r_5$	0	$\alpha\Gamma_3 +$ $\alpha\theta_2K_{f_5}r_5$	$-2\Omega_1r_4 - \Omega_3r_5$ $-K_{b_4}r_3 - K_{b_5}r_2$	$\frac{a}{b}(1 - \theta_1)K_{f_4}r_1$ $\frac{a}{b}(1 - \theta_2)K_{f_5}r_3$
0	$\Gamma_2 +$ $\frac{\theta_4}{2}K_{b_5}r_4$	$\beta\Gamma_3 +$ $\theta_3\beta K_{b_4}r_4$	$\frac{b}{a}(1 - \theta_3)K_{b_4}r_3$ $\frac{b}{a}(1 - \theta_4)K_{b_5}r_2$	$-2\Omega_2r_5 - \Omega_3r_4$ $-K_{f_4}r_1 - K_{f_5}r_3$

Now we can write the semi-implicit scheme for the first five equations in the following way:

$$S_i \frac{\rho_i^{n+1} - \rho_i^n}{\Delta t} + \frac{S_{i+1} \mathcal{L}_{i+1}^- \rho_{i+1}^{n+1} + S_i (\mathcal{L}_i^+ - \mathcal{L}_i^-) \rho_i^{n+1} - S_{i-1} \mathcal{L}_{i-1}^+ \rho_{i-1}^{n+1}}{\Delta x} = S_i \mathcal{C}_i(\rho_i^{n+1}) \rho_i^{n+1} \quad (54)$$

and using the definitions of  $G_u$ ,  $G_{u+c}$  and  $G_{u-c}$  results in:

$$\mathcal{L}_i^\pm = \text{diag} \left( u_i^\pm \frac{\beta_i}{1 + \beta_i} + \frac{(u_i + c_i)^\pm}{2(1 + \beta_i)} + \frac{(u_i - c_i)^\pm}{2(1 + \beta_i)} \right) \quad (55)$$

and the function matrix  $\mathcal{C}_i(\rho^{n+1})$  is the matrix  $\mathcal{C}$  evaluated with  $\Gamma$ ,  $\Omega$ ,  $K_f$ ,  $K_b$  computed at time level  $n$ . Note that  $\mathcal{L}_i^+$  is non-negative while  $\mathcal{L}_i^-$  is non-positive. The finite difference equation (54) constitutes a block tridiagonal system whose main diagonal block is non-linear. To solve this non-linear system, an iterative procedure has to be used. A convenient iterative scheme for (54) is:

$$S_i \frac{(\rho_i^{n+1})^{l+1} - \rho_i^n}{\Delta t} + \frac{S_{i+1} \mathcal{L}_{i+1}^- (\rho_{i+1}^{n+1})^{l+1} + S_i (\mathcal{L}_i^+ - \mathcal{L}_i^-) (\rho_i^{n+1})^{l+1} - S_{i-1} \mathcal{L}_{i-1}^+ (\rho_{i-1}^{n+1})^{l+1}}{\Delta x} = S_i \mathcal{C}_i((\rho_i^{n+1})^l) (\rho_i^{n+1})^{l+1} \quad (56)$$

starting with  $(\rho_i^{n+1})^0 = \rho_i^n$  until convergence is reached.

### POSITIVITY OF THE METHOD

The iteration formula (56) allows us to maintain positivity of the densities at every time step. To see this, we prove the following theorem:

*Theorem 5.1* Let the semi-implicit difference approximation be:

$$[I + L_i^+ - L_i^- + C_i^l] S_i \rho_i^{l+1} - L_{i-1}^+ S_{i-1} \rho_{i-1}^{l+1} + L_{i+1}^- S_{i+1} \rho_{i+1}^{l+1} = S_i \rho_i^n \quad (57)$$

with  $i = 1, 2, \dots, m-1$  where:

$$L^+ = \frac{\Delta t}{\Delta x} \mathcal{L}^+, \quad L^- = \frac{\Delta t}{\Delta x} \mathcal{L}^-, \quad C_i^l = -\Delta t \mathcal{C}_i(\rho_i^l)$$

and for sake of simplicity  $\rho_i^l = (\rho_i^{n+1})^l$ . Clearly,  $L_i^+$  and  $-L_i^-$  are non-negative diagonal matrices and the matrix  $C_i$  satisfies:

$$(C_i^l)_{kk} \geq 0, \quad (C_i^l)_{kl} \leq 0, \quad k \neq l \quad \text{and} \quad (C_i^l)_{kk} \geq - \sum_{k \neq l} (C_i^l)_{kl}$$

If  $\rho_m^{n+1} \geq 0, \rho_0^{n+1} \geq 0$  (boundary conditions) and  $\rho_i^n \geq 0$ , one has  $\rho_i^{l+1} \geq 0$  for all  $i = 1, 2, \dots, m-1$ .

