Quasi–steady–state approximation for reaction–diffusion equations

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Abstract

In this paper, we present a rigorous proof of the quasi–steady–state approximation (QSSA) used in chemistry, in two different settings: the first one corresponds to reaction–diffusion equations, while the second one is devoted to ODEs, with a particular attention to the effect of temperature.

Key words: Quasi-Steady-State Approximation, Reaction-Diffusion

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1 Introduction

1.1 Quasi–steady–state approximation

The quasi–steady–state approximation (denoted from now on by QSSA) is a standard procedure in the study of chemical reactions kinetics in situations where certain species have a very short time of existence (free radicals, very unstable molecules, etc.) with respect to other species. It consists in assuming that the variation of the unstable species is zero, so that the size of the set of equations modeling the reactions is reduced (by the number of unstable species). We refer to [17] for a detailed description of the QSSA and the assumptions underlying its validity.

When the modeling of the chemistry is done through ODEs, and the unkonown is the concentration of species, the rigorous proof of the validity

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of the QSSA is a consequence of standard theorems of singular perturbation theory. In this frame, QSSA has been studied in a lot of papers in order to build up reduction algorithms for systems appearing in chemistry (see for instance [17, 1, 6, 16] and the references therein). We also refer to [14], [2] and the references therein for a description of a related procedure in the context of ODEs, namely the fast reaction limit.

Our paper is dedicated to the proof of the validity of the QSSA when the unknowns which model the chemistry are more complicated than the time-dependent concentrations of the species. We focus on two such situations: the first one concerns a case in which the unknown is the time-space dependent concentration of the species (and ODEs are replaced by reaction-diffusion PDEs), while the second one deals with the coupling of ODEs for the concentration of the species and the temperature of the mixture. Though those two situations are quite different, we present a mathematical analysis which is based on the same concept: namely, the use of a priori estimates based on the entropy and entropy dissipation. This restricts our result to the cases when the chemistry is reversible.

We intend, in the first part of this paper, to show that the QSSA can also be rigorously established in the case when the spatial structure of the mixture is taken into account. We restrict ourselves here to the simplest possible modeling of this spatial structure: namely, when the evolution of the species is made through reaction–diffusion PDEs. We keep however the possibility of having different diffusion rates for different species, and we look for global solutions with general data in any dimension.

This problem has been investigated in [18] in cases when there is a bounded invariant region for the unknowns and, when it is not the case, for times smaller than a critical time (depending on the initial data). The methods used in [18] rely on energy bounds for parabolic PDEs, whereas our approach is rather based on Lyapounov functionals, and do not use bounded invariant regions. It is however restricted to reversible chemistry.

A related problem consists in looking to the fast reaction limit in reaction-diffusion PDEs. This has been performed both for irreversible reactions [12] and more recently also for reversible ones [3, 4]. This last paper is closest to our approach, since it uses heavily Lyapounov functionals techniques. We wish therefore to emphasize the differences with our work : First, we work in a situation in which no bounded invariant domain is available (because we consider a system of 5 equations), whereas the system of two equations appearing in [4] admits such a domain. As a consequence, we have to rely on L^2 estimates obtained by an entropy method or a duality method (Cf. [9]). Second, the limiting processes in the QSSA and the fast reaction limit are quite different. This is best seen on the limiting systems, in which nonlinear terms appear in the right-hand side (that is, outside of the derivatives) of the system obtained by the QSSA, and in the left-hand side (that is, inside the diffusion term) in the system obtained by the fast reaction scaling.

Note that there is no hope of proving the QSSA rigorously in the more realistic context of PDEs of compressible Euler or Navier–Stokes type for global solutions with general data, since existence of such solutions is not known (even in 1D without chemical reactions). There is some hope however to prove the QSSA in this context when perturbative settings (local solutions, solutions close to equilibrium (Cf. [11]), etc.) are considered. We do not investigate in this direction in this work.

Then, in a second part of the paper, we consider a situation where the evolution of the mixture is described by ODEs (the unknowns being the concentrations of the different species and the temperature of the mixture), but where the scaling that is proposed in order to describe the QSSA (and which is based on the chemical link energy of the species) does not enter in the standard formulation of the singular perturbation theory of ODEs. Namely, singularities appear in the coefficients of the ODEs (in the Arrhenius law for example), and, moreover, the scaling involves terms of the form ε^{-1}, ε^{-2} as well as terms of the form $\exp(-1/\varepsilon)$, where ε is a small parameter.

Since our approach in this part is mainly based on the entropy estimate (and is therefore restricted to a reversible chemistry mechanism), we refer to [16] for a discussion of the behavior of the entropy when the QSSA is used. In order to prove that the temperature is bounded below, we use an argument based on the entropy structure which is directly inspired from [14].

1.2 Presentation of the main result concerning reaction–diffusion equations

Our analysis will concern the mechanism

$$A + B \rightleftarrows M \ , \qquad\qquad M \rightleftarrows C + D \ ,$$

where M is a species which is much more unstable than A, B, C, D.

This mechanism has the following features, which are mandatory for our analysis:

- each reaction is reversible,

- not more than two species are involved in each side of the reaction.

