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Abstract

Numerical experiments are presented aimed at comparing the behavior of state-to-state chemical kinetics models with respect to the macroscopic thermochemical non-equilibrium models that are usually used in the numerical computation of high temperature hypersonic flows. The comparison is focused both on the differences in the numerical results and on the computational effort related to the adoption of the each approach.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{i,j}$</td>
<td>element of the state-to-state reaction rates matrix</td>
</tr>
<tr>
<td>$e_{p,i}^{s}$</td>
<td>const.-pres. specific heat for species $i$ (roto-trans.)</td>
</tr>
<tr>
<td>$E$</td>
<td>total energy per unit volume</td>
</tr>
<tr>
<td>$e_i^{v}$</td>
<td>vibrational energy of species $i$ (per unit mass)</td>
</tr>
<tr>
<td>$e_i^{eq}$</td>
<td>specific equilibrium vibrational energy of species $i$</td>
</tr>
<tr>
<td>$h$</td>
<td>mixture enthalpy</td>
</tr>
<tr>
<td>$h_i^{f}$</td>
<td>formation enthalpy of species $i$</td>
</tr>
<tr>
<td>$h_i^{p}$</td>
<td>species enthalpy (per unit mass)</td>
</tr>
<tr>
<td>$h_i^{st}$</td>
<td>stagnation enthalpy</td>
</tr>
<tr>
<td>$K$</td>
<td>time step index</td>
</tr>
<tr>
<td>$K_k$</td>
<td>chemical-equilibrium constant (concentrations)</td>
</tr>
<tr>
<td>$K_k^{f},K_k^{b}$</td>
<td>forward, backward reaction constants</td>
</tr>
<tr>
<td>$M_i$</td>
<td>component molar mass</td>
</tr>
<tr>
<td>$ar{M}$</td>
<td>average molar mass</td>
</tr>
<tr>
<td>$N$</td>
<td>cell index</td>
</tr>
<tr>
<td>$n_i$</td>
<td>number of species</td>
</tr>
<tr>
<td>$n_i^{v}$</td>
<td>number of internal energy levels of species $i$</td>
</tr>
<tr>
<td>$n_i^{b}$</td>
<td>number of vibrating species</td>
</tr>
<tr>
<td>$p$</td>
<td>pressure</td>
</tr>
<tr>
<td>$p^{st}$</td>
<td>stagnation pressure</td>
</tr>
<tr>
<td>$R_0$</td>
<td>universal gas constant</td>
</tr>
<tr>
<td>$R_i$</td>
<td>specific gas constant for the species $i$</td>
</tr>
<tr>
<td>$r$</td>
<td>number of chemical reactions</td>
</tr>
<tr>
<td>$S$</td>
<td>surface</td>
</tr>
<tr>
<td>$s$</td>
<td>number of variables in non-equilibrium</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature</td>
</tr>
<tr>
<td>$T_i^{st}$</td>
<td>vibrational temperature of species $i$</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
</tr>
<tr>
<td>$u$</td>
<td>velocity x-component</td>
</tr>
<tr>
<td>$W(V(T,T')_{VT})$</td>
<td>coupling factor (vibration on dissociation)</td>
</tr>
<tr>
<td>$W_i$</td>
<td>element of the conservative variables vector</td>
</tr>
<tr>
<td>$x$</td>
<td>x-coordinate</td>
</tr>
<tr>
<td>$\alpha_i$</td>
<td>species mass fraction</td>
</tr>
<tr>
<td>$\alpha_i,\ell$</td>
<td>mass fraction of vibrational level $\ell$ of species $i$</td>
</tr>
<tr>
<td>$\nu_{ki}$</td>
<td>global stoichiometric coefficient</td>
</tr>
<tr>
<td>$\nu_{ki},\nu_{ki}^{V}$</td>
<td>stoichiometric coefficients of reactants, products</td>
</tr>
<tr>
<td>$\xi_k$</td>
<td>chemical-reaction rate</td>
</tr>
<tr>
<td>$\rho$</td>
<td>total-mass density</td>
</tr>
<tr>
<td>$\tau_{VT}^{f}$</td>
<td>vibrational relaxation time (VT transfer)</td>
</tr>
<tr>
<td>$\Omega_i$</td>
<td>generic production rate</td>
</tr>
<tr>
<td>$\Omega_k^n$</td>
<td>species production rate</td>
</tr>
<tr>
<td>$\Omega_i^{VT}$</td>
<td>vibrational energy production rate (per unit volume)</td>
</tr>
<tr>
<td>$\Omega_{i,f}^{VT}$</td>
<td>production rate of $\rho\alpha_i,\ell$</td>
</tr>
<tr>
<td>$\omega_{ki}^{VT}$</td>
<td>production rate of $e_i^{v}$</td>
</tr>
<tr>
<td>$\omega_{ki}^{V}$</td>
<td>production rate (VT transfer)</td>
</tr>
<tr>
<td>$\omega_{ki}^{V}$</td>
<td>production rate (VV transfer)</td>
</tr>
<tr>
<td>$\omega_{ki}^{CDV}$</td>
<td>production rate (coupling dissociation $\rightarrow$ vibration)</td>
</tr>
</tbody>
</table>