*Proof*

We can regard the iteration step (57) as an inversion of a linear system of the form:

$$M(\rho^l) \rho^{l+1} = Z \quad (58)$$

where

$$\begin{aligned} Z_1 &= S_1 \rho_1^n + S_0 L_0^+ \rho_0^{n+1} \\ Z_i &= S_i \rho_i^n && \text{for } i = 2, 3, \dots, m-2 \\ Z_{m-1} &= S_{m-1} \rho_{m-1}^n \rho_{m-1}^n - S_m L_m^- \rho_m^{n+1} \end{aligned} \quad (59)$$

and

$$M(\rho^l) = \begin{bmatrix} S_1 D_1^l & S_2 L_2^- & & & & \\ -S_1 L_1^+ & S_2 D_2^l & S_3 L_3^- & & & \\ & -S_2 L_2^+ & \vdots & \vdots & & \\ & & \vdots & \vdots & & \\ & & & & S_{m-1} L_{m-1}^- & \\ & & & -S_{m-2} L_{m-2}^+ & S_{m-1} D_{m-1}^l & \end{bmatrix} \quad (60)$$

with  $D_i^l = I + L_i^+ - L_i^- + C_i^l$ . Since  $C_i^l$  are weakly diagonally dominant (along the columns), with positive elements on the main diagonal and non-positive elements elsewhere, and since  $L_i^+$  and  $-L_i^-$  are non-negative diagonal matrices, it follows that  $M$  is a strictly diagonally dominant matrix along the column with positive elements on the main diagonal and non-negative ones elsewhere. Thus  $M(\rho^l)$  is an  $M$ -matrix. Consequently,  $[M(\rho^l)]^{-1} \geq 0$  and hence  $[M(\rho^l)]^{-1} Z \geq 0$ .

The result above proves that each iteration  $(\rho^{n+1})^l$  is positive and, when convergence is achieved, the resulting  $\rho^{n+1}$  is positive as well.

When convergence is reached the source terms are:

$$\hat{w} = \mathcal{G}(\rho^{n+1}) \rho^{n+1} \quad (61)$$

For the conservation of species masses we need

$$\hat{w}_1 + \alpha \hat{w}_3 + \hat{w}_4 = 0, \quad \hat{w}_2 + \beta \hat{w}_3 + \hat{w}_5 = 0 \quad (62)$$

which are verified by straightforward computation. This means that the numerical method conserves the total amount of nitrogen and oxygen. Equations (62) are used as convergence criterion for iterations (56).

### DISCRETIZATION OF VIBRATIONAL TERMS

In the previous sections we have developed the upwind scheme for the flux, separating the vibrational energies and density from the other conserved variables. In this section we analyse the approximation of the source terms  $W(U^{n+1}, U^n)$  for the equations of vibrational energies. In order not to destroy the positivity of the resulting flux matrix, we approximate the source terms as:

$$W_{E,i} = \frac{E_{eqk,i}^n - E_{vk,i}^{n+1}}{\tau_{k,i}} + \frac{w_{k,i}^+}{\rho_{k,i}} E_{eqk,i}^n + \frac{w_{k,i}^-}{\rho_{k,i}} E_{vk,i}^{n+1} \quad (63)$$

With this choice the finite difference scheme is of the form:

$$S_i \frac{E_{vk,i}^{n+1} - E_{vk,i}^n}{\Delta t} + \frac{S_{i+1} \mathcal{M}_{i+1}^- E_{vk,i+1}^{n+1} + S_i (\mathcal{M}_i^+ - \mathcal{M}_i^-) E_{vk,i}^{n+1} - S_{i-1} \mathcal{M}_{i-1}^+ E_{vk,i-1}^{n+1}}{\Delta x} = S_i \left( \frac{E_{eqk,i}^n - E_{vk,i}^{n+1}}{\tau_{k,i}} + \frac{w_{k,i}^+}{\rho_{k,i}} E_{eqk,i}^n + \frac{w_{k,i}^-}{\rho_{k,i}} E_{vk,i}^{n+1} \right) \quad (64)$$

where:

$$\mathcal{M}_i^\pm = u_i^\pm \frac{\beta_i}{1 + \beta_i} + \frac{(u_i + c_i)^\pm}{2(1 + \beta_i)} + \frac{(u_i - c_i)^\pm}{2(1 + \beta_i)} \quad (65)$$

