THE STEADY SHOCK PROBLEM
IN REACTIVE GAS MIXTURES

BY

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Dedicated to Prof. Y. Sone on his 70th birthday

Abstract

The shock structure in a gas mixture undergoing a bimolecular chemical reaction is studied by means of a reactive kinetic model. Rankine-Hugoniot relations and entropy conditions are investigated. The role of Mach number and concentration fractions, as well as the change of chemical composition across the shock, are emphasized.

1. Introduction

Bimolecular chemical reactions in dilute gaseous systems may be rigorously studied on the basis of kinetic theory in terms of Boltzmann-like integrodifferential nonlinear equations [1]; indeed, such an approach, in spite of its intrinsic difficulties of various kinds, is gaining interest in the scientific literature. Kinetic treatments of chemical reactions go back to pioneering times [2] and have reached considerable mathematical and physical depth [3]. They are all necessarily in the frame of kinetic theory for gas mixtures, a quite uneasy field by itself [4, 5, 6, 7], with the additional feature that transfer of mass and of energy of chemical bond in each microscopic interaction have to be taken into account. A realistic modelling requires also a suitable description of non–translational degrees of freedom, as done recently by allowing either a discrete or a continuous distribution of internal energy levels

[8, 9]. Consistent relaxation-time-approximations of the cumbersome Boltzmann collision operators (the so called BGK models) have been proposed for practical and numerical purposes [10, 11].

One of the main motivation of a kinetic approach is the need for a rigorous derivation of hydrodynamic equations for the macroscopic fields to be used in real world applications. But there is simultaneously a growing interest towards the employment of the kinetic equations themselves for solving the classical fundamental problems of Fluid Dynamics, like evaporation-condensation, wave propagation, shock structure, Riemann problem [12]. Reactive detonation waves have been investigated at the Euler level [13, 14], whereas quite extensive kinetic results on all the above problems are available in the non-reactive case (see for instance [15, 16] and the books [12, 17]). To the authors' knowledge, deterministic reactive kinetic computations are restricted up to now to space-homogeneous scenarios [18] and to the one-dimensional Riemann problem [19].

This paper is aimed at moving a first step towards a kinetic approach to the steady shock wave problem in a reactive mixture. Shock wave structure has attracted a lot of attention, and has been widely studied in the frame of hydrodynamics [20] and of extended thermodynamics [21, 22], mainly for the inert problem without chemical reactions. An analytic investigation at the kinetic level of the reactive case seems to be lacking in the literature. For this purpose, we shall use here one of the simplest kinetic model, as introduced in [23], which, in spite of its simplifications, has been shown to capture the essential features of the chemical interaction. The main properties of the model are recalled in Sec. 2 in view of its specific application to the present problem. Then the reactive shock wave structure is tackled in Sec. 3, with particular emphasis on the Rankine-Hugoniot conditions following from the conservation laws and on the entropy condition. Results are discussed in Sec. 4, in comparison to the much simpler scenario occurring in the inert case. In fact, entropy condition is affected now by the upstream chemical compositions, and not only by the upstream Mach number. Moreover, the chemical reaction always proceeds in a well defined direction across the shock.

2. Reactive Kinetic Equations

A four component gas mixture of species A^i, $i = 1, \ldots, 4$, colliding among themselves and undergoing the reversible bimolecular chemical reaction

$$A^1 + A^2 \rightleftharpoons A^3 + A^4 \tag{1}$$

may be described at the kinetic level, according to the model proposed in [23] and [8], by the set of nonlinear integrodifferential Boltzmann-like equations

$$\frac{\partial f^i}{\partial t} + \mathbf{v} \cdot \frac{\partial f^i}{\partial \mathbf{x}} = Q^i[\underline{f}] \qquad i = 1, \ldots, 4 \tag{2}$$

where $\underline{f}$ is the vector of the four distribution functions $f^i(\mathbf{x}, \mathbf{v}, \mathbf{t})$. The collision term may be split into its mechanical and chemical parts

$$Q^i[\underline{f}] = \sum_{j=1}^{4} I^{ij}(f^i, f^j) + J^i[\underline{f}] \tag{3}$$

where the elastic scattering binary contributions I^{ij} have the standard form and properties (we refer for instance to the textbook [1]), while the chemical collision operator J^i may be cast as

$$
\begin{aligned}
J^i = {} & \int_{\mathbb{R}^3} \int_{S^2} \Theta(g^2 - \delta_{ij}^{hk}) g \sigma_{ij}^{hk}(g, \hat{\mathbf{\Omega}} \cdot \hat{\mathbf{\Omega}}') \\
& \times \left[\left(\frac{\mu^{ij}}{\mu^{hk}} \right)^3 f^h \left(\mathbf{v}_{ij}^{hk} \right) f^k \left(\mathbf{w}_{ij}^{hk} \right) - f^i(\mathbf{v}) f^j(\mathbf{w}) \right] d\mathbf{w} d\hat{\mathbf{\Omega}}'
\end{aligned}
\tag{4}
$$

where (i, j, h, k) is a permutation of the indices 1, 2, 3, 4, uniquely defined by the selected value of i, and the allowed permutations are respectively $(1, 2, 3, 4)$, $(2, 1, 4, 3)$, $(3, 4, 1, 2)$, $(4, 3, 2, 1)$. Here Θ is the Heaviside function, μ^{ij} stands for the reduced mass $m^i m^j / (m^i + m^j)$ and symbols g and $\hat{\mathbf{\Omega}}$ are used to denote modulus and direction of the relative velocity $\mathbf{v} - \mathbf{w}$. It is assumed for simplicity that particles are endowed with translational degrees of freedom only, and with an energy of chemical link E^i. We will conventionally assume as endothermic the direct reaction in (1), namely

$$\Delta E = -\sum_{i=1}^{4} \Lambda^i E^i = E^3 + E^4 - E^1 - E^2 > 0, \tag{5}$$

where Λ^i is a component of the string of the stoichiometric coefficients $(1, 1, -1, -1)$. Velocity vectors $\mathbf{v}_{ij}^{hk}$ and $\mathbf{w}_{ij}^{hk}$ are given by

$$
\begin{aligned}
\mathbf{v}_{ij}^{hk} &= \alpha^{ij}\mathbf{v} + \alpha^{ji}\mathbf{w} + \alpha^{kh}g_{ij}^{hk}\hat{\boldsymbol{\Omega}}' \\
\mathbf{w}_{ij}^{hk} &= \alpha^{ij}\mathbf{v} + \alpha^{ji}\mathbf{w} - \alpha^{hk}g_{ij}^{hk}\hat{\boldsymbol{\Omega}}',
\end{aligned}
\tag{6}
$$