Introduction

In this paper, we present numerical experiments aimed at comparing the behavior of state-to-state chemical kinetics models with respect to the macroscopic thermochemical non-equilibrium models that are usually adopted in the numerical computation of high temperature hypersonic flows.

The comparison is focused on two different aspects connected with the choice of one of the two approaches for modelling a reacting flow. The first aspect is related to the differences in the obtained results and it opens a discussion on the importance of accounting for the detailed description of the reaction rates introduced by the state-to-state kinetics with respect to the simpler macroscopic non-equilibrium models. The second aspect concerns the cost, in terms of complexity and, most important, in terms of memory storage and of computational time, associated with the adoption of each approach. On the one hand, the first type of comparison can put in evidence non-equilibrium effects that state-to-state kinetics is capable of revealing, but that are ignored by
the macroscopic models. Nevertheless, only a comparison with detailed experimental measurements (validation) could make it possible to say a final word on the accuracy of the chemical models. On the other hand, the second type of comparison can be very helpful to quantify the additional computational effort which is introduced by the complex state-to-state kinetics models and it opens up the way to investigations on numerical methods aimed to efficiently couple detailed chemistry to fluid dynamics.

The numerical experiments are carried out considering the air as a gas mixture composed of O$_2$, N$_2$, NO, O and N. The governing equations that are used to model the flow are the quasi-one-dimensional Euler equations, where the effects due to diffusion phenomena are neglected. Such a model is considered to be adequate to address the problem under consideration. In the case of the macroscopic thermochemical non-equilibrium models, the mass and the vibrational energy balance equations for the chemical species that form the gas mixture are added to the system of the Euler equations to take into account thermochemical non-equilibrium effects. On the contrary, when the state-to-state chemistry approach is adopted, a balance equation is written for each internal level considered for any species in the mixture.

The numerical results that will be presented are obtained using a time-dependent method that adopts a finite volume discretization scheme, an upwind flux-difference splitting technique for the evaluation of the convective fluxes.

We intend to present results about test cases that are related to the expansion of the flow inside a hypersonic nozzle with different stagnation conditions. The geometrical configuration considered is that of the Scirocco Plasma Wind Tunnel (PWT) of CIRA (Italy).

The paper runs as follows. In the following section, information about fluid dynamics and thermochemical models is provided. Next, the used numerical method is shortly described, focusing the attention on the treatment of non-equilibrium source terms mainly. Afterwards, the geometrical configuration and the test matrix are presented. Then, results obtained using the macroscopic and the state-to-state approach compressibility are displayed. Conclusions are finally drawn in the last section.

**Governing equations**

Since the interest is concentrated on the application of different thermochemical kinetics models to the flow inside hypersonic nozzles, the choice of a quasi-one-dimensional inviscid model for fluid dynamics is deemed to be appropriate.