It will become convenient to denote the chemical concentrations, depending on time $t \in \mathbb{R}^+$ and point $x \in \Omega \subset \mathbb{R}^N$, of the species A, B, C, D, M both as $a \equiv a_1$, $b \equiv a_2$, $c \equiv a_3$, $d \equiv a_4$, m. We assume that $a_i \equiv a_i(t,x)$ is the concentration of A_i at time t and point x, and satisfies the following set of reaction–diffusion equations:

$$
\begin{array}{lrcl}
i=1,2 & \partial_t a_i - d_i\,\Delta_x a_i &=& k_1\,m - k_2\,a_1\,a_2\,, \\
i=3,4 & \partial_t a_i - d_i\,\Delta_x a_i &=& k_3\,m - k_4\,a_3\,a_4\,, \\
 & \partial_t m - d_5\,\Delta_x m &=& k_2\,a_1\,a_2 + k_4\,a_3\,a_4 - (k_1+k_3)m\,,
\end{array}
\tag{1}
$$

where $d_i > 0$ $(i = 1,\dots,5)$ are the diffusion rates (they can be different for each species) and $k_i > 0$ $(i = 1,\dots,4)$ are the reaction rates corresponding respectively to $M \to A+B$, $A+B \to M$, $M \to C+D$, $C+D \to M$. We complete the system with homogeneous Neumann conditions for $x \in \partial\Omega$

$$
n(x)\cdot\nabla_x\,a_i(t,x) = 0\ , \quad i=1,\dots,4\ , \qquad n(x)\cdot\nabla_x\,m(t,x) = 0\ , \tag{2}
$$

where Ω is a regular bounded open set of $\mathbb{R}^N$ (and $n(x)$ is the outward normal vector at point $x \in \partial\Omega$), and the nonnegative initial conditions

$$
a_i(0,x) = a_{i0}(x) \geq 0\ , \quad i=1,\dots,4\ , \qquad m(0,x) = 0\ . \tag{3}
$$

Note that this corresponds to an isolated chemical reactor in which no unstable species is put initially.

We now introduce the scaling corresponding to the QSSA. Since M is unstable, we suppose that k_1, $k_3 \gg k_2$, k_4. In order to simplify notations, we consider the particular case

$$
k_1 = k_3 = \frac{1}{\varepsilon}\ , \qquad\qquad k_2 = k_4 = 1\ ,
$$

and let ε go to 0. Note that our analysis would hold for any choice of k_1, k_2, k_3, k_4 such that k_1, k_3 are of order $1/\varepsilon$, and k_2, k_4 are of order 1. Our system becomes

$$
\partial_t a^\varepsilon - d_1\,\Delta_x a^\varepsilon = \frac{1}{\varepsilon}\,m^\varepsilon - a^\varepsilon b^\varepsilon\ , \tag{4}
$$

$$
\partial_t b^\varepsilon - d_2\,\Delta_x b^\varepsilon = \frac{1}{\varepsilon}\,m^\varepsilon - a^\varepsilon b^\varepsilon\ , \tag{5}
$$

$$
\partial_t c^\varepsilon - d_3\,\Delta_x c^\varepsilon = \frac{1}{\varepsilon}\,m^\varepsilon - c^\varepsilon d^\varepsilon\ , \tag{6}
$$

$$
\partial_t d^\varepsilon - d_4\,\Delta_x d^\varepsilon = \frac{1}{\varepsilon}\,m^\varepsilon - c^\varepsilon d^\varepsilon\ , \tag{7}
$$

$$
\partial_t m^\varepsilon - d_5\,\Delta_x m^\varepsilon = a^\varepsilon b^\varepsilon + c^\varepsilon d^\varepsilon - \frac{2}{\varepsilon}\,m^\varepsilon\ . \tag{8}
$$

The initial and boundary conditions write

$$a_i^\varepsilon(0,x) = a_{i0}(x) \geq 0\,, \quad i=1,\dots,4, \qquad m^\varepsilon(0,x) = 0\,, \quad x \in \Omega\,, \tag{9}$$
$$n(x)\cdot\nabla_x a_i^\varepsilon(t,x) = 0, \quad i=1,\dots,4, \quad n(x)\cdot\nabla_x m^\varepsilon(t,x) = 0\,, \;\; x\in\partial\Omega \tag{10}$$

The formal computation corresponding to the QSSA theory is the following: when ε goes to 0, we replace the left-hand side of eq. (8) by 0, and we use the corresponding relation $a\,b + c\,d = \frac{2}{\varepsilon}\,m$ in eqs. (4)–(7). This leads formally to the following system:

$$\partial_t a - d_1\,\Delta_x a = \frac{1}{2}\,(c\,d - a\,b)\;, \tag{11}$$
$$\partial_t b - d_2\,\Delta_x b = \frac{1}{2}\,(c\,d - a\,b)\;, \tag{12}$$
$$\partial_t c - d_3\,\Delta_x c = -\frac{1}{2}\,(c\,d - a\,b)\;, \tag{13}$$
$$\partial_t d - d_4\,\Delta_x d = -\frac{1}{2}\,(c\,d - a\,b)\;, \tag{14}$$

with Neumann boundary conditions and initial data:

$$a_i(0,x) = a_{i0}(x) \geq 0\,, \quad i=1,\dots,4, \quad x\in\Omega\,, \tag{15}$$
$$n(x)\cdot\nabla_x a_i(t,x) = 0\,, \quad i=1,\dots,4, \quad x\in\partial\Omega\,. \tag{16}$$