where $\alpha^{ij} = m^i/(m^i + m^j)$ and

$$
g_{ij}^{hk} = \left[\frac{\mu^{ij}}{\mu^{hk}}(g^2 - \delta_{ij}^{hk})\right]^{1/2},
\tag{7}
$$

with

$$
\delta_{ij}^{hk} = \Lambda^i \frac{2\Delta E}{\mu^{ij}}.
\tag{8}
$$

The sign of δ_{ij}^{hk} determines whether the threshold imposed by the Heaviside function Θ in (4) is effective. The additional threshold due to the activation energy is accounted for by the differential cross sections σ_{ij}^{hk}, which obey, along with obvious symmetry and indistinguishableness properties, the microreversibility condition

$$
(\mu^{ij})^2 g^2 \sigma_{ij}^{hk}(g, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}') = (\mu^{hk})^2 \left(g_{ij}^{hk}\right)^2 \Theta\left(g^2 - \delta_{ij}^{hk}\right)\sigma_{hk}^{ij}(g_{ij}^{hk}, \hat{\boldsymbol{\Omega}} \cdot \hat{\boldsymbol{\Omega}}').
\tag{9}
$$

We recall here for convenience the main properties of equations (2). Technical details and more information may be found, for instance, in the recent survey paper [24]. Collision invariants $\underline{\varphi} = (\varphi^1, \varphi^2, \varphi^3, \varphi^4)$, defined by

$$
\sum_{i=1}^{4} \int_{\mathbb{R}^3} \varphi^i(\mathbf{v})Q^i[\underline{f}]d\mathbf{v} = 0 \qquad \forall \underline{f}
\tag{10}
$$

constitute a seven dimensional linear subspace of the continuous functions of $\mathbf{v}$, and a possible basis is provided by the strings

$$
(1, 0, 1, 0) \qquad (1, 0, 0, 1) \qquad (0, 1, 0, 1),
\tag{11}
$$

and by the additional four scalar options

$$
\varphi^i = m^i\mathbf{v}, \quad i = 1, \dots, 4; \qquad \varphi^i = \frac{1}{2}m^i v^2 + E^i, \quad i = 1, \dots, 4,
\tag{12}
$$

the latter representing conservation of momentum and total (kinetic plus chemical) energy. The former describe conservation of particles in the in-

dependent pairs of species $(1,3)(1,4)(2,4)$, and proper linear combinations reproduce conservation of total particle number and of total mass. As a consequence, the following seven, exact but not closed, macroscopic conservation equations hold

$$\frac{\partial}{\partial t}(n^1 + n^3) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^1 \mathbf{u}^1 + n^3 \mathbf{u}^3) = 0$$

$$\frac{\partial}{\partial t}(n^1 + n^4) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^1 \mathbf{u}^1 + n^4 \mathbf{u}^4) = 0$$

$$\frac{\partial}{\partial t}(n^2 + n^4) + \frac{\partial}{\partial \mathbf{x}} \cdot (n^2 \mathbf{u}^2 + n^4 \mathbf{u}^4) = 0$$

$$\frac{\partial}{\partial t}(\rho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u} + \mathbf{P}) = \mathbf{0}$$

$$\frac{\partial}{\partial t}\left(\frac{1}{2}\rho u^2 + \frac{3}{2}nKT + U^*\right) + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2}\rho u^2 + \frac{3}{2}nKT + U^*\right)\mathbf{u}\right]$$

$$+ \frac{\partial}{\partial \mathbf{x}} \cdot \left[\mathbf{P} \cdot \mathbf{u} + \mathbf{q} + \mathbf{q}^*\right] = 0,$$

(13)

where macroscopic observables are moments of the distribution functions given in Table 1. Continuity equations for number density and mass density follow as linear combinations of the first three equations in (14).

Another crucial property of the collision term $\underline{Q}$ is the extended version of Boltzmann's lemma, which reads

$$\sum_{i=1}^{4} \int_{\mathbb{R}^3} \log\left[\frac{f^i(\mathbf{v})}{(m^i)^3}\right] Q^i[\underline{f}](\mathbf{v})d\mathbf{v} \leq 0 \qquad \forall \underline{f}$$

(14)

with equal sign iff the string $\log[f^i/(m^i)^3]$ is a collision invariant. This determines in fact collision equilibria, namely the solutions $\underline{f}$ of the integral equations

$$\underline{Q}[\underline{f}](\mathbf{v}) = 0 \qquad \forall \mathbf{v} \in \mathbb{R}^3$$

(15)

as the seven parameter family of local Maxwellians

$$f_M^i(\mathbf{v}) = n^i\left(\frac{m^i}{2\pi KT}\right)^{3/2} \exp\left[-\frac{m^i}{2KT}(\mathbf{v} - \mathbf{u})^2\right] \qquad i = 1,\cdots,4$$

(16)

with $\mathbf{u}$ and T standing for mass velocity and temperature of the mixture, and where number densities n^i must be related by the mass action law

$$\frac{n^1 n^2}{n^3 n^4} = \left(\frac{\mu^{12}}{\mu^{34}}\right)^{3/2} \exp\left(\frac{\Delta E}{KT}\right)$$

(17)

expressing chemical equilibrium between direct and inverse reaction rate constants at temperature T. One might also introduce the concentration fractions

$$\chi^i = \frac{n^i}{n} \qquad \sum_{i=1}^4 \chi^i = 1 \tag{18}$$

and notice that (17) may be rewritten in equivalent forms, like for instance

$$\frac{KT}{\Delta E} = \Big[\sum_{i=1}^4 \Lambda^i \log \frac{\chi^i}{(m^i)^{3/2}} \Big]^{-1}. \tag{19}$$

Table 1. Macroscopic moments of the distribution functions f^i, $1 \le i \le 4$.