When written in integral conservation form, the quasi-one-dimensional Euler equations read like

\[
\frac{\partial}{\partial t} \int_{x_1}^{x_2} \rho S dx + (\rho u S) \bigg|_{x_1}^{x_2} = 0 \quad (1a)
\]

\[
\frac{\partial}{\partial t} \int_{x_1}^{x_2} \rho u S dx + \left[ (p + \rho u^2) S \right] \bigg|_{x_1}^{x_2} - \int_{x_1}^{x_2} \rho u \frac{dS}{dx} dx = 0 \quad (1b)
\]

\[
\frac{\partial}{\partial t} \int_{x_1}^{x_2} E S dx + \left[ (E + p) u S \right] \bigg|_{x_1}^{x_2} = 0 \quad (1c)
\]

Mass and vibrational energy balance equations for the chemical species that form the gas mixture are then added to the system in case the macroscopic non-equilibrium models are used. Otherwise, if the state-to-state chemistry approach is adopted, a balance equation must be added for each internal energy level considered for any species in the mixture. The final system of partial differential equations is thus composed of the three Euler equations plus a number of balance equations that depends on the composition of the considered gas mixture and on the used non-equilibrium model. Indicating with $\xi_i$ a generic quantity (per unit mass) in non-equilibrium conditions, the additional differential equations, written in conservation form, are

\[
\frac{\partial}{\partial t} \int_{x_1}^{x_2} \rho \xi_i S dx + (\rho \xi_i u S) \bigg|_{x_1}^{x_2} = \int_{x_1}^{x_2} \Omega_i S dx \quad (2)
\]

For instance, in this paper the number of equations hidden in Eq. (2) will be equal to eight when using the macroscopic models, but it will arrive up to eighty-five using the state-to-state approach.

The total energy per unit volume $E$ appearing in (1c) is defined as

\[
E = \rho h + p + \frac{1}{2} \rho u^2 \quad (3)
\]

and the mixture enthalpy $h$ is obtained through summation of each species enthalpy

\[
h = \sum_{i=1}^{n} \alpha_i h_i \quad (4)
\]

Species enthalpy $h_i$ is defined as

\[
h_i = h_i^0 + c_{p,i}^e T + c_i^e \quad (5)
\]

Since translational and rotational energies are assumed to be fully excited, the roto-translational contribution to the constant-pressure specific heat $c_{p,i}^e$ is equal to

\[
c_{p,i}^e = \frac{5}{2} R_i \quad \text{for mono-atomic species} \quad (6)
\]

\[
c_{p,i}^e = \frac{7}{2} R_i \quad \text{for diatomic species} \quad (7)
\]

Numerical values for the species formation enthalpy can be easily found in the literature.

The governing equations system is finally closed by the state equation

\[
p = \rho \frac{R_G}{M} T \quad (8)
\]

where the average molar mass $M$ depends on the chemical composition of the mixture according to the relation

\[
M = \left( \sum_{i=1}^{n} \frac{\alpha_i}{M_i} \right)^{-1} \quad (9)
\]

**Thermochemical models**

**Macroscopic models**

**Chemical non-equilibrium model**

High-temperature air is modelled as a gas mixture composed of five species: O, N, NO, O$_2$ and N$_2$. The partial density of each species varies in time and space according to equations

\[
\frac{\partial}{\partial t} \int_{x_1}^{x_2} \rho \xi_i S dx + (\rho \xi_i u S) \bigg|_{x_1}^{x_2} = \int_{x_1}^{x_2} \Omega_i S dx \quad (10)
\]

for any species in the mixture. The final system of partial differential equations is thus composed of the three Euler equations plus a number of balance equations that depends on the composition of the considered gas mixture and on the used non-equilibrium model. Indicating with $\xi_i$ a generic quantity (per unit mass) in non-equilibrium conditions, the additional differential equations, written in conservation form, are

\[
\frac{\partial}{\partial t} \int_{x_1}^{x_2} \rho \xi_i S dx + (\rho \xi_i u S) \bigg|_{x_1}^{x_2} = \int_{x_1}^{x_2} \Omega_i S dx \quad (2)
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where the average molar mass $M$ depends on the chemical composition of the mixture according to the relation

\[
M = \left( \sum_{i=1}^{n} \frac{\alpha_i}{M_i} \right)^{-1} \quad (9)
\]
Reaction terms of vibrational energy per unit mass are introduced. Chemical reaction rates are influenced by flow compressibility on chemical kinetics, as discussed by Park in Ref. 3. Backward reaction rates are obtained via chemical-equilibrium constants by the formula used by Park in Ref. 6.

