Numerical Evaluation of an Efficient Roe-type Flux Difference Scheme for Thermochemical Non-equilibrium Nozzle Flows

June 1991

A.C.J. Venis and S.P. Spekreijse

TU Delft
Faculty of Aerospace Engineering
Delft University of Technology
Numerical Evaluation of an Efficient Roe-type Flux Difference Scheme for Thermochemical Non-equilibrium Nozzle Flows

A.C.J. Venis and S.P. Spekreijse
NUMERICAL EVALUATION OF AN EFFICIENT ROE-TYPE
FLUX DIFFERENCE SCHEME FOR THERMOCHEMICAL
NON-EQUILIBRIUM NOZZLE FLOWS

A.C.J. Venis and S.P. Spekreijse

Report LR 624

This report is also published as TP 90099L at National Aerospace Laboratory/NLR

Juni 1991
SUMMARY

An efficient Roe-type flux-difference scheme for chemically reacting, inviscid, compressible flows in thermal nonequilibrium is presented. The numerical scheme is validated.

The testcases concerned quasi one-dimensional hypersonic nozzle flows with and without strong normal shockwaves.
CONTENTS

LIST OF SYMBOLS ......................................................... 5

1 INTRODUCTION ......................................................... 9

2 THERMO-CHEMICAL NONEQUILIBRIUM FLOW ......................... 13
  2.1 Governing equations ........................................... 13
  2.2 Modelling thermal nonequilibrium ........................... 15
  2.3 Governing equations for a quasi 1D nozzle flow in
      thermo-chemical nonequilibrium ........................... 17

3 NUMERICAL MODELLING ............................................... 19
  3.1 A Roe-type scheme for thermo-chemical nonequilibrium flow 19
  3.2 Final discretization ........................................... 22

4 NUMERICAL RESULTS .................................................. 24
  4.1 Definition of testcases ....................................... 24
  4.2 Discussion of results ......................................... 29

5 CONCLUSIONS .......................................................... 36

6 REFERENCES ............................................................ 38

30 Figures

APPENDIX A  Data on species characteristics ....................... 54

(54 pages in total)
**LIST OF SYMBOLS**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Jacobian matrix of f with respect to q</td>
<td>(df/dq)</td>
</tr>
<tr>
<td>A&lt;sub&gt;i&lt;/sub&gt;</td>
<td>constant for determining τ&lt;sub&gt;i&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>area distribution</td>
<td>(m&lt;sup&gt;2&lt;/sup&gt;)</td>
</tr>
<tr>
<td>A&lt;sub&gt;0&lt;/sub&gt;</td>
<td>throat area</td>
<td>(m&lt;sup&gt;2&lt;/sup&gt;)</td>
</tr>
<tr>
<td>a</td>
<td>speed of sound</td>
<td>(m/s)</td>
</tr>
<tr>
<td>C&lt;sub&gt;p&lt;/sub&gt;</td>
<td>mixtures specific heat at constant pressure</td>
<td>(J kg&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>(C&lt;sub&gt;p&lt;/sub&gt;)&lt;sub&gt;i&lt;/sub&gt;</td>
<td>specific heat at constant pressure of species i</td>
<td>(J kg&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>C&lt;sub&gt;v&lt;/sub&gt;</td>
<td>mixture's specific heat at constant volume</td>
<td>(J kg&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>(C&lt;sub&gt;v&lt;/sub&gt;)&lt;sub&gt;i&lt;/sub&gt;</td>
<td>specific heat at constant volume of species i</td>
<td>(J kg&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>C&lt;sub&gt;i&lt;/sub&gt;</td>
<td>mass fraction of species i</td>
<td>(kg/mol)</td>
</tr>
<tr>
<td>D&lt;sub&gt;i&lt;/sub&gt;</td>
<td>vibrational energy per unit mass of dissociating molecules i</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>E</td>
<td>total energy per unit volume</td>
<td>(J/m&lt;sup&gt;3&lt;/sup&gt;)</td>
</tr>
<tr>
<td>e&lt;sub&gt;i&lt;/sub&gt;</td>
<td>internal energy per unit mass of species i</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>ev&lt;sub&gt;i&lt;/sub&gt;</td>
<td>vibrational energy per unit mass of species i</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>Δe&lt;sub&gt;i&lt;/sub&gt;</td>
<td>heat of formation per unit mass of species i</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>ev&lt;sub&gt;i&lt;/sub&gt;</td>
<td>equilibrium vibrational energy per unit mass of species i</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>f</td>
<td>flux vector</td>
<td></td>
</tr>
<tr>
<td>f&lt;sub&gt;R&lt;/sub&gt;</td>
<td>Riemann solver, numerical function</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>flux vector</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>total enthalpy per unit mass</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>h</td>
<td>specific enthalpy; flux vector; altitude (km)</td>
<td>(J/kg)</td>
</tr>
<tr>
<td>k&lt;sub&gt;j&lt;/sub&gt;</td>
<td>equilibrium reaction constant of reaction j</td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;Fj&lt;/sub&gt;</td>
<td>forward rate of reaction j units in cgs system</td>
<td></td>
</tr>
<tr>
<td>k&lt;sub&gt;Bj&lt;/sub&gt;</td>
<td>backward rate of reaction j units in cgs system</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>Mach number</td>
<td></td>
</tr>
<tr>
<td>M&lt;sub&gt;i&lt;/sub&gt;</td>
<td>molar mass of species i</td>
<td>(kg mol&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>P</td>
<td>pressure</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>state vector</td>
<td></td>
</tr>
<tr>
<td>R</td>
<td>mixture's gas constant</td>
<td>(J kg&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
<tr>
<td>R&lt;sub&gt;i&lt;/sub&gt;</td>
<td>gas constant of species i</td>
<td>(J kg&lt;sup&gt;-1&lt;/sup&gt; K&lt;sup&gt;-1&lt;/sup&gt;)</td>
</tr>
</tbody>
</table>
LIST OF SYMBOLS (continued)

\[ R \]  eigenvector of Jacobian matrix
\[ r_j \]  production term of reaction j
\[ r_0 \]  throat radius
\[ T \]  translational/rotational temperature
\[ T_v \]  vibrational temperature
\[ t \]  time
\[ \Delta t_i \]  local time step
\[ u \]  velocity in \( x \)-direction
\[ v \]  velocity in \( y \)-direction
\[ w \]  velocity in \( z \)-direction
\[ x \]  cartesian co-ordinate
\[ \Delta x_i \]  local grid spacing \((x_{i+1} - x_i)\)
\[ \bar{x}_{ref} \]  reference nozzle length
\[ y \]  cartesian co-ordinate
\[ z \]  cartesian co-ordinate

GREEK SYMBOLS

\[ \alpha \]  parameter in nozzle geometry
\[ \alpha_1, \alpha_2 \]  coefficients in Roe scheme
\[ \omega_k \]  stage coefficient in integration scheme
\[ \gamma \]  ratio of specific heats \((C_p/C_v)\)
\[ \Delta(\cdot) \]  arbitrary jump in Roe scheme
\[ \delta_i \]  species discriminator
\[ \zeta \]  vectorial sum of all source term vectors
\[ \theta \]  Roe average parameter
\[ \Lambda \]  vibrational relaxation source term vector
\[ \mu_{ij} \]  reduced mass of colliding species \( i, j \)
\[ \rho \]  mixture density
\[ \rho_i \]  density of species \( i \)
\[ \phi_i \]  vibrational relaxation time of species \( i \)
\[ \phi_i \]  vibrational source term vector

\[ (\cdot)_R - (\cdot)_L \]
\[ (\Omega + \Omega_v + \Lambda) \]
\[ \left( \sqrt{\rho_L} / \left( \sqrt{\rho_L} + \sqrt{\rho_R} \right) \right) \]
\[ (M_i M_j / (M_i + M_j)) \]
\[ (kg \ m^{-3}) \]
\[ (kg \ m^{-3}) \]
\[ (s) \]
LIST OF SYMBOLS (continued)