$n^i = \displaystyle\int_{\mathbb{R}^3} f^i d\mathbf{v}$	number density of the i-th component
$\mathbf{u}^i = \dfrac{1}{n^i} \displaystyle\int_{\mathbb{R}^3} \mathbf{v} f^i d\mathbf{v}$	drift velocity of the i-th component
$n = \displaystyle\sum_{i=1}^4 n^i$	total number density
$\rho = \displaystyle\sum_{i=1}^4 m^i n^i$	mass density
$\mathbf{u} = \dfrac{1}{\rho} \displaystyle\sum_{i=1}^4 m^i n^i \mathbf{u}^i$	mass velocity
$\mathbf{P} = \displaystyle\sum_{i=1}^4 m^i \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})(\mathbf{v} - \mathbf{u}) f^i d\mathbf{v}$	pressure tensor
$T = \dfrac{1}{3nK} tr\mathbf{P}$	kinetic temperature
$U^* = \displaystyle\sum_{i=1}^4 E^i n^i$	excitation energy density
$\mathbf{q} = \dfrac{1}{2} \displaystyle\sum_{i=1}^4 m^i \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u})^2 (\mathbf{v} - \mathbf{u}) f^i d\mathbf{v}$	thermal heat flux
$\mathbf{q}^* = \displaystyle\sum_{i=1}^4 E^i \int_{\mathbb{R}^3} (\mathbf{v} - \mathbf{u}) f^i d\mathbf{v} = \sum_{i=1}^4 E^i n^i (\mathbf{u}^i - \mathbf{u})$	excitation heat flux

Another important consequence of (14) is that we can introduce an H-

functional

$$H[\underline{f}] = \sum_{i=1}^{4} \int_{\mathbb{R}^3} f^i \log \frac{f^i}{(m^i)^3} d\mathbf{v} \qquad (20)$$

and prove an equivalent of the H-theorem, namely that H is a strict Lyapunov functional for stability of equilibria (16), quantifying irreversibility and dissipativity of the process in agreement with the second law of thermodynamics. Entropy density s at local thermodynamical equilibrium may be defined for instance as $s = -KH/n$, and, upon using (16) into (20), reads as

$$s = -K \sum_{i=1}^{4} \chi^i \log \frac{\chi^i}{(m^i)^{3/2}} + \frac{3}{2} K \log T - K \log n \qquad (21)$$

where additive constants have been discarded and the last two addends make up formally the standard single gas entropy. It is obviously understood that macroscopic fields in (21) are bound together by the mass action law (19), so that entropy s depends only on four of them. For practical purposes, a closed set of hydrodynamic equations at macroscopic level would be desirable. The simplest approximate hydrodynamic closure of the conservation equations is provided by the Euler equations. In a collision dominated regime, like the one we will be dealing with in the present paper, such equations are obtained by expressing all redundant moments by means of the equilibrium distribution functions (16), with constraint (17). This yields

$$
\begin{aligned}
&\frac{\partial}{\partial t}(n^i + n^j) + \frac{\partial}{\partial \mathbf{x}} \cdot [(n^i + n^j)\mathbf{u}] = 0 \qquad (i,j) = (1,3), (1,4), (2,4) \\
&\frac{\partial}{\partial t}(\rho \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}} \cdot (\rho \mathbf{u} \otimes \mathbf{u}) + \frac{\partial}{\partial \mathbf{x}}(nKT) = \mathbf{0} \\
&\frac{\partial}{\partial t}\left(\frac{1}{2}\rho u^2 + \frac{3}{2}nKT + \sum_{i=1}^{4} E^i n^i\right) \\
&\qquad + \frac{\partial}{\partial \mathbf{x}} \cdot \left[\left(\frac{1}{2}\rho u^2 + \frac{5}{2}nKT + \sum_{i=1}^{4} E^i n^i\right)\mathbf{u}\right] = 0,
\end{aligned}
\qquad (22)
$$

which again must be coupled with the mass action law (17) to provide a set of eight differential-algebraic equations for the eight unknown functions n^i, $\mathbf{u}$, T. Equations (22) may be linearized around a stationary homogeneous state with zero drift in one space dimension. The equations for the five

independent small perturbations $\tilde{n}^i$, $\tilde{u}$ read as

$$\frac{\partial \tilde{n}^i}{\partial t} + \frac{\partial \tilde{n}^j}{\partial t} + n^i \frac{\partial \tilde{u}}{\partial x} + n^j \frac{\partial \tilde{u}}{\partial x} = 0 \qquad (i,j) = (1,3),(1,4),(2,4)$$

$$\frac{\partial \tilde{u}}{\partial t} + \frac{KT}{\rho} \sum_{i=1}^{4} \frac{\partial \tilde{n}^i}{\partial x} - \frac{n}{\rho} \frac{(KT)^2}{\Delta E} \sum_{i=1}^{4} \frac{\Lambda^i}{n^i} \frac{\partial \tilde{n}^i}{\partial x} = 0 \qquad (23)$$

$$\frac{\partial \tilde{n}^1}{\partial t} + \left(n^1 - \frac{nKT}{\Delta E} \right) \frac{\partial \tilde{u}}{\partial x} + \frac{3}{2} n \left(\frac{KT}{\Delta E} \right)^2 \sum_{i=1}^{4} \frac{\Lambda^i}{n^i} \frac{\partial \tilde{n}^i}{\partial t} = 0.$$

The usual ansatz $\tilde{n}^i(x,t) = \overline{n}^i \exp(\lambda t + ikx)$, $\tilde{u}(x,t) = \overline{u} \exp(\lambda t + ikx)$ yields an homogeneous algebraic system for $\overline{n}^i$, $\overline{u}$, whose determinant provides the dispersion relation $\det(A) = 0$, where the matrix A is

$$\begin{pmatrix} \lambda & 0 & \lambda & 0 & ik(n^1+n^3) \\ \lambda & 0 & 0 & \lambda & ik(n^1+n^4) \\ 0 & \lambda & 0 & \lambda & ik(n^2+n^4) \\ ik\frac{KT}{\rho}\left(1-\frac{KT}{\Delta E}\frac{1}{\chi^1}\right) & ik\frac{KT}{\rho}\left(1-\frac{KT}{\Delta E}\frac{1}{\chi^2}\right) & ik\frac{KT}{\rho}\left(1+\frac{KT}{\Delta E}\frac{1}{\chi^3}\right) & ik\frac{KT}{\rho}\left(1+\frac{KT}{\Delta E}\frac{1}{\chi^4}\right) & \lambda \\ \lambda\left[1+\frac{3}{2}\left(\frac{KT}{\Delta E}\right)^2\frac{1}{\chi^1}\right] & \lambda\frac{3}{2}\left(\frac{KT}{\Delta E}\right)^2\frac{1}{\chi^2} & -\lambda\frac{3}{2}\left(\frac{KT}{\Delta E}\right)^2\frac{1}{\chi^3} & -\lambda\frac{3}{2}\left(\frac{KT}{\Delta E}\right)^2\frac{1}{\chi^4} & ik\left(n^1-\frac{nKT}{\Delta E}\right) \end{pmatrix}$$