Conservation equations for non-equilibrium on chemical kinetics is taken into account (CVD model). Species react according to the seventeen non-ionizing reactions listed in Table 1. 

| Reaction | \( O_2 + O \rightarrow 2O + O \) | \( O_2 + N \rightarrow 2O + N \) | \( O_2 + NO \rightarrow 2O + NO \) | \( O_2 + O_2 \rightarrow 2O + O_2 \) | \( O_2 + N_2 \rightarrow 2O + N_2 \) | \( N_2 + O \rightarrow 2N + O \) | \( N_2 + N \rightarrow 2N + N \) | \( N_2 + NO \rightarrow 2N + NO \) | \( N_2 + O_2 \rightarrow 2N + O_2 \) | \( N_2 + N_2 \rightarrow 2N + N_2 \) | \( NO + O \rightarrow N + 2O \) | \( NO + N \rightarrow 2N + O \) | \( NO + NO \rightarrow N + O + NO \) | \( NO + O_2 \rightarrow N + O + O_2 \) | \( NO + N_2 \rightarrow N + O + N_2 \) | \( NO + O \rightarrow N + O_2 \) | \( N_2 + O \rightarrow N + NO \) |
| \( r \) | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 |

**Table 1 Considered chemical reactions.**

Species react according to the seventeen non-ionizing reactions listed in Table 1. Chemical production rates are computed as

\[
\dot{\Omega}_i = \sum_{k=1}^{r} \dot{\xi}_{ik} v_{ki} M_i
\]

(11)

Here, chemical reaction rates \( \dot{\xi}_{ik} \) are identified as those provided by the law of mass action

\[
\dot{\xi}_{ik} = K_{ik}^{n} \prod_{i=1}^{n} \left( \frac{p_{vi}^{1/2}}{M_i} \right) - K_{ik}^{n} \prod_{i=1}^{n} \left( \frac{p_{v_i}^{1/2}}{M_i} \right)
\]

(12)

The influence of flow compressibility on chemical-reaction rates is not taken into account.

Forward reaction rates and equilibrium constants are those suggested by Park in Ref. 3. Backward reaction rates are obtained via chemical-equilibrium constants by the formula

\[
\frac{K_{ik}^{n}}{K_{ik}^{n}} = K_{k}^{n}(T)
\]

(13)

Forward and backward reaction rates are modified as described in the next subsection in case the coupling effect of vibrational non-equilibrium on chemical kinetics is taken into account (CVD model).

Vibrational non-equilibrium models

In the macroscopic model approach, the average vibrational energy possessed by diatomic molecules is described using the truncated harmonic oscillator model. Conservation equations for the vibrational energy of species \( i \) are written as

\[
\frac{\partial}{\partial t} \int_{x} \rho_{v_i} S dx + (\rho_{v_i} u S) \bigg|_{x=1}^{x=2} = \int_{x=1}^{x=2} \Omega_{i}^{x} S dx
\]

(14)

Equation (14) can be rewritten in non-conservation form in terms of vibrational energy per unit mass \( \epsilon_{v_i}^{x} \) as

\[
\frac{\partial \epsilon_{v_i}^{x}}{\partial t} + \frac{\partial \psi_{v_i}^{x}}{\partial x} = \omega_{v_i}^{x}
\]

(15)

Source terms \( \omega_{v_i}^{x} \) describe the production/ destruction rate of specific vibrational energy. In general, they are composed of three terms

\[
\omega_{v_i}^{x} = (\omega_{v_i}^{x})_{VT} + (\omega_{v_i}^{x})_{VV} + (\omega_{v_i}^{x})_{CVD}
\]

(16)

The first addendum represents the contribution of the vibration-translation energy transfer (VT transfer)

\[
(\omega_{v_i}^{x})_{VT} = \frac{\epsilon_{v_i}^{in} - \epsilon_{v_i}^{x}}{\tau_{VT}^{x}}
\]

(17)

The VT vibrational relaxation time \( \tau_{VT}^{x} \) is computed according to the formulation by Millikan and White, corrected by an additional term proposed by Park. Some coefficients used in the original Millikan and White formulation have been substituted by those given by Park in Ref. 6.