Equations (64) can be rewritten as:

$$S_i E_{v_{k,i}}^{n+1} \left( 1 + \frac{\Delta t}{\Delta x} (\mathcal{M}_i^+ - \mathcal{M}_i^-) + \frac{\Delta t}{\tau_{k,i}} \frac{w_{k,i}^-}{\rho_{k,i}} \right) + S_{i-1} E_{v_{k,i-1}}^{n+1} \left( -\frac{\Delta t}{\Delta x} \mathcal{M}_{i-1}^+ \right) + S_{i+1} E_{v_{k,i+1}}^{n+1} \left( \frac{\Delta t}{\Delta x} \mathcal{M}_{i+1}^- \right) = S_i \left( E_{v_{k,i}}^n + \Delta t \left( \frac{E_{eqk,i}}{\tau_{k,i}} + \frac{w_{k,i}^+}{\rho_{k,i}} E_{eqk,i} \right) \right) \quad (66)$$

Note that (66) constitute a linear system whose coefficient matrix is an *M*-matrix and the vector on the right hand side is always positive. Thus the vibrational energies maintain positivity at each time step. We also note that the unknowns  $E_{v_{k,i}}^{n+1}$  are separated for every *k*, then we can solve three simpler tridiagonal systems rather than one block tridiagonal system.

### DISCRETIZATION OF REMAINING TERMS

In the momentum and total energy equations of system (1) there is no way to ensure positivity of the pressure for arbitrarily large time steps. Actually, we use a simple discretization that uses the information of already evaluated variables. Next, if a negative pressure is encountered we repeat the evaluation with a smaller time step. Explicitly, by setting  $\hat{w} = \mathcal{C}_i (\rho_i^{n+1}) \rho_i^{n+1}$ , from (20) and (21) we have:

$$W_{\mathcal{E}_i}(U_i^{n+1}, U_i^n) = - \sum_{k=1}^3 \left( h_k^0 \hat{w}_k + \frac{E_{eqk,i}^n - E_{v_{k,i}}^{n+1}}{\tau_{k,i}} + \frac{w_{k,i}^+}{\rho_{k,i}^{n+1}} E_{eqk,i}^n + \frac{w_{k,i}^-}{\rho_{k,i}^{n+1}} E_{v_{k,i}}^{n+1} \right) p(U_i^{n+1}, U_i^n) = \beta_i^{n+1} \left( \mathcal{E}_i^{n+1} - \frac{m_i^{n+1} u_i^n}{2} \right) \frac{S_{i+1} - S_{i-1}}{2 \Delta x} \quad (67)$$

Thus, by setting

$$\mathcal{P}_i = \begin{pmatrix} -\frac{S_{i+1} - S_{i-1}}{2 \Delta x} \beta_i^{n+1} \frac{u_i^n}{2} & \frac{S_{i+1} - S_{i-1}}{2 \Delta x} \beta_i^{n+1} \\ 0 & 0 \end{pmatrix} \quad (68)$$

and

$$V_i = \begin{pmatrix} m_i \\ \mathcal{E}_i \end{pmatrix} \quad (69)$$

the finite difference system for the momentum and total energy becomes:

$$S_i \frac{V_i^{n+1} - V_i^n}{\Delta t} + \frac{S_{i+1} \mathcal{N}_{i+1}^- V_{i+1}^{n+1} + S_i (\mathcal{N}_i^+ - \mathcal{N}_i^-) V_i^{n+1} - S_{i-1} \mathcal{N}_{i-1}^+ V_{i-1}^{n+1}}{\Delta x} = \mathcal{P}_i V_i^{n+1} + \begin{pmatrix} 0 \\ W_{\mathcal{E}_i} \end{pmatrix} \quad (70)$$

where  $\mathcal{N}$  is defined as in (47).