$$(24)$$

Long but standard manipulations show that it can be cast as

$$\lambda^3(\lambda^2 + k^2 c_0^2) = 0 \qquad (25)$$

where

$$c_0 = \left\{ \frac{5}{3} \frac{nKT}{\rho} \left[\sum_{i=1}^{4} \frac{1}{\chi^i} + \frac{2}{5}\left(\frac{\Delta E}{KT}\right)^2 \right] \Big/ \left[\sum_{i=1}^{4} \frac{1}{\chi^i} + \frac{2}{3}\left(\frac{\Delta E}{KT}\right)^2 \right] \right\}^{1/2} \qquad (26)$$

is thus the speed of sound for the considered reactive mixture. This expression is in agreement with thermodynamical considerations and with a result in [14] on detonation waves. It shows a deviation from the standard value for the inert mixture, $\sqrt{\frac{5}{3}\frac{nKT}{\rho}}$, determined by chemical composition (affecting also T via (17)), but, remarkably enough, independent of the jump ΔE in the energies of chemical bonds, as a consequence of (19). The deviation vanishes when concentrations χ^i are such that $\Delta E/(KT) \to 0$ (limiting case of diverging equilibrium temperature), and the correction is always a reduction on the sound speed, which anyway can never decrease beyond the lower bound $\sqrt{\frac{nKT}{\rho}}$. It might be noticed that the inert value $\sqrt{\frac{5}{3}\frac{nKT}{\rho}}$ is

approached also in the opposite limiting case $\Delta E/(KT) \to \infty$, which occurs when one of the products tends to vanish.

3. Shock Wave Structure

The steady shock problem may be formulated as follows [12]. Consider the governing equations in the simple stationary form in one space dimension

$$v_1 \frac{\partial f^i}{\partial x} = Q^i[\underline{f}] \qquad i = 1, \ldots, 4 \tag{27}$$

with $x = x_1$ and with v_1 standing for the first component of the velocity vector $\mathbf{v}$. Equation (27) has to be solved for $-\infty < x < +\infty$ with boundary conditions

$$\lim_{x \to \pm\infty} f^i(x, \mathbf{v}) = M_\pm^i(\mathbf{v}) \tag{28}$$

where $M_\pm^i$ denote families of Maxwellian distributions describing equilibrium outside the shock region, characterized by upstream $(-)$ and downstream $(+)$ parameters $n_\pm^i$, $u_\pm = u_{1\pm}$, $T_\pm$. They read as

$$M_\pm^i(\mathbf{v}) = n_\pm^i \left(\frac{m^i}{2\pi K T_\pm} \right)^{3/2} \exp\left[-m^i \frac{(v_1 - u_\pm)^2 + v_2^2 + v_3^2}{2KT_\pm} \right] \tag{29}$$

and constitute each a five parameter family, since, for instance, temperature is not independent, but follows from the mass action law

$$\frac{\chi_\pm^1 \chi_\pm^2}{\chi_\pm^3 \chi_\pm^4} = \eta \exp\left(\frac{\Delta E}{KT_\pm} \right) \tag{30}$$

where the parameter η, defined by

$$\eta = \left(\frac{m^1 m^2}{m^3 m^4} \right)^{3/2} \tag{31}$$

depends on the pre- and post-collisional masses, and turns out to be different from unity if an actual reaction takes place (due to mass conservation, $\eta = 1$ may occur only if $m^1 = m^3$, $m^2 = m^4$ or $m^1 = m^4$, $m^2 = m^3$). In addition, because of (19), this parameter is subject to the constraint

$$0 < \eta < \frac{\chi_\pm^1 \chi_\pm^2}{\chi_\pm^3 \chi_\pm^4}. \tag{32}$$

As well known, the 10 free upstream and downstream parameters cannot be chosen arbitrarily, since they must be related by the Rankine-Hugoniot conditions, which simply express the conservation laws for the present problem. In one space dimension we can rely on five collision invariants, given by the appropriate version of (11)–(12), namely

$$\underline{\varphi} = (1,0,1,0), (1,0,0,1), (0,1,0,1) \tag{33}$$

and

$$\varphi^i = m^i v_1, \qquad \varphi^i = \frac{1}{2}m^i(v_1^2 + v_2^3 + v_3^2) + E^i, \quad i = 1, \ldots, 4 \tag{34}$$

so that in principle we may deduce the five downstream parameters in terms of the set of the corresponding upstream ones. It suffices in fact to take the weak forms of (27) relevant to the test functions (33)–(34) to get rid of the collision term and to yield conservation equations for the corresponding fluxes

$$\frac{d}{dx} \sum_{i=1}^{4} \int_{\mathbb{R}^3} v_1 \varphi^i(\mathbf{v}) f^i(x, \mathbf{v}) d\mathbf{v} = 0. \tag{35}$$

Integrating on the real line and applying limiting conditions (28) leads, via easy algebra allowed by the expressions (29) for upstream and downstream equilibria, to the version of the Rankine-Hugoniot conditions pertinent to a reactive mixture

$$
\begin{aligned}
(n_-^i + n_-^j)u_- &= (n_+^i + n_+^j)u_+ \qquad (i,j) = (1,3), (1,4), (2,4) \\
n_- KT_- + \rho_- u_-^2 &= n_+ KT_+ + \rho_+ u_+^2 \\
\frac{1}{2}\rho_- u_-^3 + \frac{5}{2}n_- KT_- u_- &+ \sum_{i=1}^{4} E^i n_-^i u_- \\
&= \frac{1}{2}\rho_+ u_+^3 + \frac{5}{2}n_+ KT_+ u_+ + \sum_{i=1}^{4} E^i n_+^i u_+,
\end{aligned}
\tag{36}
$$

with $T_\pm$ defined by (30). The first three of them may be rewritten as

$$(\chi_+^i + \chi_+^j)n_+ u_+ = (\chi_-^i + \chi_-^j)n_- u_-, \qquad (i,j) = (1,3), (1,4), (2,4), \tag{37}$$

and simple manipulations show that $n_+ u_+ = n_- u_-$, and that the variations of concentrations $\Delta\chi^i = \chi_+^i - \chi_-^i$ must be related by $\Delta\chi^1 = \Delta\chi^2 = -\Delta\chi^3 =$

$-\Delta\chi^4$. Introducing $\Delta\chi = \Delta\chi^1$ as independent variable, we may write

$$\chi_+^i = \chi_-^i + \Lambda^i\Delta\chi, \quad i = 1,\ldots, 4; \qquad \frac{n_+}{n_-} = \frac{u_-}{u_+} = \frac{\rho_+}{\rho_-}. \qquad (38)$$

Therefore, it is easily realized that, for given upstream parameters n_-^i, u_-, all downstream quantities are determined from the knowledge of only two unknowns, namely $\Delta\chi$ and the ratio n_+/n_-, that can be in turn evaluated as solution of the last two equations in (36).