\( \varphi \) arbitrary function

\( \psi \) nozzle half angle \((\text{deg})\)

\( \Omega \) chemical source term vector

\( \Omega_i \) chemical source term of species

\( \Omega_v \) chemical reactive vibrational source term vector

Superscripts

\( n \) denotes time level \((t = n\Delta t)\)

\( t \) transpose

\( (k) \) stage number

Subscripts

\( i \) species \( i \); volume number

\( \text{in} \) inlet conditions

\( \text{ex} \) exit conditions

\( L \) left

\( R \) right

\( j \) number of reaction; species \( j \)

\( k \) stage number

\( v \) vibrational mode only

\( \infty \) infinity

\( o \) stagnation conditions

Other

\( \sim \) (tilde) denotes Roe-average

\( - \) (overbar) dimensional quantity

\( + \) (arrow) vector
Intentionally left blank.
1 INTRODUCTION

The urge of man to continuously shift the boundaries of his environment has developed the will to transport himself beyond the restrictions of classical airplanes. Re-entry vehicles like the Space Shuttle, Hermes, Sänger and the National Aerospace Plane (NASP) were developed or are under current research. The accurate prediction of the behaviour of these hypervelocity transportational vehicles is of greatest importance for safety and economic reasons. Research in hypersonic aerodynamics contributes to a large extent to the fulfilling of the need for modern hypersonic transportation.

Re-entry vehicles are all constructed as blunt bodies to avoid excessive aerodynamic heating or even ablation of the body at hypersonic velocities. Blunt body flow is characterized by a very strong detached bow shock wave. The enormous amount of kinetic energy released by the deceleration of the flow through the shock wave is transferred to the internal energy modes of the gas. This causes the translational temperature to rise to an extremely high level. In these high temperature flow fields the classical assumption of calorically perfect gases no longer hold, due to dissociation/recombination effects and excitation of internal energy modes.

The difficulty in the solution of hypersonic flow problems lies in the fact that the high temperature effects may occur as nonequilibrium processes. The processes that we will consider are governed by molecular inelastic collisions. Each process requires a certain number of collisions to occur and thus a certain amount of time. If we consider a fluid element travelling through the flow field and compare the fluid element's residence time with the characteristic time of a process to reach equilibrium we can distinguish three situations. First, if the characteristic time of the process is much smaller than the residence time the process is said to be in equilibrium.

Second, if the characteristic time of the process is much larger than the residence time the process is said to be frozen, i.e. nothing happens. All situations in between are called nonequilibrium situations; the characteristic process time is of the same order of magnitude as the fluid element's residence time.
Nonequilibrium chemistry is one of the aspects that play a dominant role in high temperature flow fields. The composition of the gas changes as the fluid elements travel through the flow field. The change in chemical composition of the gas affects the amount of internal energy that is stored as formation (chemical) energy. As a result, flow properties, such as temperature, pressure, density etc., may be strongly influenced compared to ideal gas flow where the chemical composition is assumed to be constant. To account for nonequilibrium or finite rate chemistry appropriate modelling of chemistry is necessary. Three different chemical models were studied in [10].

In [10] we presented calculations of quasi 1D hypersonic nozzle flows where the flow was assumed to be in thermal equilibrium. Thermal equilibrium is the situation in which we assume that the translational, rotational and vibrational energy modes are in equilibrium at one temperature. Then the particles are distributed over the available energy states according to the most probable (Boltzmann) distribution which is characterized by one temperature only: translational/rotational temperature $T$.

However, it is well known that the vibrational energy mode takes more time to reach equilibrium than the translational/rotational modes. In certain flow fields the characteristic vibrational relaxation time may become of the same order of magnitude as the characteristic flow time. In that case the flow is in thermal nonequilibrium.

We characterize the vibrational nonequilibrium by its own temperature: the vibrational temperature $T_v$. It is defined as the temperature at which the distribution of molecules over the vibrational energy states is according to a Boltzmann distribution; the vibrational system is considered as an equilibrium system in itself. If the vibrational temperature becomes equal to the translational/rotational temperature, the flow is in thermal equilibrium.

The effect of vibrational (thermal) nonequilibrium is that the transfer of energy to or from the vibrational energy mode takes a certain time to occur. This directly affects the translational temperature which may be quite different from the thermal equilibrium case.
Also finite rate chemistry may be influenced by the assumption of thermal nonequilibrium. First, due to the effect on translational temperature, since the reaction rates are functions of temperature only. Second, the assumption of preferential dissociation/recombination could be made. Preferential dissociation means that it is assumed that molecules which are in a highly excited vibrational state are more likely to dissociate than molecules which do not carry a large amount of vibrational energy. Preferential recombination means that recombining atoms are likely to produce vibrationally highly excited molecules.

In the literature several models can be found to account for preferential dissociation/recombination. The Park $T_T$ model uses an alternate temperature in the forward reaction rates. In the Treanor & Marrone model vibration-weighted alterations are made on the reaction rates. For details, see also Gnooffo et. al. [4]. However, here we assume no vibration-chemistry coupling.

The importance of thermal nonequilibrium may be qualitatively illustrated by considering fast expanding high enthalpy nozzle flows or hypervelocity flows with very strong normal shock waves. In a rapidly expanding nozzle flow the required increase of kinetic energy of the gas is partly provided by the internal energy modes. Since the translational and rotational modes are considered to be in equilibrium the translational temperature immediately starts to decrease. Nonequilibrium chemistry becomes relevant since the predissociated high enthalpy flow starts to recombine due to the decreasing translational temperature, thus yielding chemical energy.

If we compare thermal equilibrium and thermal nonequilibrium expanding flow we observe the following. In the equilibrium case the transfer of internal energy from translational, rotational and vibrational energy modes occurs instantaneously. In the thermal nonequilibrium case the transfer of vibrational energy takes time, thus requiring more translational and rotational energy for the expansion of the flow. Translational temperature will be lower than for the thermal equilibrium case. Furthermore, freezing of the vibrational mode may occur as the flow expands and the flow time decreases. A higher level of storage of vibrational energy may be the result.
For problems with normal shock waves the situation is opposite. Over the shock wave the flow rapidly decelerates to subsonic velocities causing a release of a large amount of kinetic energy, which is to be partly transferred to the internal energy modes. Due to the thermo-chemical nonequilibrium assumption the translational temperature just behind the shock wave will almost reach the ideal gas flow value. The vibrational energy mode and chemistry will not have time to consume any energy when the flow passes a very thin shock wave. When thermal equilibrium is assumed the vibrational energy mode will instantaneously consume a certain amount of energy released over the shock wave.

The present investigation will govern the solution of quasi 1D thermo-chemical nonequilibrium nozzle flow by a cell centered finite volume numerical method. The steady state solution of the governing time-dependent equations is found by applying a point-implicit three-stage time integration scheme using local timestepping. In the point-implicit approach (see [1]), the vibrational and chemical source terms are treated implicitly whereas the flux differences are treated explicitly. Thus, the computational timestep depends only on the fluid time scales.

The calculation of the fluxes at cell interfaces is performed by a Roe-type flux difference splitting scheme for thermo-chemical nonequilibrium flow. In [10] we presented an efficient Roe-type scheme for chemically reacting flow in thermal equilibrium. Here, we have used the same concept to derive a scheme for thermo-chemical nonequilibrium flow. The scheme shows to be more simple than the scheme presented in [10]. The derivation is analogous to the derivation of the scheme for thermal equilibrium flow [10].