### BOUNDARY CONDITIONS

As an inflow condition, supersonic inflow is chosen. All the characteristic lines are entering and consequently all the variables have to be specified. The outlet is subsonic and thus one eigenvalue has opposite sign. This represents the disturbance coming from downstream. In this case one condition must be specified and therefore the pressure at the outlet is prescribed. The boundary

conditions are applied using the method of Courant–Isaacson and Rees<sup>6</sup>. For the actual calculations it is advantageous to rewrite the equations for  $m$  and  $\mathcal{E}$  as equations in  $u$  and  $p$ ,

$$\begin{cases} u_t + uu_x + \frac{p_x}{\rho} = \frac{p}{\rho} \frac{S_x}{S} \\ p_t + p(1 + \beta)u_x + up_x = W_{\mathcal{E}} \end{cases} \tag{71}$$

where

$$W_{\mathcal{E}} = \sum_{i=1}^5 (py_i - \beta h_j^0)w_i - up \left( 1 + \frac{3}{2}\beta \right) \frac{1}{S} \frac{dS}{dx} - \beta \sum_{k=1}^3 \left( \frac{E_{eqk} - E_{\iota k}}{\tau_k} + \frac{w_k^+}{\rho_k} E_{eqk} + \frac{w_k^+}{\rho_k} E_{eqk} + \frac{w_k^-}{\rho_k} E_{\iota k} \right) \tag{72}$$

using matrix notation we can rewrite system (71) as:

$$\begin{pmatrix} u \\ p \end{pmatrix}_t + A \begin{pmatrix} u \\ p \end{pmatrix}_x = B \tag{73}$$

where

$$A = \begin{pmatrix} u & \frac{1}{\rho} \\ p(1 + \beta) & u \end{pmatrix}, \quad B = \begin{pmatrix} \frac{p}{\rho} \frac{S_x}{S} \\ W_{\mathcal{E}} \end{pmatrix} \tag{74}$$

Next we multiply this system by the matrix  $T$ :

$$T = \begin{pmatrix} 1 & \frac{1}{\rho c} \\ 1 & -\frac{1}{\rho c} \end{pmatrix} \tag{75}$$

obtaining the new system:

$$T \begin{pmatrix} u \\ p \end{pmatrix}_t + TA \begin{pmatrix} u \\ p \end{pmatrix}_x = TB \tag{76}$$

Observing that:

$$TA = \Lambda T \tag{77}$$

where  $\Lambda = \text{diag}(u + c, u - c)$ , we obtain:

$$\begin{cases} u_t + p_t \frac{1}{\rho c} + (u + c) \left[ u_x + p_x \frac{1}{\rho c} \right] = \frac{p}{\rho} \frac{S_x}{S} + \frac{1}{\rho c} W_{\mathcal{E}} \\ u_t - p_t \frac{1}{\rho c} - (u - c) \left[ u_x - p_x \frac{1}{\rho c} \right] = \frac{p}{\rho} \frac{S_x}{S} - \frac{1}{\rho c} W_{\mathcal{E}} \end{cases} \tag{78}$$

Using the directional derivative:

$$D_{\lambda} = \frac{\partial}{\partial t} + \lambda \frac{\partial}{\partial x} \tag{79}$$



after some manipulations the complete system takes the form:

$$\left\{ \begin{aligned} D_u \rho_i + \frac{W_g - D_u p}{p(1 + \beta)} \rho_i &= w_i - \rho_i \frac{D_u S}{S} \\ D_u E_{ck} + \frac{W_g - D_u p}{p(1 + \beta)} E_{ck} &= \frac{E_{eqk} - E_{tk}}{\tau_k} + \frac{w_k^+}{\rho_k} E_{eqk} + \frac{w_k^-}{\rho_k} E_{tk} - E_{tk} \frac{D_u S}{S} \\ D_{u+c} u + \frac{1}{\rho c} D_{u+c} p &= \frac{p S_x}{\rho S} + \frac{1}{\rho c} W_g \\ D_{u-c} u - \frac{1}{\rho c} D_{u-c} p &= \frac{p S_x}{\rho S} - \frac{1}{\rho c} W_g \end{aligned} \right. \quad (80)$$

Using this relation it is easy to construct the one step method of characteristic. But because of the very stiffness of the problem we assume that at the outlet the gas is in chemical equilibrium so that  $W_g = 0$ .

### NUMERICAL RESULTS

The code was tested with two different problems: the Antibes nozzle, defined during Antibes Workshop I, January 1990 and Antibes workshop II, April 1990 and the Chiang and Offmann nozzle<sup>14</sup>.