In order to achieve explicit expressions for the results of the present manipulations, it proves convenient resorting to an equivalent but slightly different strategy, which consists in assigning instead all n_-^i and $\Delta\chi$, and in considering u_- as an unknown, like the other downstream quantities. In this way, we see that (38) still solves the Rankine-Hugoniot conditions, provided we are able to determine the unknowns u_- and n_+/n_-, for given $\Delta\chi$, from the last two equations in (36). It is then matter of some standard algebra to deduce the quadratic algebraic equation

$$KT_+\left(\frac{n_+}{n_-}\right)^2 + 2\left[\Delta E\Delta\chi - 2K(T_+ - T_-)\right]\frac{n_+}{n_-} - KT_- = 0 \qquad (39)$$

where again $T_\pm$ follows from (30) with all χ_+^i given by (38). This equation, by its own structure, always admits a unique meaningful solution

$$\frac{n_+}{n_-} = 2\left(1 - \frac{T_-}{T_+}\right) - \frac{\Delta E}{KT_+}\Delta\chi + \sqrt{\left[2\left(1 - \frac{T_-}{T_+}\right) - \frac{\Delta E}{KT_+}\Delta\chi\right]^2 + \frac{T_-}{T_+}}. \qquad (40)$$

Assuming conventionally $u_- > 0$, we have then

$$u_- = \sqrt{\frac{n_-KT_-}{\rho_-}}\left[\frac{n_+}{n_-}\frac{1 - (n_+/n_-)(T_+/T_-)}{1 - (n_+/n_-)}\right]^{1/2} \qquad (41)$$

provided

$$\left(1 - \frac{n_+}{n_-}\frac{T_+}{T_-}\right)\left(1 - \frac{n_+}{n_-}\right) > 0 \qquad (42)$$

which may be considered as "a posteriori" constraint on the choice of $\Delta\chi$. Finally, from (38), we have $u_+ = u_-/(n_+/n_-)$, which completes the procedure and determines uniquely all downstream parameters and u_- in terms of n_-^i and $\Delta\chi$.

Along with the Rankine-Hugoniot conditions, there is another crucial physical feature of the shock wave problem that follows from the mathematical properties of the collision operator, and is related to the H-theorem and to the second law of thermodynamics. Such an entropy condition is quantified by Boltzmann's lemma (14) which, applied to the governing equation (27), leads to a weak form of (27) itself that can be cast as a differential inequality for the entropy flux

$$\frac{d}{dx} \sum_{i=1}^{4} \int_{\mathbb{R}^3} v_1 f^i \log \left[\frac{f^i}{(m^i)^3} \right] d\mathbf{v} \leq 0. \tag{43}$$

Again, integration from $-\infty$ to $+\infty$, accounting for limiting values (29), yields a relationship between upstream and downstream entropy fluxes of the kind

$$n_+ u_+ \sum_{i=1}^{4} \chi_+^i \log \left[n_+^i (2\pi m^i K T_+)^{-3/2} \right]$$

$$\leq n_- u_- \sum_{i=1}^{4} \chi_-^i \log \left[n_-^i (2\pi m^i K T_-)^{-3/2} \right] \tag{44}$$

from which, on account of (38) and of the fact that $u_- > 0$,

$$\sum_{i=1}^{4} \chi_+^i \log \left[\frac{\chi_+^i}{(m^i)^{3/2}} \right] - \frac{3}{2} \log T_+ + \log n_+$$

$$\leq \sum_{i=1}^{4} \chi_-^i \log \left[\frac{\chi_-^i}{(m^i)^{3/2}} \right] - \frac{3}{2} \log T_- + \log n_-. \tag{45}$$

It can be noticed that the last inequality, bearing in mind the expression (21) for entropy at local thermodynamical equilibrium, amounts to the requirement

$$\Delta s = s_+ - s_- \geq 0, \tag{46}$$

of clear physical meaning.

It is worth comparing the results of the previous investigation to the corresponding ones relevant to the case of a non reacting gas. In fact, it is well known [12] that the pertinent version of the entropy condition (46) can

be worked out, and that it is equivalent to the requirement

$$Ma_- \geq 1, \tag{47}$$

implying in turn $Ma_+ \leq 1$, where $Ma_\pm$ denote the up- and downstream Mach numbers

$$Ma_\pm = u_\pm/c_{0\pm}. \tag{48}$$

Here c_0 denotes the sound speed corresponding to the relevant asymptotic equilibrium state, which in the present reactive case would be provided by (26). So, in the inert case, the shock problem has a meaning only if it describes transition from a supersonic to a subsonic flow. The proof of the above statements follows simply from the fact that the inert Rankine–Hugoniot conditions read as

$$\frac{n_+^i}{n_-^i} = \frac{n_+}{n_-} = \frac{u_-}{u_+} = \frac{4Ma_-^2}{Ma_-^2 + 3} \qquad \frac{T_+}{T_-} = \frac{(Ma_-^2 + 3)(5Ma_-^2 - 1)}{16Ma_-^2}, \tag{49}$$

while the entropy jump takes the explicit form

$$\Delta s = \frac{K}{2} \log \frac{(Ma_-^2 + 3)^5 (5Ma_-^2 - 1)^3}{4^8 Ma_-^{10}}, \tag{50}$$

so that it depends solely on the upstream Mach number, $\Delta s = \Delta s(Ma_-)$, with

$$\Delta s(1) = 0, \qquad \Delta s \geq 0 \Longleftrightarrow Ma_- \geq 1. \tag{51}$$

Indeed, the plot of Δs versus Ma_- shows a typical piecewise monotonically–increasing trend with flex point at $Ma_- = 1$.

4. Discussion

For our problem, it would be interesting to investigate whether a complicated inequality like (45), involving in principle all upstream parameters (or, in our strategy, the five independent variables $\Delta \chi, n_-$ and three out of the χ_-^i), can be linked to a form like (47), possibly modified, or to some other specific parameter. Actually, since the ratio n_+/n_- is determined by (40), it can be easily verified that the entropy jump Δs depends actually only on four parameters, which may be chosen as $\Delta \chi$ and three independent fractions χ_-^i.