We give a rigorous result corresponding to the formal computation above. It constitutes our first main theorem :

Theorem 1.1 *Let $N\geq 1$, Ω be a bounded regular open set of $\mathbb{R}^N$, and a_{i0}, $i=1,\dots,4$, be nonnegative functions from Ω to $\mathbb{R}$ satisfying $\displaystyle\int_\Omega |a_{i0}|^2\left(1+|\ln a_{i0}|^2\right)dx < +\infty$. Let d_i, $i=1,\dots,5$ be strictly positive diffusion rates. Then,*

1. *For any $\varepsilon>0$, there exists a weak solution a^ε, b^ε, c^ε, d^ε, m^ε in $\left(L^2_{loc}([0,+\infty[\;;\;L^2(\Omega))\right)^5$ to system (4)–(10).*

2. *When $\varepsilon\to 0$, there exists a subsequence of $a^\varepsilon, b^\varepsilon, c^\varepsilon, d^\varepsilon, m^\varepsilon$ (still denoted by $a^\varepsilon, b^\varepsilon, c^\varepsilon, d^\varepsilon, m^\varepsilon$) which converges to $a,b,c,d,0$ in $\left(L^1_{loc}([0,+\infty[\;;\;L^1(\Omega))\right)^5$. Moreover, this limit is a weak solution of system (11)–(16) belonging to $\left(L^2_{loc}([0,+\infty[\;;\;L^2(\Omega))\right)^4$.*

3. *When* $N = 1$*, the solution of (4)–(10) and (11)–(16) is strong and unique as soon as the initial data* $a_{i0}, i = 1, ..., 4$ *are smooth* $(C^2(\bar{\Omega}))$ *and compatible with the Neumann boundary conditions. Then, the whole sequence* $a^\varepsilon, b^\varepsilon, c^\varepsilon, d^\varepsilon, m^\varepsilon$ *converges to* $a, b, c, d, 0$.

The proof of this theorem is based on a priori estimates mainly coming out of the entropy and entropy dissipation related to system (4)–(10). In this respect, it is reminiscent of the papers [4, 7, 8]. When $N > 1$, it also uses the method of duality proposed by M. Pierre (cf. [15, 9]) in order to prove an "$L^2 (\ln L)^2$" bound.

1.3 Presentation of the main result concerning ODEs

We introduce again the simple chemical mechanism treated in the first part of our work. Precisely, we consider a mixture of four gases A, B, C, D undergoing a reversible bimolecular chemical reaction through an unstable state, that is

$$A + B \rightleftarrows M, \qquad M \rightleftarrows C + D, \tag{17}$$

where M is an unstable species.

We recall that the fact that this mechanism is reversible plays a decisive role in our analysis.

The number densities of species A, B, C, D and M are denoted, respectively, by n_A, n_B, n_C, n_D and n_M. Moreover, the total number density is defined as $n = n_A + n_B + n_C + n_D + n_M$.

Finally, E_A, E_B, E_C, E_D and E_M denote the (constant) chemical bond energies of species A, B, C, D and M (they can all be supposed to be nonnegative), and we introduce the notations

$$E_\alpha = E_A + E_B - E_M\,, \qquad E_\beta = E_C + E_D - E_M\,, \tag{18}$$

for the strength of reactions (17), respectively, and

$$\Delta E = E_\beta - E_\alpha = E_C + E_D - E_A - E_B. \tag{19}$$

Here we assume $\Delta E \geq 0$ (the other case being similar, since the species A, B, C, D can be ordered in such a way that $\Delta E \leq 0$).

The chemical energy of the mixture is defined as

$$e_{ch} = E_A n_A + E_B n_B + E_C n_C + E_D n_D + E_M n_M\ . \tag{20}$$

We assume that the state equations for pressure and energy are those of monoatomic perfect gases (though other laws could be treated in the same way). The total energy of the system, which takes into account the thermal and chemical contributions, is therefore

$$e_{tot} = \frac{3}{2} n\Theta + e_{ch} \ , \tag{21}$$

where Θ is the temperature of the mixture.

The evolution of the mixture is governed by the following set of ODEs [10]:

$$n'_A = n'_B = -\varphi(\Theta)\, S_1, \tag{22}$$
$$n'_C = n'_D = -\psi(\Theta)\, S_2, \tag{23}$$
$$n'_M = \varphi(\Theta)\, S_1 + \psi(\Theta)\, S_2, \tag{24}$$
$$e'_{tot} = 0, \tag{25}$$

where

$$S_1 = n_A\, n_B - n_M\, e^{-E_\alpha/\Theta + \frac{3}{2}\ln\Theta - \frac{5}{2}} \ , \tag{26}$$
$$S_2 = n_C\, n_D - n_M\, e^{-E_\beta/\Theta + \frac{3}{2}\ln\Theta - \frac{5}{2}} \ , \tag{27}$$

and φ, ψ are given by a heuristic formula such as the one proposed in [10]:

$$\varphi(\Theta) = \mathcal{A}_1 \Theta^{\mathcal{B}_1} \exp\left(-\frac{\mathcal{E}_1}{\Theta}\right) \ , \qquad \psi(\Theta) = \mathcal{A}_2 \Theta^{\mathcal{B}_2} \exp\left(-\frac{\mathcal{E}_2}{\Theta}\right) \ , \tag{28}$$

where $\mathcal{A}_1, \mathcal{A}_2, \mathcal{E}_1, \mathcal{E}_2 > 0$ and $\mathcal{B}_1, \mathcal{B}_2 \in \mathbb{R}$.