We will present calculations of quasi 1D nozzle flows with and without a normal shock wave. The results will be compared with the results of Sagnier & Maraffa [7] and of the Antibes workshop [12].
2 THERMO-CHEMICAL NONEQUILIBRIUM FLOW

2.1 Governing equations

Inviscid thermo-chemical nonequilibrium flow is described by the modified set of the Euler equations of motion. The system of nonlinear partial differential equations is composed of the species continuity equations, the global momentum equations, the global energy equation and the vibrational energy equations. For an n-species gas, consisting of m molecular species, the set of equations in conservative form reads:

\[
\frac{\partial q}{\partial t} + \frac{\partial f}{\partial x} + \frac{\partial g}{\partial y} + \frac{\partial h}{\partial z} = \Omega(q) + \Phi(q)
\]  

where \( q \) is defined as the statevector as:

\[
q = (\rho_1, \rho_2, \ldots, \rho_n, \rho_u, \rho_v, \rho_w, E, \rho_{n-m+1} e_{vn-m+1}, \ldots, \rho_n e_{vn})^t
\]  

The flux vectors \( f, g \) and \( h \) are given as:

\[
f = (\rho_1 u, \rho_2 u, \ldots, \rho_n u, \rho u^2 + p, \rho u v, \rho u w, (E+p)u, \rho_{n-m+1} e_{vn-m+1})
\]

\[
U, \ldots, (\rho_n e_{vn})^t
\]

\[
g = (\rho_1 v, \rho_2 v, \ldots, \rho_n v, \rho u v, \rho v^2 + p, \rho v w, (E+p)v, (\rho_{n-m+1} e_{vn-m+1})
\]

\[
v, \ldots, (\rho_n e_{vn})^t
\]

\[
h = (\rho_1 w, \rho_2 w, \ldots, \rho_n w, \rho u w, \rho v w, \rho w^2 + p, (E+p)w, (\rho_{n-m+1} e_{vn-m+1})
\]

\[
w, \ldots, (\rho_n e_{vn})^t
\]

The chemical source vector \( \Omega(q) \) is defined as

\[
\Omega(q) = (\Omega_1, \ldots, \Omega_n, 0, 0, 0, 0, \ldots, 0)^t
\]
and the vibrational source vector as:

\[ \Phi(q) = (0, 0, \ldots, 0, 0, 0, 0, \phi_{n-m+1}, \ldots, \phi_n)^t \]  

(2.5)

The global density \( \rho \) is defined as the sum of partial densities \( \rho_i \):

\[ \sum_{i=1}^{n} \rho_i = \rho \]  

(2.6)

\( E \) is total energy of the gas mixture per unit volume:

\[ E = \rho e + \frac{p}{\rho} (u^2 + v^2 + w^2) \]  

(2.7)

Specific enthalpy \( h \) is defined as

\[ h = e + \frac{p}{\rho} \]  

(2.8)

and total enthalpy \( H \) as:

\[ H = \frac{E + p}{\rho} \]  

(2.9)

For a mixture of perfect gases in thermal nonequilibrium the internal energy \( e \) becomes:

\[ e = \sum_{i=1}^{n} c_i e_i \]  

(2.10)

where \( c_i \) denotes the species mass fractions and \( e_i \) the species \( i \) contribution to internal energy:

\[ e_i = \frac{3}{2} R_i T + \delta_i R_i T + \delta_i e_{v_i} + \Delta e_i \]  

(2.11)

In equation (2.11) \( R_i \) denotes the gas constant, \( \Delta e_i \) the heat of formation and \( e_{v_i} \) the vibrational energy of species \( i \). \( \delta_i \) is the species discriminator, equal to one for diatomic species and equal to zero for monatomic species.
The gas is considered as a mixture of perfect gases, consequently the pressure \( p \) is given by

\[
p = \sum_{i=1}^{n} \rho_i R_i T
\]

(2.12)

The source terms in equation (2.4) account for the production and depletion of species due to finite rate chemistry. The source terms are explicitly given by:

\[
\Omega_i = M_i \sum_{j=1}^{r} \left( \nu_{ij}^' - \nu_{ij} \right) K_{F,j} \prod_{\alpha=1}^{\Pi} \left( \frac{\rho_{\alpha}}{M_{\alpha}} \right)^{\nu_{ij,\alpha}} - K_{B,j} \prod_{\alpha=1}^{\Pi} \left( \frac{\rho_{\alpha}}{M_{\alpha}} \right)^{\nu_{ij,\alpha}}
\]

(2.13)

A detailed description of the terms \( \Omega_i \) can be found in [10].

The source terms \( \Phi_i \) in the vibrational energy conservation equations, account for vibrational relaxation and are given by:

\[
\Phi_i = \left( \rho_i \dot{e}_{vi} \right) = \dot{\rho}_i e_{vi} + \rho_i \dot{e}_{vi}
\]

(2.14)

where the dots denote changes in time. Equation (2.14) expresses the time rate of change of the vibrational energy of molecular species \( i \).

### 2.2 Modelling thermal nonequilibrium

As stated in the previous paragraph, vibrational relaxation is governed by vibrational energy conservation equations

\[
\frac{3}{\partial t} (\rho_i e_{vi}) + \nabla \left( \rho_i e_{vi} \mathbf{u} \right) = (\rho_i \dot{e}_{vi})
\]

(2.15)

In equation (2.15) \( \rho_i e_{vi} \) denotes vibrational energy per unit volume of molecules \( i \). \( \nabla \) is the divergence operator and \( \mathbf{u} = (u, v, w)^t \) the velocity vector. The right-hand side of equation (2.15) expresses the time rate of change of vibrational energy. The source term is split into two parts, a chemical
reactive vibration source term $\dot{\rho}_i e_{\nu i}$, and a relaxation source term $\rho_i \dot{e}_{\nu i}$.

The chemical reactive vibration source term denotes the amount of vibrational energy that is destroyed or gained by dissociation or recombination processes respectively. It is modelled by:

$$\dot{\rho}_i e_{\nu i} = \Omega_i(q) \Delta_i$$

(2.16)

where $\Omega_i(q)$ is the time rate of change of molecules $i$ due to dissociation or recombination (cf. eq.(2.13)). $\Delta_i$ denotes the energy per unit of mass which is destroyed or created at rate $\Omega_i(q)$. If preferential dissociation/recombination is assumed $\Delta_i$ must be chosen larger than $e_{\nu i}$ (see Gnooffo et. al. [4]). As mentioned in section 1, we will not invoke preferential dissociation/recombination, hence we choose

$$\Delta_i = e_{\nu i}$$

(2.17)

Equation (2.17) states that the amount of energy destroyed or created at rate $\Omega_i$ equals the average vibrational energy of molecules $i$.

The vibrational relaxation source terms are modelled by a so-called Landau-Teller relation:

$$\rho_i \dot{e}_{\nu i} = \frac{\rho_i e_{\nu i}^* - \rho_i e_{\nu i}}{<\tau_i>}$$

(2.18)

where $e_{\nu i}^*$ denotes the equilibrium vibrational energy and, $<\tau_i>$ denotes the vibrational relaxation time. Relation (2.18) expresses the tendency of the vibrational energy mode towards equilibrium by means of inelastic molecular collisions in a characteristic time $<\tau_i>$. The vibrational relaxation time is defined by a relation due to Millikans & White (see Gnooffo et. al. [4]):
\[
p \tau_i = \frac{\sum_{j=1}^{n} \frac{\rho_j}{M_j} \exp \left( A_i \left( T^{-1/3} - 0.015 \mu_{ij}^{1/4} \right) - 18.42 \right)}{\sum_{j=1}^{n} \frac{\rho_j}{M_j}} \quad (2.19)
\]

where \( \mu_{ij} \) is the reduced mass of the colliding species \( i \) and \( j \):

\[
\mu_{ij} = \frac{M_i M_j}{M_i + M_j} \quad (2.20)
\]

The pressure \( p \) must be specified in atmospheres. The above correlation is valid for a temperature range of 300 to 8000 K. Above 8000 K the correlation must be altered (see [4]). The constants \( A_i \) are given for a five species gas in appendix A.