Let us remark preliminarily that the jump $\Delta\chi$ must imply a positive and finite T_+. Some algebra shows that this leads to the restriction

$$-\chi_-^* < \Delta\chi < \min\{\chi_-^3, \chi_-^4\} \tag{52}$$

where $\chi_-^* > 0$ is given by

$$
\chi_-^* = \frac{1}{2(1-\eta)}\Big\{\chi_-^1 + \chi_-^2 + \eta\chi_-^3 + \eta\chi_-^4
$$
$$
-\sqrt{(\chi_-^1 + \chi_-^2 + \eta\chi_-^3 + \eta\chi_-^4)^2 - 4(1-\eta)(\chi_-^1\chi_-^2 - \eta\chi_-^3\chi_-^4)}\Big\}, \tag{53}
$$

valid for any $\eta \neq 1$; in particular, $\chi_-^* < \min\{\chi_-^1, \chi_-^2\}$. Once T_+ and n_+/n_- are computed, the variable $\Delta\chi$ must be tested also versus condition (42), so that the procedure can be completed by computing u_-. It should be born in mind that the chosen $\Delta\chi$ turns out to represent the change of chemical composition that would be determined in the shock, if that u_- were chosen as input datum together with the other upstream parameters. Also, it should be noticed that the case of no chemical variations, $\Delta\chi = 0$, is always included in the range (52). At this point, however, one is able to test if the crucial condition (45) is fulfilled by the considered choice of the independent variables.

Let us consider first the very special case $\Delta E = 0$, which requires a modified approach. In fact, temperatures $T_\pm$ are not determined by concentrations $\chi_\pm^i$ any more, and should be regarded as independent variables themselves. On the other hand, chemical equilibrium reads now as

$$\frac{\chi_\pm^1\chi_\pm^2}{\chi_\pm^3\chi_\pm^4} = \eta, \tag{54}$$

so that only two out of the χ^i are independent, both up- and downstream. For fixed upstream conditions, downstream equilibrium reads as a quadratic equation for $\Delta\chi$, with roots $\Delta\chi = 0$ and, with $\eta \neq 1$,

$$\Delta\chi = \frac{\chi_-^1 + \chi_-^2 + \eta\chi_-^3 + \eta\chi_-^4}{\eta - 1}. \tag{55}$$

It is immediately realized that (55) always violates (52), so that only the solution with no chemical changes is left. The remaining Rankine-Hugoniot conditions yield then the same relationships as for an inert mixture, namely equation (49). It can be then easily verified that the entropy condition

(45) yields exactly the same constraint of a non reactive mixture, namely inequality (47). In conclusion, the chemical compositions of the upstream and downstream equilibria coincide for $\Delta E = 0$ and the jump conditions are exactly the same that would occur if the four species were non reactive. Therefore, since species may always be ordered in such a way that ΔE is non negative, we shall stick below only to the option $\Delta E > 0$.

Since $\Delta \chi = 0$ implies $T_+ = T_-$ and $n_+ = n_-$ (see (40)), and

$$\Delta s = \frac{3}{2} \log \frac{T_+}{T_-} - \log \frac{n_+}{n_-} - \frac{\Delta E}{KT_+} \Delta \chi - \sum_{i=1}^{4} \chi_-^i \log \left(1 + \Lambda^i \frac{\Delta \chi}{\chi_-^i}\right), \qquad (56)$$

it is immediately realized that $\Delta s = 0$ for $\Delta \chi = 0$ (indeed, states at $\pm \infty$ are identical in this case). It is interesting to evaluate the upstream velocity u_- that actually induces a chemical variation $\Delta \chi = 0$. This can be done by taking the limit of (41) for $\Delta \chi \to 0$, formally an indeterminate form $0/0$. It is not difficult to show that

$$\frac{T_-}{T_+} = 1 + \left(\frac{KT_-}{\Delta E} \sum_{i=1}^{4} \frac{1}{\chi_-^i}\right) \Delta \chi + O(\Delta \chi^2) \qquad (57)$$

$$\frac{n_+}{n_-} = 1 - \left(\frac{\Delta E}{KT_-} + \frac{3}{2} \frac{KT_-}{\Delta E} \sum_{i=1}^{4} \frac{1}{\chi_-^i}\right) \Delta \chi + O(\Delta \chi^2), \qquad (58)$$

from which

$$\lim_{\Delta \chi \to 0} \frac{n_+}{n_-} \frac{1 - (n_+/n_-)(T_+/T_-)}{1 - (n_+/n_-)} = \frac{\left(\dfrac{\Delta E}{KT_-}\right)^2 + \dfrac{5}{2} \displaystyle\sum_{i=1}^{4} \dfrac{1}{\chi_-^i}}{\left(\dfrac{\Delta E}{KT_-}\right)^2 + \dfrac{3}{2} \displaystyle\sum_{i=1}^{4} \dfrac{1}{\chi_-^i}}, \qquad (59)$$

and then finally

$$\lim_{\Delta \chi \to 0} u_- = c_{0-} \qquad \text{or} \qquad \lim_{\Delta \chi \to 0} Ma_- = 1. \qquad (60)$$

In other words, also for a reactive mixture, sonic upstream conditions determine no variations downstream (in fact, $\Delta \chi = 0$, $T_+ = T_-$, $n_+ = n_-$, $u_+ = u_-$), namely a constant solution all over the real line. It is then natural to conjecture that moving u_- across the critical value c_{0-} should produce a change of sign in Δs, as well as in $\Delta \chi$, so that, at least locally in a neighborhood of the sound speed, only one side will be allowed to the upstream

velocity in order to fulfill the entropy condition (45), and, correspondingly, the allowed chemical transition will be characterized by a well defined sign of $\Delta\chi$. The situation is rather tricky since, if $\Delta\chi$ is used again as independent variable, it is possible to prove, on account of (56)$-$(58), that

$$\lim_{\Delta\chi\to 0}\frac{\partial(\Delta s)}{\partial(\Delta\chi)}=0. \tag{61}$$

An analytical proof of the previous conjecture seems very difficult, because of complicated dependence on so many parameters, but there is indeed numerical evidence that it holds true, and that it turns out to be valid not only locally, but also globally. More precisely, following again our strategy, extensive computations, randomly covering the whole range allowed to each parameter, indicate that both Δs and u_- are monotonically decreasing functions of $\Delta\chi$ (the former only piecewise, due to the horizontal tangent in $\Delta\chi=0$ implied by (61)). Therefore, we have $\Delta s > 0$ only in the interval $-\chi_-^* < \Delta\chi < 0$, and in that range u_- always exceeds c_{0-}, namely Ma_- always exceeds unity. The remaining part of the interval (52), corresponding to $Ma_- < 1$, must be discarded, since it yields $\Delta s < 0$. In addition, the observed one-to-one correspondence between u_- and $\Delta\chi$ indicates the uniqueness of the downstream equilibrium state once the upstream one has been given. Thus, like for an inert shock, there are exactly two kinetic equilibria sharing the same conserved quantities.