#### Antibes nozzle

In the Antibes test case the nozzle shape is as follows: the throat radius,  $r_0 = 0.003$  m; the half cone angle  $\Theta = 10^\circ$ ; length = 1.13 m, with the boundary conditions:

	$C_{N_2} = 69.53\%$
$p_{in} = 84590000$ Pa	$C_{O_2} = 6.89\%$
$u_{in} = 1621$ m/sec	$C_{NO} = 14.78\%$
$\rho_{in} = 46.21$ Kg/m <sup>3</sup>	$C_N = 0.27\%$
	$C_O = 8.53\%$

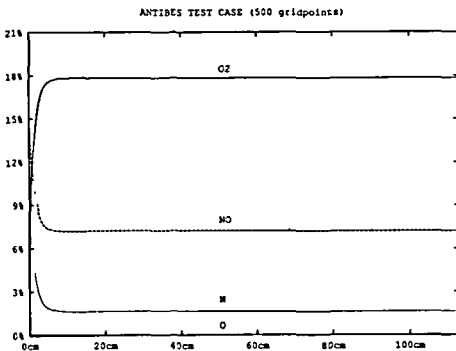


Figure 1a Mass fraction

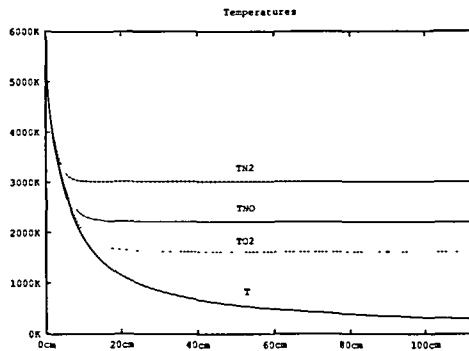


Figure 1b Temperatures

The outlet pressure has not been specified because the outlet flow is expected to be supersonic. The results are shown in *Figures 1a* and *1b*. *Figure 1a* represents the mass fraction of the species NO, O<sub>2</sub>, N and O, *Figure 1b* represents the vibrational temperature of species N<sub>2</sub>, O<sub>2</sub>, NO and the translational temperature. These results have been obtained over 500 grid points in only 20 sec of CPU time of a 4.2MFLOPS workstation. The results compared with that in Reference 9 show agreement.

*Chiang and Hoffmann nozzle*

This nozzle is described and shaped as<sup>14</sup>:

$$S(x) = 1.398 + 0.347 \tanh(0.8x - 0.4)$$

where  $x$  is in cm. The nozzle starts at 1.2 cm and ends at 8 cm with the flux from left to right. The boundary conditions are the inlet density, velocity, pressure, and the outlet pressure. The first test case is parametrized by:

- |                                      |                     |
|--------------------------------------|---------------------|
| $p_{in} = 5529 \text{ Pa}$           | $C_{N_2} = 76.71\%$ |
| $p_{out} = 2500000 \text{ Pa}$       | $C_{O_2} = 23.29\%$ |
| $u_{in} = 6125 \text{ m/sec}$        | $C_{NO} = 0\%$      |
| $\rho_{in} = 0.08245 \text{ Kg/m}^3$ | $C_N = 0\%$         |
|                                      | $C_O = 0\%$         |