The second addendum \( (\omega_{v_i}^{x})_{VV} \) in the right-hand side of Equation (16) is the contribution of the vibration-vibration energy transfer (VV transfer). In the present work, this term is modelled according to Candler and MacCormack.

**Coupling between vibrational and chemical non-equilibrium**

The third addendum \( (\omega_{v_i}^{x})_{CVD} \) in the right-hand side of Equation (16) takes into account the fact that, when a diatomic molecule dissociates, it removes a certain amount of vibrational energy and conversely, when a new diatomic molecule is created by recombination processes, it adds vibrational energy to the mixture. This effect, originally introduced by Marrone and Treanor, is called dissociation-vibration coupling.

The complementary effect, called vibration-dissociation coupling, is based on the observation that "...the use of the chemical equilibrium constant to relate the forward and the backward rates is justified only when vibrational equilibrium obtains...". In vibrational non-equilibrium conditions, it is necessary to modify the classical Arrhenius description of reaction rates by means of a coupling factor \( V(T, T_{v}) \)

\[
K_{k}^{v_{x}} = V(T, T_{v})K_{k}^{v_{x}}
\]

(18)

This formulation was proposed for the first time by Hammerling et al. in Ref. 10. When exchange reactions are considered, the coupling factor should be used to alter the backward reaction rates of the involved species.

In the literature, the contemporary use of the CDV and the CVD models is defined as the CVDV model.

**State-to-state Chemistry**

Macroscopic models cannot take into account the possibility to have non-Boltzmann distributions of the internal energy levels. To model such an occurrence, it is necessary to use the so-called "state-to-state chemistry", where a continuity equation is written for each considered internal energy level \( \ell \) for every species \( i \) in the mixture

\[
\frac{\partial}{\partial t} \int_{x_{1}}^{x_{2}} \rho_{o_{i,\ell}} S dx + (\rho_{o_{i,\ell}} u S) \bigg|_{x_{1}}^{x_{2}} = \int_{x_{1}}^{x_{2}} \Omega_{i,\ell}^{x} S dx
\]

(19)

Equation (19) can be rewritten in non-conservation form in terms of detailed internal energy exchange. State-to-state chemistry models...
have been applied to different mixtures, in particular air, nitrogen and oxygen.\textsuperscript{16-20}

In this paper we will discuss the microscopic vibrational kinetics for air. Such as in the macroscopic approach, the considered species are O, N, NO, O\textsubscript{2} and N\textsubscript{2}. The vibrational energy is the only internal energy mode considered in non-equilibrium conditions. The number of vibrational energy levels used in this study is 1 for O, N, and NO, 34 for O\textsubscript{2} and 48 for N\textsubscript{2}, for a total of 85 non-equilibrium variables. Considering NO only in the ground state is an approximation justified by the radiative decay of the vibrational excited molecules. On the other hand, such an hypothesis can fail if the radiative lifetimes are comparable with the flow characteristic time. In any case, this point deserves to be addressed to in the future.

In summary, the number of balance equations that must be added to the three fluid dynamics ones is, in this case, equal to 85. Making a preliminary rough estimate, one could anticipate that the additional computational cost requested by state-to-state kinetics with respect to perfect gas computations is at least about ten times larger than the additional cost requested by macroscopic non-equilibrium models.

The considered state-to-state processes are displayed in Tab.2, where N\textsubscript{2}(v), O\textsubscript{2}(v) represent the molecule in the v\textsuperscript{th} energy level. Rate coefficients for internal energy exchange processes can be taken from Ref. 21, where many references about available data can also be found.

Dissociation rate coefficients have been calculated using the ladder climbing approximation, where such rates are considered as the extrapolation to a virtual level of the internal state transition rate coefficients. The state-to-state dissociation is still an open problem. The ladder climbing model gives only qualitative values for the dissociation, far to be sufficient for accurate models. Further studies are in due course to improve the dissociation-recombination model by using QCT calculation.\textsuperscript{22} Other rates, such as those related to NO formation, have been calculated using the QCT approach by Bose and Candler.\textsuperscript{23,24}

### Numerical method

Governing equations are discretized in space according to a cell-centered finite volumes approximation and they are integrated in time using a forward explicit method for the convected fluxes and an implicit method for the chemical source terms (see the following subsections).