In conclusion, necessary and sufficient condition for occurrence of the shock turns out to be given again by (47), like for inert mixtures, with equal sign only for the degenerate case of no discontinuity. However, an important difference with respect to the non reactive case actually occurs, namely a change of chemical composition definitely takes place ($\Delta\chi \neq 0$). And it is remarkable that the variation always goes in a well defined direction, characterized by $\Delta\chi < 0$, which corresponds to an enhancement of the products at the expenses of the reactants (macroscopically endothermic shift). The downstream chemical equilibrium carries then a larger chemical energy ($\Delta E > 0$, $\Delta\chi < 0$) as well as a larger thermal energy ($T_+ > T_-$, as follows from (19) and from $\Delta\chi < 0$).

As a sample of the above numerical investigation, we report in the following figures some trends of Δs and $\Delta\chi$ versus the upstream Mach number Ma_-. First, we consider a case for which $\eta = 0.6125 < 1$, relevant to the following choice of masses [10]: $m^1 = 11.7$, $m^2 = 3.6$, $m^3 = 8$,

$m^4 = 7.3$, with $\Delta E = 10$, and select different values for upstream concentrations (Figures 1−3). Then we change masses according to the reaction $H_2 + Cl \rightleftharpoons HCl + H$ [11], namely $m^1 = 0.335$, $m^2 = 5.886$, $m^3 = 6.054$, $m^4 = 0.167$, and obtain a case for which $\eta = 2.7237 > 1$ (Figures 4−5); here $\Delta E = 3.98$. In all cases, the physically allowed region corresponds to an abscissa ranging from 1 to $+\infty$, and the limiting values of $\Delta\chi$ at the two edges correspond to 0 and to its lower bound $-\chi_-^*$, respectively. In the unphysical (subsonic) region, the variable Ma_- can not range down to 0, since other consistency (positivity) requirements would be violated. Its lower bound is given by

$$\left(\frac{\frac{1}{5}}{1 + \frac{2}{3}\frac{\Delta E}{KT_-}\min\{\chi_-^3, \chi_-^4\}} \frac{\frac{2}{3}\left(\frac{\Delta E}{KT_-}\right)^2 + \sum_{i=1}^{4}\frac{1}{\chi_-^i}}{\frac{2}{5}\left(\frac{\Delta E}{KT_-}\right)^2 + \sum_{i=1}^{4}\frac{1}{\chi_-^i}} \right)^{1/2}, \qquad (62)$$

and the corresponding limit for $\Delta\chi$ turns out to be just $\min\{\chi_-^3, \chi_-^4\}$ (see equation (52)). It can be noted that the bound (62) can never exceed the value $1/\sqrt{3}$, and that, in both limiting cases when $\Delta E/KT_- \to 0$ and $\Delta E/KT_- \to \infty$, it tends to the typical value $1/\sqrt{5}$, which characterizes the inert case.
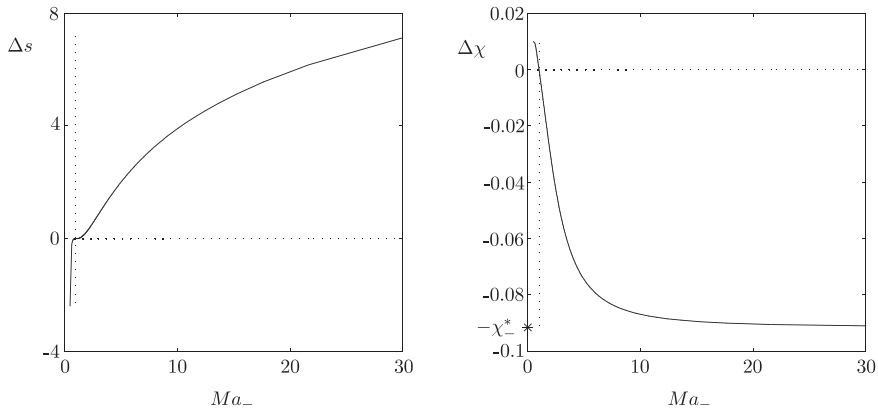

Figure 1. Δs (left) and $\Delta\chi$ (right) versus Ma_- for the first reaction considered in the text. Upstream concentrations: $\chi_-^1 = 0.25$, $\chi_-^2 = 0.3$, $\chi_-^3 = 0.01$, $\chi_-^4 = 0.44$ ($\chi_-^* = 0.0915$).
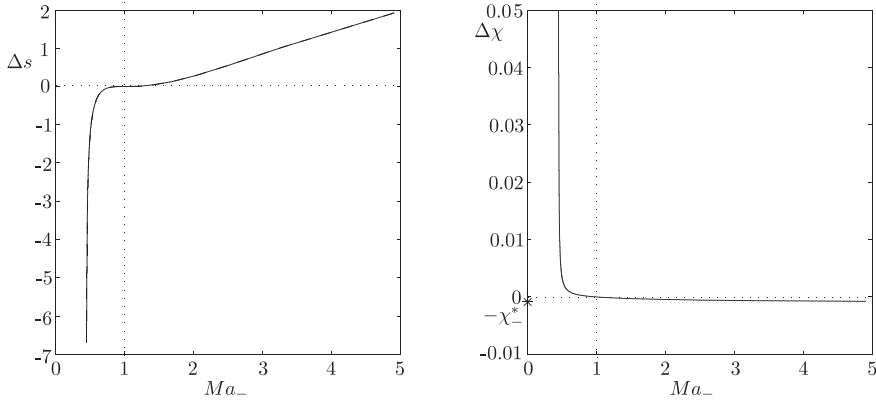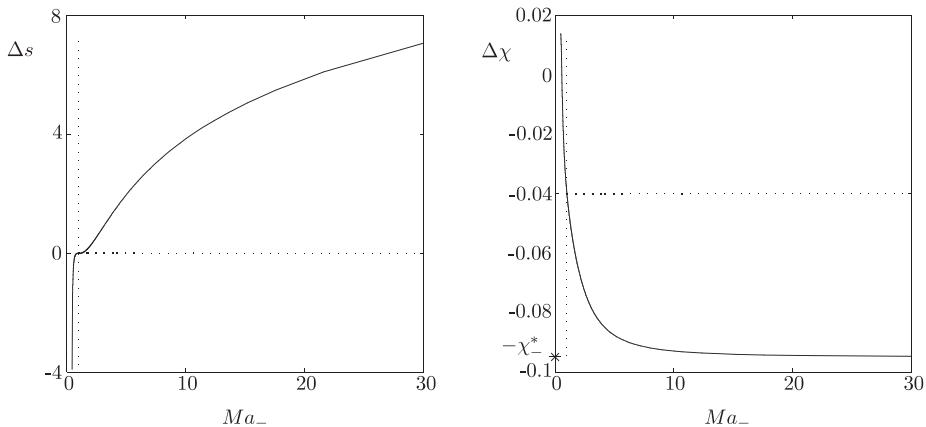
Figure 2. Δs (left) and $\Delta \chi$ (right) versus Ma_- for the first reaction considered in the text. Upstream concentrations: $\chi^1_- = 0.05$, $\chi^2_- = 0.35$, $\chi^3_- = 0.05$, $\chi^4_- = 0.55$ ($\chi^*_- = 8.55 \times 10^{-4}$).