Eq. (25) can be written under the explicit form

$$\left(E_A n_A + E_B n_B + E_C n_C + E_D n_D + E_M n_M + \frac{3}{2} n\Theta\right)' = 0 \ , \tag{29}$$

as well as under the form of time evolution of pressure:

$$(n\Theta)' = \frac{2}{3}\left(E_\alpha \varphi(\Theta) S_1 + E_\beta \psi(\Theta) S_2\right) \ , \tag{30}$$

or, finally, under the form of time evolution of temperature:

$$\Theta' = \left(\Theta + \frac{2}{3} E_\alpha\right) \frac{\varphi(\Theta) S_1}{n} + \left(\Theta + \frac{2}{3} E_\beta\right) \frac{\psi(\Theta) S_2}{n} \ . \tag{31}$$

Nonnegative initial conditions are imposed on system (22)-(25):

$$\begin{array}{lll} n_A(0) = n_{A0} > 0 \ , & n_B(0) = n_{B0} > 0 \ , & \Theta(0) = \Theta_0 > 0 \ , \\ n_C(0) = n_{C0} \geq 0 \ , & n_D(0) = n_{D0} \geq 0 \ , & n_M(0) = 0 \ . \end{array} \tag{32}$$

In particular, as in the previous subsection, the number density of the unstable species, n_M, is supposed to be initially zero, while the assumption of strict positivity of n_{A0} and n_{B0} is needed in order to ensure the existence of non trivial (that is, non constant) solutions (we could have chosen instead $n_{C0} > 0$ and $n_{D0} > 0$, without changing much in our analysis).

Since we are supposing that M is an unstable species, its chemical bond energy is much larger than those of the other species. Therefore, we propose a scaling consisting in choosing $E_\alpha = -1/\varepsilon$, and hence $E_\beta = \Delta E - 1/\varepsilon$. The system (22)-(25), after this rescaling, writes as

$$(n_A^\varepsilon)' = (n_B^\varepsilon)' = -\varphi(\Theta^\varepsilon) S_1^\varepsilon, \tag{33}$$

$$(n_C^\varepsilon)' = (n_D^\varepsilon)' = -\psi(\Theta^\varepsilon) S_2^\varepsilon, \tag{34}$$

$$(n_M^\varepsilon)' = \varphi(\Theta^\varepsilon) S_1^\varepsilon + \psi(\Theta^\varepsilon) S_2^\varepsilon, \tag{35}$$

$$\left[E_A n_A^\varepsilon + E_B n_B^\varepsilon + E_C n_C^\varepsilon + E_D n_D^\varepsilon + \left(E_A + E_B + \frac{1}{\varepsilon} \right) n_M^\varepsilon \right. \\ \left. + \frac{3}{2} n^\varepsilon \Theta^\varepsilon \right]' = 0 \ , \tag{36}$$

where

$$\begin{aligned} S_1^\varepsilon &= n_A^\varepsilon n_B^\varepsilon - n_M^\varepsilon \exp\left(\frac{1}{\varepsilon \Theta^\varepsilon} + \frac{3}{2} \ln \Theta^\varepsilon - \frac{5}{2} \right) , \\ S_2^\varepsilon &= n_C^\varepsilon n_D^\varepsilon - n_M^\varepsilon \exp\left(\frac{1}{\varepsilon \Theta^\varepsilon} - \frac{\Delta E}{\Theta^\varepsilon} + \frac{3}{2} \ln \Theta^\varepsilon - \frac{5}{2} \right) . \end{aligned} \tag{37}$$

The initial conditions imposed on the rescaled system (33)-(36) are supposed to be independent of ε:

$$\begin{array}{lll} n_A^\varepsilon(0) = n_{A0} > 0 \ , & n_B^\varepsilon(0) = n_{B0} > 0 \ , & n_M^\varepsilon(0) = 0 \ , \\ n_C^\varepsilon(0) = n_{C0} \geq 0 \ , & n_D^\varepsilon(0) = n_{D0} \geq 0 \ , & \Theta^\varepsilon(0) = \Theta_0 > 0 \ . \end{array} \tag{38}$$