Fluxes at cell interfaces are evaluated using an upwind Flux Difference Splitting (FDS) Riemann solver.\textsuperscript{25} Upwind methods present the appealing feature of introducing the elements of the wave propagation phenomenology in the integration of the conservation laws. In particular, the adopted FDS technique consists in defining and solving a special initial-value problem, called the Riemann problem,\textsuperscript{26} at each lateral surface. The Riemann problem, that is, the evolution in time of the flow discontinuities that are present at each lateral surface due to the discretization, is solved here in an approximate way: shock waves that could be generated by the collapse of the initial discontinuities are approximated by compression waves. The conservative form of the equations insures that the correct jump and entropy conditions are satisfied.

Second order accuracy in space and time is achieved following the guidelines of the Essentially Non Oscillatory schemes for shock capturing techniques,\textsuperscript{27} which are capable of avoiding spurious oscillations at flow discontinuities.

### Implicit treatment of thermochemical source terms

#### Macroscopic approach

To improve the robustness of the numerical method, thermochemical source terms are computed using the implicit scheme

\[
\left(\frac{\partial (\rho u_i)}{\partial t}\right)_n^k = \Delta x_n \left(\rho \xi_i u_i\right)_n^k - \left(\rho \xi_i u_i\right)_{n+1}^k = (\Omega_i)_n^k + \left(\frac{\partial \Omega_i}{\partial W_j}\right)_n W_j \frac{\Delta t}{2} (20)
\]

where \(W_i\) are the elements of the conservative variables vector \(W = (\rho, \rho u, E, \rho \xi_i)\). The resulting scheme is implicit in \(\frac{\partial (\rho \xi_i)}{\partial t}\), so that the dimension of the algebraic system to solve is, in this case, equal to eight. The partial derivatives of the thermochemical production terms are evaluated numerically using forward first order differences. Such a procedure results in 12 evaluations of each thermochemical source term per cell per time step, for a total of 96 source terms evaluations per cell per time step.

#### State-to-state approach

For computational simplicity, mass fractions and production terms related to the internal energy levels \(\ell\) of species \(i\) are stored in a single vector of dimension

\[
n_i^\ell = \sum_{i=1}^{n} n_i^\ell \quad (21)
\]

<table>
<thead>
<tr>
<th>#</th>
<th>Reaction</th>
<th>(i)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>(N_2(3) + N_2)</td>
<td>(v)</td>
</tr>
<tr>
<td>2</td>
<td>(N_2(v) + N_2)</td>
<td>(v)</td>
</tr>
<tr>
<td>3</td>
<td>(N_2(v) + N_2(M))</td>
<td>(v)</td>
</tr>
<tr>
<td>4</td>
<td>(N_2(v) + N_2(w-1))</td>
<td>(v)</td>
</tr>
<tr>
<td>5</td>
<td>(N_2(v) + N)</td>
<td>(v)</td>
</tr>
<tr>
<td>6</td>
<td>(N_2(v) + N)</td>
<td>(v)</td>
</tr>
<tr>
<td>7</td>
<td>(O_2(v) + O_2(w-1))</td>
<td>(v)</td>
</tr>
<tr>
<td>8</td>
<td>(O_2(v) + O_2(M))</td>
<td>(v)</td>
</tr>
<tr>
<td>9</td>
<td>(O_2(v) + O_2)</td>
<td>(v)</td>
</tr>
<tr>
<td>10</td>
<td>(O_2(M) + O_2)</td>
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<td>(N_2(v) + O_2)</td>
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<td>(N_2(v) + O)</td>
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<td>16</td>
<td>(N_2(v) + O)</td>
<td>(v)</td>
</tr>
<tr>
<td>17</td>
<td>(O_2(v) + N_2)</td>
<td>(v)</td>
</tr>
<tr>
<td>18</td>
<td>(O_2(v) + N_2)</td>
<td>(v)</td>
</tr>
<tr>
<td>19</td>
<td>(O_2(v) + N)</td>
<td>(v)</td>
</tr>
<tr>
<td>20</td>
<td>(O_2(v) + N)</td>
<td>(v)</td>
</tr>
<tr>
<td>21</td>
<td>(O_2(v) + N_2(w-1))</td>
<td>(v)</td>
</tr>
<tr>
<td>22</td>
<td>(NO(0) + O)</td>
<td>(v)</td>
</tr>
<tr>
<td>23</td>
<td>(NO(0) + N)</td>
<td>(v)</td>
</tr>
<tr>
<td>24</td>
<td>(NO(0) + NO)</td>
<td>(v)</td>
</tr>
<tr>
<td>25</td>
<td>(NO(0) + O_2)</td>
<td>(v)</td>
</tr>
<tr>
<td>26</td>
<td>(NO(0) + N_2)</td>
<td>(v)</td>
</tr>
</tbody>
</table>