2.3 Governing equations for a quasi-1D nozzle flow in thermo-chemical nonequilibrium

For a five species gas \( \text{(N, O, N}_2, \text{O}_2, \text{NO)} \); i.e. \( n=5 \), \( m=3 \) in Eqs. (2.2) - (2.5) the equations for quasi-1D nozzle flow in thermal nonequilibrium may be found from equation (2.1):

\[
\frac{\partial q}{\partial t} + \frac{\partial f}{\partial x} = W(q) + \Omega(q) + \Omega_v(q) + \Lambda(q) \quad (2.21)
\]

where the state vector \( q \) is given as

\[
q = (\rho_1, \ldots, \rho_5, \rho u, E, \rho_3 e_{v3}, \rho_4 e_{v4}, \rho_5 e_{v5})^t \quad (2.22)
\]

and flux vector \( f \) as

\[
f = (\rho_1 u, \ldots, \rho_5 u, \rho u^2 + p, (E + p)u, \rho_3 e_{v3} u, \rho_4 e_{v4} u, \rho_5 e_{v5} u)^t \quad (2.23)
\]

The nozzle geometry is accounted for by the terms \( W(q) = -\frac{1}{A} \frac{dA}{dx} G(q) \) where \( A = A(x) \) denotes the nozzle area distribution and \( G(q) \) is given by:
\[ G(q) = (\rho_1 u, \ldots, \rho_5 u, \rho u^2, (E + p)u, \rho_3 u e_{v_3}, \ldots, \rho_5 u e_{v_5})^T \]  

(2.24)

The chemical sourceterms \( \Omega(q) \) are given by:

\[ \Omega_1(q) = M_1 (2r_2 + r_3 + r_1 + r_5) \]

\[ \Omega_2(q) = M_2 (2r_1 + r_3 - r_1 - r_3) \]

\[ \Omega_3(q) = M_3 (-r_2 - r_5) \]  

(2.25)

\[ \Omega_4(q) = M_4 (-r_1 + r_4) \]

\[ \Omega_5(q) = M_5 (-r_3 + -r_4 + r_5) \]

where \( r_1 \) to \( r_5 \) are given as:

\[ r_1 = \left\{ \sum_{i=1}^{5} \frac{\rho_1}{M_1} k_{F_{1,i}} \right\} \{ \frac{\rho_4}{M_4} - \frac{1}{k_1} \left( \frac{\rho_2}{M_2} \right)^2 \} \]

\[ r_2 = \left\{ \sum_{i=1}^{5} \frac{\rho_3}{M_3} k_{F_{2,i}} \right\} \{ \frac{\rho_3}{M_3} - \frac{1}{k_2} \left( \frac{\rho_1}{M_1} \right)^2 \} \]

\[ r_3 = \left\{ \sum_{i=1}^{5} \frac{\rho_5}{M_5} k_{F_{3,i}} \right\} \{ \frac{\rho_3}{M_3} - \frac{1}{k_3} \left( \frac{\rho_1 \rho_2}{M_1 M_2} \right) \} \]  

(2.25)

\[ r_4 = k_{F_4} \left( \frac{\rho_2}{M_2} \frac{\rho_5}{M_5} - \frac{1}{k_4} \frac{\rho_1 \rho_4}{M_1 M_4} \right) \]

\[ r_5 = k_{F_5} \left( \frac{\rho_2}{M_2} \frac{\rho_3}{M_3} - \frac{1}{k_5} \frac{\rho_1 \rho_5}{M_1 M_5} \right) \]

Data on the reaction constants \( k_F \) and \( k^* \) can be found in [10].
The vibrational reactive source terms $\Omega_v(q)$ are chosen as in equation (2.16) with $\hat{d}_i$ as given in equation (2.17). The vibrational relaxation source term $\Lambda$ are chosen according to equation (2.18) with $<\tau_i>$ as specified in equation (2.19) for a five species gas.

3 NUMERICAL MODELLING

The equations of motion for quasi one-dimensional nozzle flows (Eq. (2.21)) are numerically solved by an upwind, cell centered, finite volume method.

The spatial discretization is based on the one-dimensional Riemann problem. The ideas of Roe [5] are used to develop an approximate Riemann solver. The fluxes on cell intersections are given by a numerical flux function $f_R(q_L, q_R)$, with $q_L$ and $q_R$ the interpolated state vectors respectively to the left and to the right of the intersection.

In the next section we present an efficient algorithm for the numerical flux function of the Roe-type for thermo-chemical nonequilibrium flows. In section 3.2 the spatial accuracy of the scheme is discussed and a point-implicit three-stage integration procedure is given.

3.1 A Roe-type scheme for thermo-chemical nonequilibrium flow

In the following paragraph we give the algorithm for the numerical flux function for thermo-chemical nonequilibrium flow of a five component gas with three molecular species. Basically, the procedure is the same as presented in [10] for thermal equilibrium flow

Let $q_L$ and $q_R$ be the left and right states (in 3D)

$q_L = (\rho_1, \ldots, \rho_5, \rho u, \rho v, \rho w, E, \rho_3 e_{v3}, \ldots, \rho_5 e_{v5})^T_L$

$q_R = (\rho_1, \ldots, \rho_5, \rho u, \rho v, \rho w, E, \rho_3 e_{v3}, \ldots, \rho_5 e_{v5})^T_R$. 
The flux function then becomes:

\[ f_r(q_L, q_R) = \frac{1}{2} \left( f(q_L) + f(q_R) - (\tilde{u} b + \tilde{a}_1 \tilde{u} a) \tilde{R}_1 + \tilde{a}_2 \tilde{u} a \tilde{R}_2 \right) \]  

(3.1)

where

\[ \tilde{R}_1 = (\tilde{c}_1, \ldots, \tilde{c}_5, \tilde{u} - \tilde{a}, \tilde{v}, \tilde{w}, \tilde{H} - \tilde{u} \tilde{a}, (\rho \\tilde{e}_v)_3, \ldots, (\rho \tilde{e}_v)_5)^\tau \]

\[ \tilde{R}_2 = (\tilde{c}_1, \ldots, \tilde{c}_5, \tilde{u} + \tilde{a}, \tilde{v}, \tilde{w}, \tilde{H} + \tilde{u} \tilde{a}, (\rho \tilde{e}_v)_3, \ldots, (\rho \tilde{e}_v)_5)^\tau \]

and

\[ \tilde{a}_1 = \frac{1}{2a^2} (\Delta p - \tilde{\rho} \tilde{a} \Delta \omega), \quad \tilde{a}_2 = \frac{1}{2a^2} (\Delta p + \tilde{\rho} \tilde{a} \Delta \omega) \]

The operator \( \Delta \) is defined as:

\[ \Delta(\cdot) = (\cdot)_R - (\cdot)_L \]

and, furthermore

\[ \tilde{\rho} = \sqrt{\rho_L \rho_R}, \quad \theta = \frac{\rho_L}{\sqrt{\rho_L + \rho_R}} \]

\[ \tilde{u} = \theta u_L + (1-\theta) u_R, \quad \tilde{v} = \theta v_L + (1-\theta) v_R, \quad \tilde{w} = \theta w_L + (1-\theta) w_R \]

\[ \tilde{H} = \theta H_L + (1-\theta) H_R, \quad \tilde{c}_i = \theta c_i^L + (1-\theta) c_i^R, \]

\[ (\rho \tilde{e}_v)_j = \theta (\rho_j \tilde{e}_v^j)_L + (1-\theta) (\rho_j \tilde{e}_v^j)_R \]

The vector \( b \) is computed according to

\[ b = \Delta q - \tilde{a}_1 \tilde{R}_1 - \tilde{a}_2 \tilde{R}_2 \]
As a result, \( f_R (q_L, q_R) \) can be written as:

\[
f_R (q_L, q_R) = \frac{1}{2} \{ f(q_L) + f(q_R) \} - (|\vec{u}| \Delta q + \tilde{a}_1 (|\vec{u} - \tilde{a}| - |\vec{u}|) \tilde{R}_1 \\
\quad + \tilde{a}_2 (|\vec{u} + \tilde{a}| - |\vec{u}|) \tilde{R}_2 \tag{3.2}
\]