We now present the formal computation associated to the QSSA. Note first that system (33)-(36) can also be written in the following form:

$$(n_A^\varepsilon)' = (n_B^\varepsilon)' = F^\varepsilon - \frac{\varphi^\varepsilon}{\varphi^\varepsilon + \psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \, (n_M^\varepsilon)', \tag{39}$$

$$(n_C^\varepsilon)' = (n_D^\varepsilon)' = -F^\varepsilon - \frac{\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon + \psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \, (n_M^\varepsilon)', \tag{40}$$

$$(n_M^\varepsilon)' = \varphi^\varepsilon n_A^\varepsilon n_B^\varepsilon + \psi^\varepsilon n_C^\varepsilon n_D^\varepsilon - \zeta^\varepsilon n_M^\varepsilon, \tag{41}$$

$$\begin{aligned} \frac{3}{2}\,(n^\varepsilon \Theta^\varepsilon)' = \Delta E \;F^\varepsilon + \frac{(E_A+E_B)\,\varphi^\varepsilon + (E_C+E_D)\,\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon + \psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} (n_M^\varepsilon)' \\ - \left(E_A + E_B + \frac{1}{\varepsilon}\right)(n_M^\varepsilon)', \end{aligned} \tag{42}$$

where $\varphi^\varepsilon = \varphi(\Theta^\varepsilon)$ and $\psi^\varepsilon = \psi(\Theta^\varepsilon)$,

$$F^\varepsilon = F\left(n_A^\varepsilon, n_B^\varepsilon, n_C^\varepsilon, n_D^\varepsilon, \Theta^\varepsilon\right) \equiv \frac{\varphi^\varepsilon \psi^\varepsilon}{\varphi^\varepsilon + \psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \left(n_C^\varepsilon n_D^\varepsilon - n_A^\varepsilon n_B^\varepsilon e^{-\Delta E/\Theta^\varepsilon}\right),$$

and

$$\zeta^\varepsilon = \zeta(\Theta^\varepsilon) \equiv \left(\varphi^\varepsilon + \psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}\right) \exp\left(\frac{1}{\varepsilon \Theta^\varepsilon} + \frac{3}{2}\ln \Theta^\varepsilon - \frac{5}{2}\right) .$$

In the limit $\varepsilon \to 0$, n_M^ε is expected to tend to 0 more rapidly than ε (more precisely, it is expected to be of order $e^{-\frac{1}{\varepsilon \Theta^\varepsilon}}$). Therefore, the quantities n_A^ε, n_B^ε, n_C^ε, n_D^ε and Θ^ε are expected to tend to n_A, n_B, n_C, n_D, Θ, defined as the solution of the formal limit of system (39)-(42):

$$n_A' = n_B' = F\,, \tag{43}$$

$$n_C' = n_D' = -F\,, \tag{44}$$

$$\frac{3}{2}\,(n\,\Theta)' = \Delta E \;F\,, \tag{45}$$

where $n = n_A + n_B + n_C + n_D$ and

$$F = F\left(n_A, n_B, n_C, n_D, \Theta\right) \equiv \frac{\varphi(\Theta)\psi(\Theta)}{\varphi(\Theta) + \psi(\Theta)e^{-\Delta E/\Theta}} \left(n_C n_D - n_A n_B e^{-\Delta E/\Theta}\right) \;,$$

together with the initial conditions

$$\begin{aligned} &n_A(0) = n_{A0} > 0\;, \qquad n_B(0) = n_{B0} > 0\;, \\ &n_C(0) = n_{C0} \geq 0\;, \qquad n_D(0) = n_{D0} \geq 0\;, \qquad \Theta(0) = \Theta_0 > 0\;. \end{aligned} \tag{46}$$

We now present our second main theorem, which makes rigorous this formal asymptotics:

Theorem 1.2 *We assume that $\varepsilon \in]0,1[$, that φ, ψ are C^1 functions of the temperature such that $\Theta > 0 \Longrightarrow \varphi(\Theta), \psi(\Theta) > 0$ (this assumption includes formulas such as (28)). We consider energies $E_A, E_B, E_C, E_D > 0$ and initial data $n_{A0}, n_{B0} > 0$, $n_{C0}, n_{D0} \geq 0$, $\Theta_0 > 0$. Then,*

1. *There exists a unique solution n_A^ε, n_B^ε, n_C^ε, n_D^ε, n_M^ε, Θ^ε in $C^1([0,+\infty[)$ to the Cauchy problem (33)-(38).*

2. *For all $t > 0$,*
$$n_A^\varepsilon(t), n_B^\varepsilon(t), n_C^\varepsilon(t), n_D^\varepsilon(t), n_M^\varepsilon(t), \Theta^\varepsilon(t) > 0. \tag{47}$$

3. *There exist constants $c_1, c_2, \ldots > 0$ (depending only on the data and independent of ε) such that for all $t > 0$,*
$$n_A^\varepsilon(t), n_B^\varepsilon(t), n_C^\varepsilon(t), n_D^\varepsilon(t), n_M^\varepsilon(t) \leq c_1, \tag{48}$$
$$c_2 \leq n^\varepsilon(t) \leq c_3, \tag{49}$$
$$c_4 \leq \Theta^\varepsilon(t) \leq c_5. \tag{50}$$

4. *There exists a unique solution n_A, n_B, n_C, n_D, Θ in $C^1([0,+\infty[)$ to the Cauchy problem (43)-(46).*

5. *For all $t > 0$,*
$$n_A(t), n_B(t), n_C(t), n_D(t), \Theta(t) > 0. \tag{51}$$

6. *For the same constants $c_1, c_2, \ldots > 0$ as in point 3, and for all $t > 0$,*
$$n_A(t), n_B(t), n_C(t), n_D(t) \leq c_1, \tag{52}$$
$$c_2 \leq n(t) \leq c_3, \tag{53}$$
$$c_4 \leq \Theta(t) \leq c_5. \tag{54}$$