Table 2 Chemical processes in the state-to-state approach.
In this way, the double subscript can be eliminated and the production terms $\Omega^\nu_i$ can be easily defined as

$$\Omega^\nu_i = C_{i,j} \frac{M_i}{M_j} (\rho \alpha_j)_j$$

(22)

In principle, nothing prevents from using the same implicit treatment of the source terms used with the macroscopic models, but in this case each source term should be evaluated 89 times per cell per time step, for a total of 7565 source terms evaluations per cell per time step.

To improve the efficiency of the method, loosing something in robustness, is thus preferable to discretize the equations as

$$\frac{(\rho \alpha_i)_n^{k+1} - (\rho \alpha_i)_n^k}{\Delta t} A_n \Delta x_n + (\rho \alpha_j u)_n^{k+1} - (\rho \alpha_j u)_n^k = (\Omega^\nu_i)_n^{k+1}$$

(23)

and to adopt the approximation

$$(\Omega^\nu_i)_n^{k+1} = (\Omega^\nu_i)_n^k + \left( \frac{\partial \Omega_i}{\partial W_j} \right)_n^k \left( \frac{\partial W_i}{\partial t} \right)_n^k \Delta t$$

$$\approx (C_{i,j})_n^k \frac{M_i}{M_j} (\rho \alpha_j)_n^{k+1}$$

(24)

The resulting scheme is implicit in $(\rho \alpha_j)_n^{k+1}$ and the dimension of the algebraic system to solve is 85. The approximation made when computing the source terms at step $K+1$ permitted to evaluate matrix $C_{i,j}$ just once, which corresponds to 85 source terms evaluations per cell per time step.

**Geometrical configuration and test matrix**

Numerical tests are carried out considering the expanding flow inside a hypersonic nozzle. In particular, the geometrical configuration of the Scirocco plasma wind tunnel of the Italian Center for Aerospace Research (CIRA) is considered in this case (Fig. 1).

The used numerical grid is composed of 178 cells, clustered in particular at the corner where the nozzle begins and in the throat region. A preliminary grid convergence study demonstrated that numerical results do not change if the mesh is further refined.

Here, we present numerical tests carried out considering two different stagnation conditions, which mainly differ in the magnitude of the total enthalpy (Table 3).

### Table 3 Test matrix

<table>
<thead>
<tr>
<th>T.C.</th>
<th>$h^o$ [MJ/kg]</th>
<th>$p^o$ [bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.305</td>
<td>5.68</td>
</tr>
<tr>
<td>2</td>
<td>6.802</td>
<td>3.52</td>
</tr>
</tbody>
</table>

**Computational efficiency**

In our numerical experiments, we noticed that a state to state computation costs, *per time step*, about 18.5 times more than a macroscopic one. However, the time consumed to reach steady state solutions was even larger, because CFL numbers in a range from 1.6 to 2.5 times smaller than those used with the macroscopic models had to be used for state-to-state computations. Thus, in our experience, a state-to-state computation costed, depending on the test case, something between 30 to 46 times more than one where a macroscopic thermochemical non-equilibrium model was adopted.

**Problems with the CVDV model**

CVDV models are widely used in the simulation of flows where strong compressions across shock waves occur. In those cases, the amount of vibrational energy of diatomic species is normally lower than the equilibrium value and the coupling factor $V$ that alters reaction rates controlling dissociation is smaller than one.