In the present formulation there is still one degree of freedom left: the choice of the Roe average of the frozen speed of sound \( \tilde{a} \). In [11] it was shown that the expression for \( \tilde{a} \) is given by:

\[
\tilde{a}^2 = \frac{\tilde{R}}{\tilde{\rho}} \left\{ \frac{\tilde{\rho} \tilde{T}}{\Sigma \tilde{c}_i R_i} \left( \frac{5}{i=1} \right) + \frac{5}{\Sigma \tilde{c}_i R_i} \right\} \tag{3.3}
\]

where \( R_i \) denotes the gas constant of species \( i \), and

\[
\tilde{\rho} = \tilde{\rho} (\tilde{H} - \tilde{e} - 1/2 (\tilde{u}^2 + \tilde{v}^2 + \tilde{w}^2)) \\
\tilde{e} = \Theta e_L + (1-\Theta)e_R, \quad \tilde{T} = \Theta T_L + (1-\Theta)T_R.
\]

For a gas in thermal nonequilibrium it follows that

\[
\frac{5}{\Sigma \tilde{c}_i \Delta T_i} = 3/2 \tilde{c}_1 R_1 + 3/2 \tilde{c}_2 R_2 + 5/2 \tilde{c}_3 R_3 + 5/2 \tilde{c}_4 R_4 + 5/2 \tilde{c}_5 R_5
\]

The expression for \( \tilde{a} \) may be put in a more familiar form if we furthermore define

\[
\tilde{c}_v = \Sigma \tilde{c}_i \Delta e_i / \Delta T_i, \quad \tilde{R} = \Sigma \tilde{c}_i R_i, \quad \tilde{c}_p = R + \tilde{c}_v, \quad \gamma = \frac{\tilde{c}_p}{\tilde{c}_v}
\]

by which \( \tilde{a}^2 \) becomes

\[
\tilde{a}^2 = (\gamma - 1) \left( \frac{\tilde{c}_v \tilde{T} + \tilde{\rho}}{\tilde{\rho}} \right) \tag{3.4}
\]
By defining \( \tilde{a} \) as in equation (3.3) or equation (3.4), it can be proved that if two states \( q_L \) and \( q_R \) obey the Rankine-Hugoniot relations then there exists a one-parameter family of intermediate states \( q_m \), such that

\[
f(q_L) = f_R(q_L, q_m) = f_R(q_m, q_R) = f(q_R).
\]

The above property implies (at least in one dimension) that steady shock waves are captured by the scheme with only one interior grid point.

Finally, it can easily be seen that for the special case of a one-component gas, the scheme presented here is identical to the original Roe-scheme presented in [5].

### 3.2 Final discretization

The semi-discretized form of the governing equations of motion (Eq. (2.21)) reads:

\[
\frac{d}{dt} q_i(t) = -F_i - \frac{d}{dt} \left( W_i(q_i(t)) + \Omega(q_i(t)) + \Lambda(q_i(t)) + \Omega_v(q_i(t)) \right)
\]

where \( q_i(t) \) is the mean value of the state \( q \) in volume \( i \) at time \( t \). The flux differences are denoted by \( F_i \):

\[
F_i = \frac{1}{\Delta x_i} \left[ f_R \left( q_{i+\frac{1}{2}}^L(t), q_{i+\frac{1}{2}}^R(t) \right) - f_R \left( q_{i-\frac{1}{2}}^L(t), q_{i-\frac{1}{2}}^R(t) \right) \right]
\]

where \( f_R \left( q_{i+\frac{1}{2}}^L(t), q_{i+\frac{1}{2}}^R(t) \right) \) denotes the flux at the intersection of volume \( i \) and \( i+1 \) at time \( t \). The left and right states \( q_{i+\frac{1}{2}}^L(t) \) and \( q_{i+\frac{1}{2}}^R(t) \) are found by using the van Albada limiter which combines second order spatial accuracy and monotonicity. The interpolation formulae can be found in [8, 10]. The limiter is applied to the variables \( \rho_1, \ldots, \rho_5, u, T, e_v^3, e_v^4 \) and \( e_v^5 \). A first order accurate scheme is found when the left and right states are simply taken as the states in the cell center of the volume to the left and to the right of the intersection.
The integration in time is performed by a point-implicit three-stage scheme. The scheme reads:

\[ q^{(0)} = q_1^n, \quad \Delta t = \Delta t_i \]

\[ (I - a_1 \Delta t \frac{\partial^2}{\partial q^2} (q^{(0)})) (q^{(1)} - q^{(0)}) = a_1 \Delta t \{ -F^{(0)} + \zeta(q^{(0)}) + \dot{\omega}(q^{(0)}) \} \]

\[ (I - a_2 \Delta t \frac{\partial^2}{\partial q^2} (q^{(0)})) (q^{(2)} - q^{(0)}) = a_2 \Delta t \{ -F^{(1)} + \zeta(q^{(0)}) + \dot{\omega}(q^{(1)}) \} \]

\[ (I - a_3 \Delta t \frac{\partial^2}{\partial q^2} (q^{(0)})) (q^{(3)} - q^{(0)}) = a_3 \Delta t \{ -F^{(2)} + \zeta(q^{(0)}) + \dot{\omega}(q^{(2)}) \} \]

\[ q_1^{n+1} = q^{(3)} \]

The source terms due to vibrational and chemical processes were linearized according to

\[ \zeta(q^{(k)}) = \zeta(q^{(0)}) + \frac{\partial \zeta}{\partial q} (q^{(0)}) (q^{(k)} - q^{(0)}) \]

where \( \zeta(q^{(k)}) \) is the vectorial sum of \( \Omega(q^{(k)}) \), \( \Omega_v(q^{(k)}) \) and \( \Lambda(q^{(k)}) \). The stage coefficients were taken from [6] as

\[ a_1 = 0.2, \quad a_2 = 0.5, \quad a_3 = 1.0. \]

The presently proposed approach requires the inversion of the 10 x 10 full matrix,

\[ I - a_i \Delta t \frac{\partial^2}{\partial q^2} (q^{(0)}) \]

at each volume and in each stage.
4 NUMERICAL RESULTS

4.1 Definition of testcases

The numerical scheme will be validated for four testcases yielding several testproblems. All cases concern quasi 1D-nozzle flows. The flows considered may be either shock-free or a normal shock wave may be encountered somewhere in the nozzle.

Testcases A–C concern the flow in a linearly diverging nozzle. The nozzle geometry is fully defined by the length \( l \), the throat radius \( r_0 \) or the throat area \( A_0 = \pi r_0^2 \), and the cone half angle \( \psi \) (Fig. 4.1).