7. *There exist constants $c_6, c_7, c_8, c_9 > 0$ (depending on the data and independent of ε) such that for any $\varepsilon \in]0,1[$ and $T > 0$,*
$$\sup_{t\in[0,+\infty[} n_M^\varepsilon(t) \leq c_6\, e^{-\frac{1}{\varepsilon\,\Theta^\varepsilon}} \leq c_6\, e^{-\frac{1}{c_4\,\varepsilon}}, \tag{55}$$
$$\sup_{t\in[0,T]} \left| n^\varepsilon_{A,B,C,D}(t) - n_{A,B,C,D}(t) \right| \leq\ c_7\, e^{c_8\,T}\, \varepsilon^{-1}\, e^{-\frac{1}{c_4\,\varepsilon}}, \tag{56}$$
$$\sup_{t\in[0,T]} |\, \Theta^\varepsilon(t) - \Theta(t)| \leq\ c_9\, e^{c_8\,T}\, \varepsilon^{-1}\, e^{-\frac{1}{c_4\,\varepsilon}}. \tag{57}$$

The proof of this theorem is based on the entropy and entropy dissipation estimates, which allow to bound from below the temperature of the mixture, and on an estimate showing that the concentration $n_M^\varepsilon(t)$ of the unstable species is bounded by a constant times $\exp(-1/(\varepsilon\,\Theta^\varepsilon(t)))$. Note that standard theorems of singular perturbation for ODEs cannot be applied a priori because of the singularities in the data (this problem disappears once it is shown that the temperature is bounded below) and because of the interplay of different scales (this is apparent for example in formulas (35)–(37), where ε^{-1} and $e^{-\frac{1}{\varepsilon\,\Theta^\varepsilon}}$ appear).

2 Proof of Theorem 1.1

For the basic functional analysis results involved in the sequel, the reader is referred to [5].

We begin by recalling that for a given $\varepsilon > 0$, the existence of a weak solution $a^\varepsilon, b^\varepsilon, c^\varepsilon, d^\varepsilon, m^\varepsilon$ in $\Big(L^2_{loc}\big([0,+\infty[\ ;\ L^2(\Omega)\big)\Big)^5$ to system (4)–(10) is a direct consequence of the results of [9], based on the duality method described in [15].

2.1 A priori estimates

We begin with the obvious partial conservation of concentrations:

Lemma 2.1 *The solutions of (4)–(10) conserve the quantities*

$$M_{13} \equiv \int_\Omega (a^\varepsilon(t,x) + c^\varepsilon(t,x) + m^\varepsilon(t,x))\,dx = \int_\Omega (a_0(x) + c_0(x))\,dx\,, \quad (58)$$

$$M_{14} \equiv \int_\Omega (a^\varepsilon(t,x) + d^\varepsilon(t,x) + m^\varepsilon(t,x))\,dx = \int_\Omega (a_0(x) + d_0(x))\,dx\,, \quad (59)$$

$$M_{23} \equiv \int_\Omega (b^\varepsilon(t,x) + c^\varepsilon(t,x) + m^\varepsilon(t,x))\,dx = \int_\Omega (b_0(x) + c_0(x))\,dx\,. \quad (60)$$

Proof: The proof follows immediately by integrating over Ω suitable linear combinations of eqs. (4)–(8). $\square$

Next we turn to the consequence of the entropy structure of the chemical reactions (this structure is directly related to the reversible character of the problem under consideration). We denote by C any constant, by C_T any constant depending on T, etc.

Lemma 2.2 *Let a_i^ε, $i=1,\dots,4$, and m^ε be solutions of the system (4)-(10), with initial data $a_{i0}\ln(a_{i0}) \in L^1(\Omega)$. Then, for all $T>0$*

$$i=1,\dots,4, \qquad \|\nabla_x \sqrt{a_i^\varepsilon}\|^2_{L^2([0,T]\times\Omega)} \le C_T\,, \tag{61}$$

$$\|\nabla_x \sqrt{m^\varepsilon}\|^2_{L^2([0,T]\times\Omega)} \le C_T\,, \tag{62}$$

$$i=1,\dots,4, \qquad \sup_{t\in[0,T]} \|a_i^\varepsilon \ln a_i^\varepsilon\|_{L^1(\Omega)} \le C_T\,, \tag{63}$$

$$\sup_{t\in[0,T]} \|m^\varepsilon \ln(m^\varepsilon/\varepsilon)\|_{L^1(\Omega)} \le C_T\,, \tag{64}$$

$$\int_0^T \int_\Omega (a^\varepsilon b^\varepsilon - m^\varepsilon/\varepsilon)\,(\ln(a^\varepsilon b^\varepsilon) - \ln(m^\varepsilon/\varepsilon))\,dx dt \le C_T\,, \tag{65}$$

$$\int_0^T \int_\Omega (c^\varepsilon d^\varepsilon - m^\varepsilon/\varepsilon)\,(\ln(c^\varepsilon d^\varepsilon) - \ln(m^\varepsilon/\varepsilon))\,dx dt \le C_T\,. \tag{66}$$