Figure 3. Δs (left) and $\Delta \chi$ (right) versus Ma_- for the first reaction considered in the text. Upstream concentrations: $\chi^1_- = 0.2$, $\chi^2_- = 0.2$, $\chi^3_- = 0.036$, $\chi^4_- = 0.564$ ($\chi^*_- = 0.0366$).

The trend of $\Delta \chi$ versus Ma_- is monotonic, as anticipated. The trend of Δs versus Ma_- closely resembles the inert one, whose analytical expression is given by (50). There is now a further dependence of Δs on the upstream chemical composition, described by three independent concentrations χ^i_-. Such a dependence is clearly shown by the numerical outputs of the different cases, though hardly visible on the figures, where the universal inert curve is plotted as a dashed line. However, it does not affect the general and

crucial implications of the entropy condition, and turns out to be quite weak, in the sense that discrepancies of the different Δs at fixed Ma_- range typically from zero to few percents for varying boundary data of the upstream concentrations. An example is provided in Figure 6.
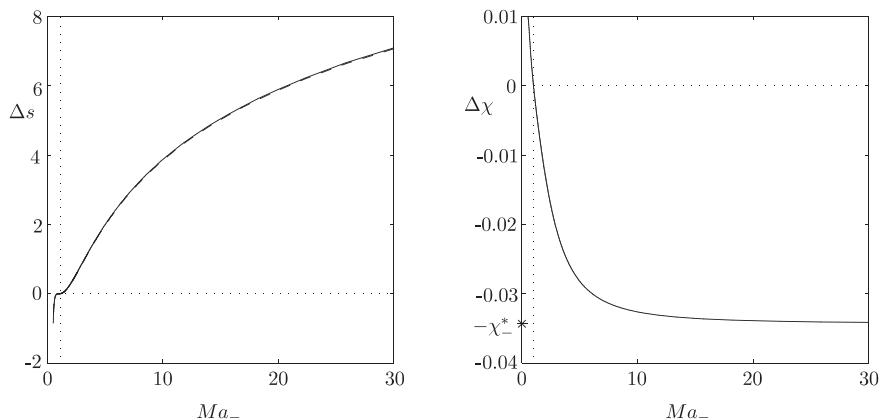

Figure 4. Δs (left) and $\Delta \chi$ (right) versus Ma_- for the second reaction considered in the text. Upstream concentrations: $\chi_-^1 = 0.25$, $\chi_-^2 = 0.3$, $\chi_-^3 = 0.01$, $\chi_-^4 = 0.44$ ($\chi_-^* = 0.0343$).
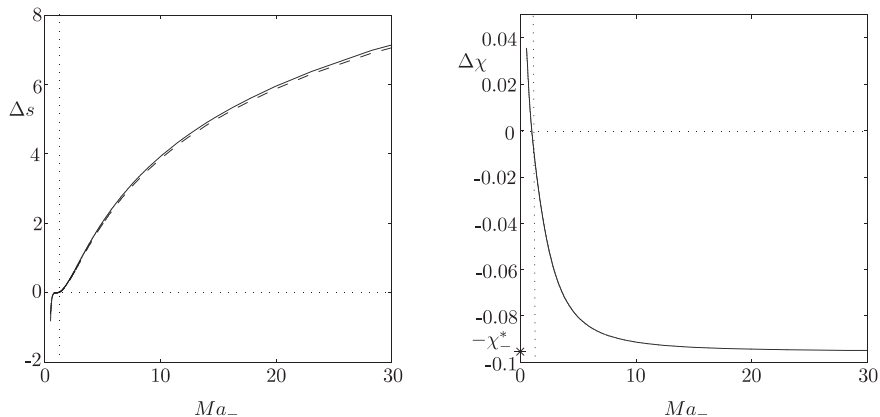

Figure 5. Δs (left) and $\Delta \chi$ (right) versus Ma_- for the second reaction considered in the text. Upstream concentrations: $\chi_-^1 = 0.4$, $\chi_-^2 = 0.4$, $\chi_-^3 = 0.036$, $\chi_-^4 = 0.164$ ($\chi_-^* = 0.0954$).

Actual determination of the reactive shock wave profiles and of their properties will be subject of further investigation. Kinetic computations by

means of a suitable BGK model [10] are scheduled as future work and will be matter of a next paper.
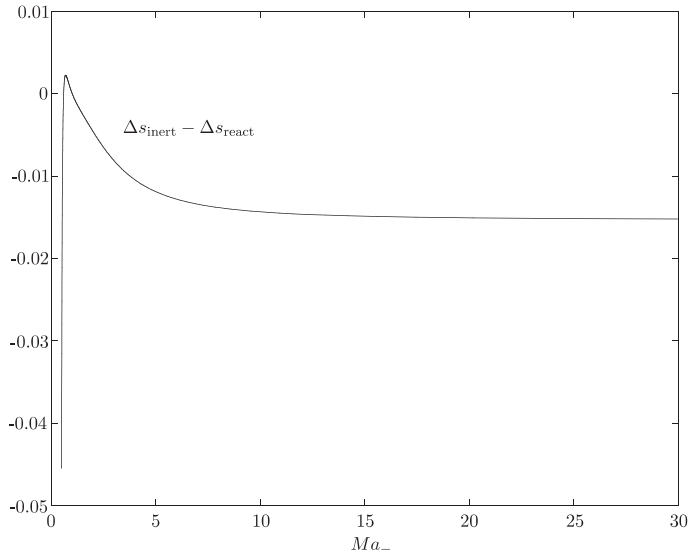

Figure 6. Difference between Δs as evaluated in the inert case (Δs_{inert}) and Δs as computed for the reactive case of Figure 5 (Δs_{react}).

Acknowledgments

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