![Fig. 4.1 Linear nozzle; geometry](image)

For the linear nozzle we completely specify the reservoir and throat conditions for the Dunn & Kang chemistry model. The reservoir or stagnation conditions are represented by pressure, temperature, density, total enthalpy, and species mass fractions. The throat conditions are easily computed under the assumption that in the region between reservoir and throat the flow is in complete (thermodynamical) equilibrium. The throat conditions are used as the inlet boundary conditions for the flow computations in the nozzles. In the throat the velocity is such that the Mach number based on the equilibrium speed of sound equals one.
TESTCASE A (Sagnier & Maraffa [7])

Problem I:

Geometry

\[ \psi = 11.3^\circ \]
\[ l = 19.0 \text{ cm} \]
\[ r_0 = 0.56 \text{ cm at } x = 3.5 \text{ cm} \]
\[ A_o = 1 \text{ cm}^2 \]

Reservoir Conditions:

\[ p_o = 50 \text{ bar} \]
\[ T_o = 4800 \text{ K} \]
\[ \rho = 3.26 \text{ kg m}^{-3} \]
\[ H = 8.01 \text{ MJ/kg} \]
\[ C_N = 0.13 \% \]
\[ C_O = 10.93 \% \]
\[ C_{N2} = 71.70 \% \]
\[ C_{O2} = 6.79 \% \]
\[ C_{NO} = 10.45 \% \]

Throat conditions

\[ p = 28.15 \text{ bar} \]
\[ T = 4404 \text{ K} \]
\[ \rho = 2.03 \text{ kg/m}^3 \]
\[ H = 8.01 \text{ MJ/kg} \]
\[ u = 1293 \text{ m/s} \]
\[ C_N = 0.05 \% \]
\[ C_O = 9.22 \% \]
\[ C_{N2} = 72.00 \% \]
\[ C_{O2} = 8.78 \% \]
\[ C_{NO} = 9.95 \% \]

TESTCASE B (Sagnier & Macaffa [7])

Problem II:

Geometry

\[ \psi = 10^\circ \]
\[ l = 200 \text{ cm} \]
\[ r_0 = 1 \text{ cm at } x = 0 \text{ cm} \]
\[ A_o = 3.14 \text{ cm}^2 \]
Reservoir Conditions:
\[ p_0 = 600 \text{ bar} \]
\[ T_0 = 10000 \text{ K} \]
\[ \rho = 14.59 \text{ kg m}^{-3} \]
\[ H = 24.42 \text{ MJ/kg} \]
\[ C_N = 23.0 \% \]
\[ C_O = 20.64 \% \]
\[ C_{N2} = 51.59 \% \]
\[ C_{O2} = 0.25 \% \]
\[ C_{NO} = 4.52 \% \]

Throat conditions
\[ p = 337.99 \text{ (bar)} \]
\[ T = 9275 \text{ K} \]
\[ \rho = 9.09 \text{ kg/m}^3 \]
\[ H = 24.42 \text{ MJ/kg} \]
\[ u = 2118 \text{ (m/s)} \]
\[ C_N = 19.40 \% \]
\[ C_O = 20.76 \% \]
\[ C_{N2} = 55.29 \% \]
\[ C_{O2} = 0.24 \% \]
\[ C_{NO} = 4.31 \% \]

TESTCASE C (Antibes workshop, problem 8, [12])

Problem III:
Geometry
\[ \psi = 10^\circ \]
\[ \ell = 113 \text{ cm} \]
\[ r_0 = 0.6 \text{ cm} \]
\[ A_0 = 1.13 \text{ cm}^2 \text{ at } x = 0 \text{ cm} \]

Reservoir Conditions:
\[ p_0 = 1530 \text{ bar} \]
\[ T_0 = 6500 \text{ K} \]
\[ \rho = 73.21 \text{ kg m}^{-3} \]
\[ H = 10.45 \text{ MJ/kg} \]
\[ C_N = 0.65 \% \]
\[ C_O = 10.23 \% \]
\[ C_{N2} = 69.15 \% \]
\[ C_{O2} = 5.19 \% \]
\[ C_{NO} = 14.78 \% \]
Throat conditions

\[ \begin{align*}
 p &= 850.41 \text{ bar} \\
 T &= 5865 \text{ K} \\
 \rho &= 45.95 \text{ kg/m}^3 \\
 H &= 10.45 \text{ MJ/kg} \\
 u &= 1515 \text{ m/s} \\
 C_N &= 0.32 \% \\
 C_O &= 9.16 \% \\
 C_{N_2} &= 69.83 \% \\
 C_{O_2} &= 6.66 \% \\
 C_{N_O} &= 14.03 \%
\end{align*} \]

Problem IV:

Geometry

\[ \begin{align*}
 \psi &= 10^\circ \\
 l &= 113 \text{ cm} \\
 r_0 &= 0.6 \text{ cm at } x = 0 \text{ cm} \\
 A_0 &= 1.13 \text{ cm}^2
\end{align*} \]

Reservoir Conditions:

\[ \begin{align*}
 p_0 &= 1000 \text{ bar} \\
 T_0 &= 10000 \text{ K} \\
 \rho &= 25.33 \text{ kg m}^3 \\
 H &= 22.59 \text{ MJ/kg} \\
 C_N &= 18.15 \% \\
 C_O &= 19.15 \% \\
 C_{N_2} &= 55.78 \% \\
 C_{O_2} &= 0.39 \% \\
 C_{N_O} &= 5.93 \%
\end{align*} \]

Throat conditions

\[ \begin{align*}
 p &= 562.21 \text{ bar} \\
 T &= 9241 \text{ K} \\
 \rho &= 15.77 \text{ kg/m}^3 \\
 H &= 22.59 \text{ MJ/kg} \\
 u &= 2077 \text{ m/s} \\
 C_N &= 14.90 \% \\
 C_O &= 19.89 \% \\
 C_{N_2} &= 59.15 \% \\
 C_{O_2} &= 0.39 \% \\
 C_{N_O} &= 5.67 \%
\end{align*} \]
Testcase D concerns a nonlinear nozzle geometry, where the area distribution $A(x)$ is given by

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

where $x$ is in cm. The nozzle inlet is located at $x = 1.2$ cm, the nozzle exit at $x = 8.0$ cm.

![Non-linear nozzle; geometry](image)

**Fig. 4.2** Non-linear nozzle; geometry

The conditions in the inlet and the pressure in the exit are specified. The inlet conditions correspond to a Mach number $M_\infty$ and an altitude above earth’s surface ($h$, in km's).

**TESTCASE D** (Chiang & Hoffmann, '21)

Problem V (low altitude case)

Inlet conditions

- $h = 20$ km
- $M_\infty = 20$
- $p_\infty = 5.529 \times 10^{-2}$ bar
- $T_\infty = 230.44$ K
- $\rho_\infty = 8.245 \times 10^{-2}$ kg/m$^3$
- $e_\infty = 167.46$ kJ/kg
- $U_\infty = 6125$ m/s

- $C_{N_\infty} = 0$ %
- $C_{O_\infty} = 0$ %
- $C_{N_2_\infty} = 76.71$ %
- $C_{O_2_\infty} = 23.29$ %
- $C_{N_O_\infty} = 0$ %
\( P_{\text{exit}}/P_\infty = 429.46 \)

Problem VI (High altitude case)

\[
\begin{align*}
  h &= 70 \text{ km} \\
  M_\infty &= 20 \\
  p_\infty &= 5.52 \times 10^{-5} \text{ bar} \\
  T_\infty &= 230.44 \text{ K} \\
  \rho_\infty &= 8.241 \times 10^{-5} \text{ kg/m}^3 \\
  e_\infty &= 167.46 \text{ kJ/kg} \\
  U_\infty &= 6125 \text{ m/s} \\
  P_{\text{exit}}/P_\infty &= 429.46
\end{align*}
\]

4.2 Discussion of results

Problem I

The results on the "short" nozzle (\( l = 19.0 \text{ cm} \)) are shown in figures (1-6). For thermal equilibrium as well as thermal nonequilibrium flow. Also a comparison is made with results of Sagnier & Maraffa [7]. The present flow computations are performed on a 200 volumes mesh with a stretching such that more volumes are located in the first part of the nozzle.

In the shock-free expanding flow through a linearly diverging nozzle, the influence of thermal nonequilibrium, compared to thermal equilibrium, shows a further decrease of pressure and temperature (Fig. 1,2). The expansion of the flow requires internal energy to increase the gas kinetic energy. Energy is instantaneously released by the equilibrium translational and rotational modes only. The assumption of thermal nonequilibrium and the rapidly decreasing characteristic flow time cause a freezing of the vibrational modes of \( N_2 \), \( O_2 \) and NO (Fig. 3, \( T_{v,N_2} = 3600 \text{ K}, T_{v,O_2} = 2000 \text{ K}, T_{v,NO} = 2700 \text{ K} \)).
This results in a storage of vibrational energy above the equilibrium level. As a consequence, more energy must be released by the equilibrium translational and rotational modes, hence temperature and pressure decrease.