Proof: Calculating the time-derivative of the entropy-functional, E,

$$E\,(t) \equiv \int_\Omega \sum_{i=1}^4 (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon)\,dx + \int_\Omega (m^\varepsilon \ln(m^\varepsilon/\varepsilon) - m^\varepsilon)\,dx \tag{67}$$

yields

$$\begin{aligned}
&\int_\Omega \sum_{i=1}^4 (a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon)(T)\,dx + \int_\Omega (m^\varepsilon \ln(m^\varepsilon/\varepsilon) - m^\varepsilon)(T)\,dx \\
&+ \sum_{i=1}^4 4d_i \int_0^T \int_\Omega |\nabla_x \sqrt{a_i^\varepsilon}|^2\,dx dt + 4d_5 \int_0^T \int_\Omega |\nabla_x \sqrt{m^\varepsilon}|^2\,dx dt \\
&+ \int_0^T \int_\Omega (a^\varepsilon\, b^\varepsilon - m^\varepsilon/\varepsilon)\,(\ln(a^\varepsilon\, b^\varepsilon) - \ln(m^\varepsilon/\varepsilon))\,dx dt \\
&+ \int_0^T \int_\Omega (c^\varepsilon\, d^\varepsilon - m^\varepsilon/\varepsilon)\,(\ln(c^\varepsilon\, d^\varepsilon) - \ln(m^\varepsilon/\varepsilon))\,dx dt \\
&= \int_\Omega \sum_{i=1}^4 \left(a_{i0}\ln a_{i0} - a_{i0}\right)\,dx \le \int_\Omega \sum_{i=1}^4 \left(a_{i0}\ln a_{i0}\right)\,dx\,.
\end{aligned}$$

Then, (61)-(66) follow from the facts that $-(y\ln y - y)\,1_{\{y\ln y - y\le 0\}} \le 1$ and $(x-y)(\ln x - \ln y) \ge 0$. $\square$

2.2 Interpolation

We use here the a priori estimates of the previous subsection in order to prove that a^ε, b^ε, c^ε, d^ε are bounded in $L^2\,\ln L([0,T]\times\Omega)$, so that $a^\varepsilon b^\varepsilon$ and

$c^\varepsilon d^\varepsilon$ are well defined (and weakly compact in L^1, thanks to Dunford-Pettis theorem). More precisely, we have the

Lemma 2.3 *For $i = 1, \dots, 4$, and all $T > 0$,*

$$\int_0^T \int_\Omega |\, a_i^\varepsilon|^2 \, \ln a_i^\varepsilon \, dxdt \le C_T \ . \tag{68}$$

Proof:

In the case $N = 1$, the proof follows from direct computations, bearing in mind that, since Ω is a bounded interval of $\mathbb{R}$, there exists C such that (for all functions $g \equiv g(x)$) the following Sobolev estimate holds:

$$\sup_{x\in\Omega} |\, g(x)| \le C \left[\left(\int_\Omega |\partial_x g(x)|^2 \, dx \right)^{1/2} + \int_\Omega |g(x)| \, dx \right].$$

Then,

$$\begin{aligned}
\int_0^T \int_\Omega |\, a_i^\varepsilon|^2 \, |\ln a_i^\varepsilon| \, dxdt &= \int_0^T \int_\Omega (a_i^\varepsilon)(a_i^\varepsilon \, |\ln a_i^\varepsilon|) \, dxdt \\
&\le \int_0^T \left(\sup_{x\in\Omega} |\, a_i^\varepsilon| \right) \left(\int_\Omega a_i^\varepsilon \, |\ln a_i^\varepsilon| \, dx \right) \, dt \\
&\le \left(\int_0^T \sup_{x\in\Omega} |\, a_i^\varepsilon| \, dt \right) \sup_{t\in[0,T]} \left(\int_\Omega a_i^\varepsilon \, |\ln a_i^\varepsilon| \, dx \right) \\
&= \int_0^T \left(\sup_{x\in\Omega} |\sqrt{a_i^\varepsilon}| \right)^2 dt \ \sup_{t\in[0,T]} \left(\int_\Omega a_i^\varepsilon \, |\ln a_i^\varepsilon| \, dx \right) \\
&\le C \int_0^T \left(\int_\Omega |\, \partial_x \sqrt{a_i^\varepsilon}|^2 dx + \left[\int_\Omega \sqrt{a_i^\varepsilon} dx \right]^2 \right) dt \ \sup_{t\in[0,T]} \left(\int_\Omega a_i^\varepsilon \, |\ln a_i^\varepsilon| \, dx \right).
\end{aligned}$$

We conclude thanks to (61) and (63). Note that in this case, it is enough to know that $a_{i0} \in L \ln L$. The hypothesis that $a_{i0} \in L^2 (\ln L)^2$ is used only when $N > 1$.