The resulting effect is that dissociation behind a shock wave is slowed down. The opposite happens when a flow expanding inside a hypersonic nozzle is concerned. In such an occurrence, it is common that the vibrational energy of diatomic species remain frozen to values definitely higher than the equilibrium ones. Now, the coupling factor $V$ is larger than one, meaning that dissociation is promoted. The more the dissociation, the more highly excited vibrational energy is extracted from the mixture via the CDV effect, so that in principle the CVD and the CDV effects should finally equilibrate. Unfortunately, the mathematical formulation of the coupling factor $V$ makes the latter grow up to non-physical exceedingly high values for the non-equilibrium conditions typical of hypersonic nozzles. The final result is that computations cannot proceed.

For the reason indicated above, only VT transfer and VV transfer models have been used in the numerical simulations that adopted the macroscopic approach.

**Test case #1**

The comparison between results obtained using macroscopic models and the state-to-state approach doesn’t show very important discrepancies. Temperature and mixture composition are slightly different in the stagnation chamber already, due to the fact that different equilibrium constant are used in the two models. The state-to-state approach is characterized by a larger amount of recombination for $N_2$ with respect to the macroscopic model, which can also explain the slightly larger value of the temperature.
1.2E+06
1.5E+07
1.4E+06
1.6E+06

by the recombination process.

This can be interpreted saying V-T processes dominate the vibrational distribution at low vibrational quantum numbers, while the tail of the distribution is dominated by the recombination process.

In test case #2 differences between the state-to-state and the macroscopic approach are even smaller. In this case, however, oxygen recombination and nitric oxide dissociation are more effective using the macroscopic approach than the state-to-state model.

Non-Boltzmann distributions

Mass fraction distributions of the vibrational energy levels are shown in Figures 6 and 7. In both test cases, distributions are almost-Boltzmann for low vibrational quantum numbers, but strongly deviate towards a non-Boltzmann behavior for high vibrational quantum numbers. This can be interpreted saying V-T processes dominate the vibrational distribution at low vibrational quantum numbers, while the tail of the distribution is dominated by the recombination process.

Non-Boltzmann distributions

The comparison between numerical results about high-temperature flows obtained using different thermochemical models could lead to satisfactory conclusions if a sufficiently large amount of experimental data about chemical composition and internal energy excitation were available. Unfortunately, this is not usually the case in hypersonics, and therefore it is normally very difficult to say in practice whether a particular thermochemical model behaves better than another or not.

In this paper, we compared results obtained using classical macroscopic thermochemical non-equilibrium models with those arising from the adoption of the state-to-state approach. The differences resulting from the use of the two methodologies are not very large, at least in the considered test cases. In general, such discrepancies fall in the same range of uncertainty produced by the choice of particular macroscopic model rather than another.

With respect to the macroscopic approach, state-to-state kinetic models present the appealing capability of simulating the internal energy of a gas without the constraint of using the Boltzmann distribution. This is a very important quality that permits to advance in the understanding of the complex phenomena occurring in flows in thermochemical non-equilibrium conditions. The possibility of adding single state-to-state chemical processes and of checking their effect on the flow-field is also very appealing and could be successfully used to build more sophisticated macroscopic models also.

This study made it possible to obtain useful information about the numerical behavior of state-to-state kinetic models and to make an estimate of the computational cost added by the adoption of such an approach. Computational efficiency is the major reason why the state-to-state approach is not commonly used in hypersonic CFD applications. In our quasi-one-dimensional exercises, we measured a rise in the CPU time per integration step of 18 when using state-to-state models. In addition, state-to-state models appear to increase the stiffness of the system, possibly also because an approximate implicit procedure for computing source terms had to be used to limit the computational cost to reasonable values.

Thus, if on the one hand state-to-state kinetic models are def-

Fig. 4 Test case #1. Temperature distribution and chemical composition.

Fig. 5 Test case #2. Temperature distribution.

References

Fig. 6 Test case #1. Vibrational energy levels distribution.


Fig. 7 Test case #2. Vibrational energy levels distribution.