Finite rate chemistry does not show to be very much affected by the assumption of thermal nonequilibrium. Figures (4,5) show the most affected species.

The Mach number (Fig. 6) based on the frozen speed of sound shows to be one of the strongest influenced flow parameters. An increase of about 18 % is observed in the exit in comparison with thermal equilibrium flow. In [7] also an experimental value of the Mach number in the exit is given: $M_{exit} \sim 6.4$. Hence, it is clear that the assumption of thermal nonequilibrium is relevant for this problem.

A comparison with numerical results presented in [7] is made on pressure and temperature (Figs. 1,2). It must be noted here, that Sagnier & Maraffa used a different modelling of vibrational nonequilibrium. First, they applied a vibration - chemistry coupling as suggested by Treanor & Marrone (non-preferential coupling). Second, Sagnier & Maraffa did not consider the vibrational mode of NO out of equilibrium. Nevertheless, a comparison does not show any obvious differences. Differences in vibrational temperatures were to be expected. Sagnier & Maraffa found a freezing of $Tv_{N2}$ at 3000 K ($Tv_{N2} \sim 3600$ K in present computations) and $Tv_{O2}$ at 2000 K ($Tv_{O2} \sim 2000$ K in present computations). Also Flamant [3] showed some results for the same problem. His results agree very well with the present computations. Flamant considered non-preferential vibration-chemistry coupling but he also considered the nonequilibrium vibrational mode of NO. Almost identical frozen vibrational temperatures are found as a result.

The location at which freezing occurs was found to be slightly different compared to [7]. In [7] freezing of $N_2$-vibrational mode occurs at $x = 8$ cm whereas the present computations show freezing of $N_2$-vibrational mode at about $x = 6$ cm. The presently obtained results agree very well with Flamant. Freezing of $O_2$-vibrational mode did not show these large discrepancies.
Problem II

Problem II covers the computation of the flow in the "long" (x = 200 cm) Sagnier & Maraffa nozzle with rather severe stagnation conditions (p_o = 600 bar, T_o = 10000 K). The high pressure and temperature give rise to a high collision frequency and therefore high relaxation rates of chemistry and vibrational modes. The computation is performed on a mesh identical to that of problem I.

A comparison between thermal equilibrium and thermal nonequilibrium flow for pressure and temperature is depicted in figures (7,8). The tendency of decreasing pressure and temperature as found for problem I is again observed. The results are almost identical with those found in [7], see figures (7,8).

Due to the small relaxation times compared to the characteristic flow time, in the first part of the nozzle, freezing of vibrational modes requires a relatively long path to occur, especially for O_2 (Fig. 9). Vibrational modes are in equilibrium with the translational/rotational modes up to the point where freezing occurs. Despite the long path before freezing, the level at which it occurs is relatively high (T_v N_2 ~ 4000 K, T_v O_2 ~ 2200 K, T_v NO ~ 3000 K).

The influence of vibrational nonequilibrium will be mainly due to N_2. nitric-oxide and molecular oxygen exist in only very small amounts, thus not requiring large amounts of vibrational energy. Figures (10,11) show the influence in the composition of the gas. It is seen that the assumption made in [7] i.e. not to consider the nonequilibrium vibrational mode of NO is not a major one.

The Mach number, depicted in figure 12 again shows that a higher value in the exit is reached when thermal nonequilibrium is considered.

Problem III

Problem III concerns the nominal case of problem 8 of the Antibes Workshop [12]. The stagnation conditions are high pressure (p_o = 1530 bar) and moderate high temperature (T_o = 6500 K). The comparison of temperature and pressure for thermal equilibrium and nonequilibrium flow shows the well known effects (Figs. 13, 14).
Due to the high pressure, the relaxation processes will initially be very fast. This is shown by the rapid decrease of translational temperature. Temperature is strongly affected by finite rate chemistry which shows a strong tendency towards equilibrium gas composition. On the other hand, the flow rapidly expands. Hence, the flow time decreases rapidly. Along with the "low" temperature and pressure this results in an early freezing of the composition of the gas and of vibrational modes (Fig. 13). Due to the early freezing of the relaxation processes the composition of the gas is not affected by the thermal nonequilibrium assumption.

The major effects are found in the Mach number distribution (Fig. 14). Differences are observed in almost the entire nozzle. The maximum difference occurs in the nozzle exit, about 10% higher Mach number for thermal nonequilibrium flow.

Comparison of present computations with results listed in [12] do not reveal any relevant discrepancies. The agreement with Zeihoun et. al. and Gnoffo is very good (see [12]). Differences are observed in chemical composition due to different chemical models (Park for Antibes Workshop, Dunn & Kang for the present computations).

Problem IV

In figures (15-17) the results of the computation of the flow in the nozzle with a high stagnation temperature \( T_0 = 10000 \text{ K} \) are shown. Computations are performed on a 200 volumes mesh with a stretching as discussed for problem I. The results will be briefly discussed.

The main difference with problem III is that the high temperature level causes a higher level of freezing of vibrational modes (Fig. 15). Nevertheless, the effects in pressure and temperature appear to be qualitatively the same. The finite rate chemistry is not much affected by thermal nonequilibrium as depicted by figure 16. The composition of the gas in the exit is merely different from the thermal equilibrium case.
As was expected, the Mach number (Fig. 17) shows a major dependence on thermal nonequilibrium. In the exit, the Mach number is about 18% higher than for the thermal equilibrium case.

The present results are in good agreement with numerical results presented in [12].

Problem V

Results of the computation of the flow through a nonlinear nozzle with a severe shock wave are given in figures (18-22). The computations are performed on a 200 volumes equidistant mesh. The conditions specified in the nozzle inlet are such that a very narrow relaxation zone develops downstream of the shock wave.

In the relaxation zone, pressure and temperature are such that small relaxation times occur. Since the flow is decelerated through the shock to subsonic speed, the characteristic flow time will be large compared to the relaxation times. As a result, the relaxation processes will be limited to very narrow regions in the flow field.

The relaxation zone appears to be represented by only 2 volumes (Fig. 18). The tendency towards frozen flow values first behind the shock is visible, though actual values are incorrect. It is observed that the solution downstream of the relaxation zone is not affected by the incorrect representation of the relaxation zone.

From figures (18, 19) we observe that the thermal nonequilibrium processes develop so fast that the influence of vibrational nonequilibrium is negligible.

The distribution of N and NO species is depicted in figures (20, 21). An almost instant increase in mass fractions was to be expected at the high pressure and density conditions.
The insensitivity of the flow for the vibrational nonequilibrium modes is nicely shown in figure 22. From this graph we observe that in front of the shock wave vibrational modes are frozen (increasing vibrational temperatures with decreasing translational temperature). Downstream of the relaxation zone, the vibrational modes are in equilibrium with the translational/rotational modes. It is observed that the NO-vibrational mode is in equilibrium with the translational/rotational modes immediately behind the shock. $T_{v\text{NO}}$ exactly follows the translational temperature $T_{\text{neq}}$.

Problem VI

Problem VI is more appropriate to show the influence of thermal nonequilibrium on flows with strong shock waves. The inlet conditions yield post-shock conditions such that the collision frequency is much smaller than for problem V. As a consequence, a more extensive relaxation zone will develop. The computations are performed on a 200 volumes equidistant mesh.

The temperature distribution (Fig. 23) shows the more extensive relaxation zone. It is also seen that downstream of the shock wave the thermal nonequilibrium temperature peak is significantly higher than the equilibrium value. This was to be expected since the assumption of vibrational nonequilibrium causes the vibrational modes and the chemical comparison to freeze as the flow passes the shock. Hence, the kinetic energy released over the shock is almost entirely consumed by the equilibrium translational/rotational modes. The temperature will tend towards the ideal gas value ($T_{\text{ideal}} \sim 18500$ K). Furthermore, it is observed that differences between thermal equilibrium and nonequilibrium are restricted to the relaxation zone.