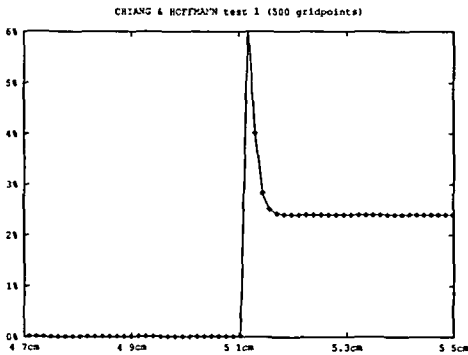


Figure 2a NO mass fraction

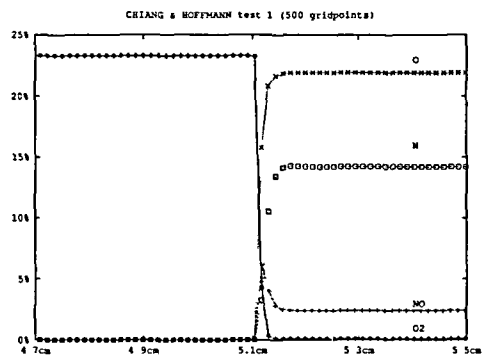


Figure 2b Mass fractions

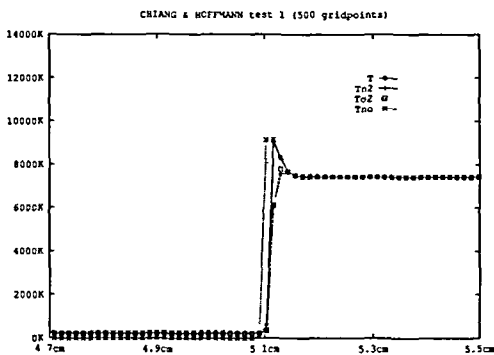


Figure 2c Temperatures

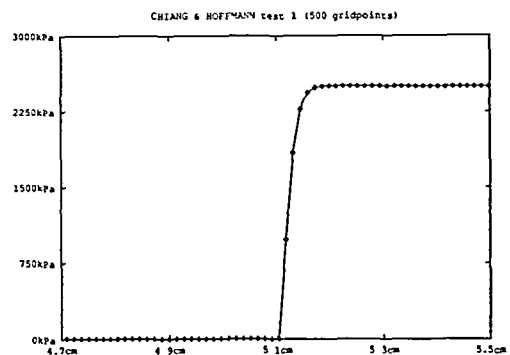


Figure 2d Pressure

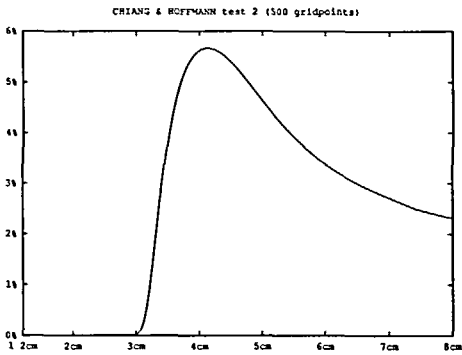


Figure 3a NO mass fraction

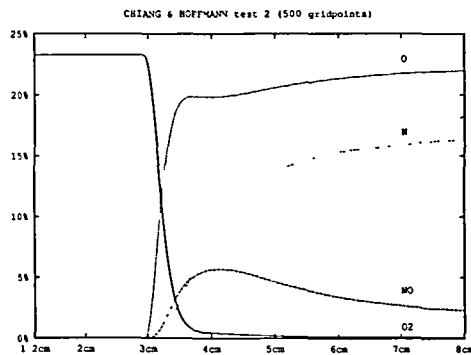


Figure 3b Mass fractions

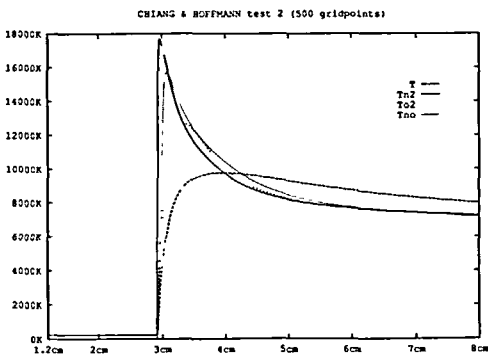


Figure 3c Temperatures

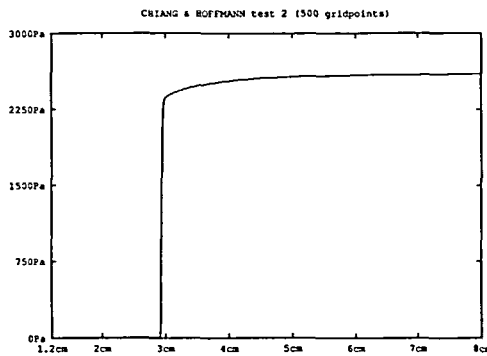


Figure 3d Pressure

and simulates the free flight conditions at 20 km altitude. The results are illustrated in *Figures 2a–2d*. *Figure 2a* shows the mass fraction of NO and *Figure 2b* show the mass fraction of O<sub>2</sub>, NO, N and O. In *Figure 2c* the vibrational temperatures of species N<sub>2</sub>, O<sub>2</sub>, NO and the translational temperature are illustrated. *Figure 2d* depicts the pressure. These results have been obtained over 500 grid points in 190 CPU sec on a 4.2MFLOPS workstation. The second test case is parametrized by:

$$\begin{aligned}
 p_{in} &= 5.529 \text{ Pa} & C_{N_2} &= 76.71\% \\
 p_{out} &= 2600 \text{ Pa} & C_{O_2} &= 23.29\% \\
 u_{in} &= 6125 \text{ m/sec} & C_{NO} &= 0\% \\
 \rho_{in} &= 0.00008254 \text{ Kg/m}^3 & C_N &= 0\% \\
 & & C_O &= 0\%
 \end{aligned}$$

and simulates the free flight conditions at 70 km altitude. The results are illustrated in *Figures 3a–3d*. *Figure 3a* represents the mass fraction of NO and *Figure 3b* the mass fraction of O<sub>2</sub>, NO, N and O. In *Figure 3c* the vibrational temperatures of species N<sub>2</sub>, O<sub>2</sub>, NO and translational temperature are illustrated. *Figure 3d* depicts the pressure. The CPU time required for this simulation is of 145 CPU sec.

## CONCLUSIONS

The numerical method developed in this paper permits the solution of hypersonic flow at a relatively low computational cost. Positivity of the densities and vibrational energies is assured even when large time steps are used. The method is quite general and can be extended to two or three dimensional problems where the low computational cost is essential. The resulting code is based on the inversion of linear systems of a sparse structure where vectorizable algorithms are available.

## ACKNOWLEDGEMENTS

We are indebted to Jochem Häuser who provided many hours of helpful advice and assistance.

## REFERENCES

- 1 Anderson Jr. J., *Hypersonic and High Temperature Gas Dynamics*, McGraw-Hill, New York (1990)
- 2 Anderson Jr. J., *Modern Compressible Flow*, McGraw-Hill, New York (1990)
- 3 Hirsch, C. *Numerical Computations of Internal and External Flows*, Wiley and Sons, New York (1991)
- 4 Vincenti, W. G. and Kruger Jr. C. H. *Introduction to Physical Gas Dynamics*, Krieger, Malabar, FL (1967)
- 5 Bertolazzi, E. and Casulli, V. *On Numerical Methods for Aerothermodynamic Applications*, Univ. Trento, *U.T.M.* 418 (1990)
- 6 Courant, R., Isaacson, E. and Rees, M. On the solution of nonlinear hyperbolic differential equation by finite difference, *Commun. Pure Appl. Math.*, 5, 243–255 (1952)
- 7 Vinckier, A. *Qoneq, A First Step Towards 2D Nonequilibrium Flow*, Inst. für Luftfahrttechn. und Leichtabu, Univ. Bundeswehr München (1990)
- 8 Häuser, J., Vinckier, A., Zemsch, S. and Paap, H. G. Supercomputing in hypersonic flow with non-equilibrium effects, *Proc. Conf. Supercomputing in Fluid Flow*, Lowell, MA (1989)
- 9 Walpot, L. Quasi one dimensional inviscid nozzle flow in vibrational and chemical non-equilibrium, T U Delft Dept Aersp. Eng. High Speed Aerodyn. Delft, The Netherlands (1991)
- 10 Millikan, R. C. and White, D. R. Systematics of vibrational relaxation, *J. Chem. Phys.* 39, 3209–3212 (1963)
- 11 Shuen, J. S. and Yoon, S. Numerical study of chemical reacting flows using lower-upper symmetric successive overrelaxation scheme, *AAIA J.* 27, (12) (1989)
- 12 Williams, F. A. *Combustion Theory*, 2nd edn., Benjamin/Cummings, Menlo Park, CA (1985)
- 13 Dunn, M. G. and Kang, S. W. Theoretical and experimental studies on reentry plasmas, *NASA CR2232* (April 1973)
- 14 Chiang, T. L. and Hoffmann, K. A. Determination of computational timestep for chemically reacting flows, *AIAA-89* (1855)
- 15 Problem 8: Non-Equilibrium Flow in an Arc Jet. *Workshop on Hypersonic Flows for Reentry Problems*, INRIA (1990)
- 16 Steger, J. L. and Warming, R. F. Flux vector splitting of the inviscid gasdynamic equations and application to finite-difference methods, *J. Comput. Phys.* 40, 263–293 (1981)
- 17 Candler, G. The computation of weakly ionized hypersonic flows in thermo-chemical nonequilibrium, *PhD Thesis*. Dept. of Aeronautics and Astronautics, Stanford University (1988)