The same behaviour is observed for the density (Fig. 24). Immediately behind the shock wave the density is lower (close to the ideal gas value) for the thermal nonequilibrium case.

The behaviour of the vibrational modes of molecules is nicely shown in figure 35. Upstream of the shock the vibrational energy is frozen at inlet level. Downstream of the shock wave it is observed that the vibrational mode of NO
behaves differently compared with the vibrational modes of N₂ and O₂. It is stated that the vibrational mode of molecules of a certain species that occur in only very small amounts, easily equilibrate. This explains the behaviour of the vibrational mode of NO first behind the shock. Furthermore, the O₂-molecules are found to be in thermal equilibrium from the point where almost all O₂-molecules are dissociated. N₂ takes a longer path, up to the nozzle exit, to reach thermal equilibrium.

Convergence history

In figures (29, 30) we present the convergence history of computations of respectively, shock free nozzle flows and flows with a strong shock wave. Compared with the results for thermal equilibrium flow (see [10]) it appears that about the same number of iterations is needed to converge to a steady state solution.

The convergence strategy is almost identical as presented in [10]. For the shock free flows we used a uniform flow field as an initial solution for the first-order computations. The CFL-path is set according to:

iteration  0 - 999          CFL = 10⁻¹
           1000 - 1500        CFL = 10⁰

After about 1500 iterations a fully converged first-order solution is achieved. The first-order solution is used as an initial solution for the second order computation. With the CFL-number set to 10⁰, convergence is accomplished after about 500 iterations. A three-step time integration has been applied for shock free flows.

The strategy for flows with normal shock waves is somewhat different. First, a frozen flow solution, where vibrational modes are in equilibrium with the translational/rotational mode is obtained and used as an initial solution for computation of thermal nonequilibrium flow.
A converged first-order solution was obtained using the following CFL-strategy

<table>
<thead>
<tr>
<th>Iteration</th>
<th>CFL</th>
<th>Integration scheme</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 - 499</td>
<td>$10^{-3}$</td>
<td>forward Euler</td>
</tr>
<tr>
<td>500 - 999</td>
<td>$10^{-1}$</td>
<td>forward Euler</td>
</tr>
<tr>
<td>1000 - 12000</td>
<td>$10^0$</td>
<td>three-stages</td>
</tr>
</tbody>
</table>

The thermal nonequilibrium code is considerably more expensive than the thermal equilibrium code [9]. On a NEC-SX2 super computer, 1000 iterations by the equilibrium code take approximately 7 CPU secs on a 200 volumes mesh whereas the full nonequilibrium code consumes about 100 CPU secs for 1000 iterations on a 200 volumes mesh.

Analysis of the time consumption showed that about 90% is used for the inversion of a $10 \times 10$ matrix on each volume for the thermal nonequilibrium code.

5 CONCLUSIONS

Chemically reacting flow in thermal nonequilibrium has been modelled in a straightforward manner. No coupling between chemistry and vibration has been applied. Dissociation and recombination are considered as nonpreferential chemical processes.

An efficient Roe type flux difference scheme has been presented. A three-stage point-implicit time integration scheme is applied to converge to steady state solutions.

A set of testproblems has been computed for both thermal equilibrium and nonequilibrium quasi 1D nozzle flow. Shock free flows as well as flows with strong normal shock waves have been considered.

Numerical results for the shockfree nozzle flows show a freezing of vibrational energy modes. As a result, pressure and temperature are relatively lower than
for thermal equilibrium flows. The Mach number, based on the frozen speed of sound, is found to be significantly higher than the thermal equilibrium value.

The chemistry in the flow appears to be almost unaffected by vibrational relaxation processes.

Comparison of the present numerical results with results listed in literature show a very good agreement. Although differences in modelling vibrational nonequilibrium were present. From the comparison it seems that vibration-chemistry coupling and preferential dissociation are not essential to obtain correct flow solutions.

The computational results for flows with strong normal shock waves show the excellent shock capturing capabilities of the Roe scheme.

Computation of the flow field with a strong shock wave followed by a very narrow relaxation zone shows that the flow is insensible to thermal nonequilibrium. Although the flow is not well represented in the relaxation zone, the length of the relaxation zone is of the order of one mesh cell, it appears that downstream of the relaxation zone the solution is correct.

The results for the flow field with a normal shock wave and a more extensive relaxation zone show a better representation of the flow in the relaxation zone. Just behind the shock wave the expected ideal gas temperature and density are achieved. Although vibrational nonequilibrium exists it appears to have almost no influence on the composition of the gas.

For the given convergence strategy the numerical scheme appears to be robust for both shock free flows and flows with strong normal shock waves. The code appears to be much more expensive than the thermal equilibrium code [10]. Computational CPU-times are increased by a factor 15.
6 REFERENCES

Fig. 1 Thermo-chemical and chemical nonequilibrium: pressure

Fig. 2 Thermo-chemical and chemical nonequilibrium: temperature
Fig. 3 Vibrational and translational temperatures

Fig. 4 Molar concentration: atomic oxygen
Fig. 5  Molar concentration: nitric oxide

Fig. 6  Thermo-chemical and chemical nonequilibrium: Mach number
Fig. 7 Thermo-chemical and chemical nonequilibrium: pressure

Fig. 8 Thermo-chemical and chemical nonequilibrium: temperature
Fig. 9 Vibrational and translational temperatures

Fig. 10 Molar concentration: molecular oxygen
Fig. 11  Molar concentration: nitric oxide

Fig. 12  Thermo-chemical and chemical nonequilibrium:
Mach number
Fig. 13 Vibrational and translational temperatures

Fig. 14 Thermo-chemical and chemical nonequilibrium: Mach number
Fig. 15 Vibrational and translational temperatures

Fig. 16 Mass fraction: atomic oxygen
Fig. 17 Thermo-chemical and chemical nonequilibrium: Mach number

Fig. 18 Thermo-chemical and chemical nonequilibrium: temperature
Fig. 19 Thermo-chemical and chemical nonequilibrium: pressure

Fig. 20 Mass fraction: atomic nitrogen
Fig. 21 Mass fraction: nitric oxide

Fig. 22 Vibrational and translational temperatures
Fig. 23 Thermo-chemical and chemical nonequilibrium: temperature

Fig. 24 Thermo-chemical and chemical nonequilibrium: density
Fig. 25 Vibrational and translational temperatures

Fig. 26 Mass fraction: nitric oxide
Fig. 27 Mass fraction: molecular oxygen

Fig. 28 Mass fraction: molecular nitrogen
Fig. 29 Convergence history: shock-free flow

Fig. 30 Convergence history: flow with strong normal shockwave
### APPENDIX A

Data on species characteristic

<table>
<thead>
<tr>
<th></th>
<th>( m_i ) (g mol(^{-1}))</th>
<th>( \theta_i ) (K)</th>
<th>( \Delta e_i ) ((10^{10}) cm(^2) s(^{-2}))</th>
<th>( A_i )</th>
<th>( R_i ) ((10^6) cm(^2) s(^{-2}) K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>14</td>
<td>15.4</td>
<td>33.6</td>
<td>-</td>
<td>5.94</td>
</tr>
<tr>
<td>O</td>
<td>16</td>
<td>-</td>
<td>15.4</td>
<td>-</td>
<td>5.20</td>
</tr>
<tr>
<td>(\text{N}_2)</td>
<td>28</td>
<td>3390</td>
<td>-</td>
<td>220</td>
<td>2.97</td>
</tr>
<tr>
<td>(\text{O}_2)</td>
<td>32</td>
<td>2270</td>
<td>-</td>
<td>129</td>
<td>2.59</td>
</tr>
<tr>
<td>(\text{NO})</td>
<td>30</td>
<td>2740</td>
<td>2.99</td>
<td>168</td>
<td>2.77</td>
</tr>
</tbody>
</table>