In the case $N > 1$, we have to resort to the duality method proposed by M. Pierre (cf. [15, 9]). Let us set

$$\begin{aligned}
z^\varepsilon &= \sum_{i=1}^4 \left(a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon \right) + \left(m^\varepsilon \ln(m^\varepsilon/\varepsilon) - m^\varepsilon \right), \\
z_d^\varepsilon &= \sum_{i=1}^4 d_i \left(a_i^\varepsilon \ln a_i^\varepsilon - a_i^\varepsilon \right) + d_5 \left(m^\varepsilon \ln(m^\varepsilon/\varepsilon) - m^\varepsilon \right).
\end{aligned} \tag{69}$$

By evaluating $\partial_t z^\varepsilon$ using equations (4)–(8), it can be easily checked that

$$\partial_t z^\varepsilon - \Delta_x (A^\varepsilon z^\varepsilon) \le 0 \tag{70}$$

where $A^\varepsilon = z_d^\varepsilon / z^\varepsilon$ (computations are very similar to those in previous subsection, relevant to time derivative of the entropy functional). At this point, if w^ε denotes the positive solution of the dual problem:

$$\begin{aligned} &-\big(\partial_t w^\varepsilon + A^\varepsilon \Delta_x w^\varepsilon\big) = H \in C_0^\infty([0,T] \times \Omega, \mathbb{R}_+)\,, \\ &w^\varepsilon(T) = 0\,, \qquad n(x) \cdot \nabla_x w^\varepsilon = 0 \quad \text{on } \partial\Omega\,, \end{aligned} \tag{71}$$

it can easily be proven [9] that (by integrating by parts),

$$\int_0^T \int_\Omega z^\varepsilon \, H \, dx \, dt \le C_T \, \|z^\varepsilon(0)\|_{L^2(\Omega)} \, \|H\|_{L^2([0,T]\times\Omega)}\,, \tag{72}$$

which, by duality, gives a bound for z^ε in $L^2([0,T] \times \Omega)$. From the definition of z^ε, the statement (68) follows (in fact, a_i^ε is bounded not only in $L^2 \ln L$, but also in $L^2 (\ln L)^2$). Note that the hypothesis that $a_{i0} \in L^2(\ln L)^2$ is used here. $\square$

Then, we show the strong compactness properties of the system:

Lemma 2.4 *For $i = 1, \dots, 4$, a_i^ε converges (up to the extraction of a subsequence) for a.e. $(t,x) \in [0,+\infty[\times\Omega$ to some a_i (belonging to $L^2 \ln L([0,T] \times \Omega)$ for all $T > 0$).*

Proof: Since the proof is rather intricate, we divide it in five steps.

First step: According to (65) (or, equivalently, to (66)) and the elementary inequality

$$(z_1 - z_2)\,(\ln z_1 - \ln z_2) \ge C\,\left(\sqrt{z_1} - \sqrt{z_2}\right)^2\,,$$

we get that

$$\int_0^T \int_\Omega \left|\sqrt{a^\varepsilon b^\varepsilon} - \sqrt{m^\varepsilon/\varepsilon}\,\right|^2 dxdt \le C_T\,,$$

$$\int_0^T \int_\Omega \left|\sqrt{c^\varepsilon d^\varepsilon} - \sqrt{m^\varepsilon/\varepsilon}\,\right|^2 dxdt \le C_T.$$

Since a_i^ε are bounded in L^2, then $\sqrt{a^\varepsilon b^\varepsilon}$ (and $\sqrt{c^\varepsilon d^\varepsilon}$) is bounded in L^2. This ensures that $\sqrt{m^\varepsilon/\varepsilon}$ is also bounded in L^2, and hence $m^\varepsilon/\varepsilon$ is bounded in L^1. In particular, m^ε converges to 0 in $L^1_{loc}(\mathbb{R}^+; L^1(\Omega))$.

Second step: We denote by ω_ν the set $\{x \in \Omega \;:\; d(x, \partial\Omega) > \nu\}$. Let $x \in \omega_\nu$ (with ν positive and such that ω_ν is not an empty set), and $k \in \mathbb{R}^N$, with $|k| \leq \nu$. Using now (61), we have for all $i = 1, \ldots, 4$,

$$\int_0^T \int_{\omega_\nu} \left| \sqrt{a_i^\varepsilon}(t, x+k) - \sqrt{a_i^\varepsilon}(t,x) \right|^2 \, dx dt \leq C_T \, |k|^2.$$

Using Cauchy-Schwarz inequality and the fact that a_i^ε is bounded in L^1, we obtain

$$\begin{aligned}
&\int_0^T \int_{\omega_\nu} |\, a_i^\varepsilon(t, x+k) - a_i^\varepsilon(t,x)| \, dx dt \\
&= \int_0^T \int_{\omega_\nu} \left| \sqrt{a_i^\varepsilon}(t, x+k) - \sqrt{a_i^\varepsilon}(t,x) \right| \left| \sqrt{a_i^\varepsilon}(t, x+k) + \sqrt{a_i^\varepsilon}(t,x) \right| \, dx dt \\
&\leq C_T \, |k| \; .
\end{aligned}$$

Third step: We use equations (4) and (8) in order to get

$$\partial_t \left(a^\varepsilon + \frac{1}{2} m^\varepsilon \right) - d_1 \, \Delta_x a^\varepsilon - \frac{d_5}{2} \, \Delta_x m^\varepsilon = \frac{1}{2} \, (c^\varepsilon d^\varepsilon - a^\varepsilon b^\varepsilon) \;\; .$$

Then, introducing any smooth function $\varphi \equiv \varphi(x)$, with compact support in Ω, we have

$$\begin{aligned}
\partial_t \int_\Omega \left(a^\varepsilon + \frac{1}{2} m^\varepsilon \right) \varphi \, dx \;\; &= \;\; d_1 \int_\Omega a^\varepsilon \, \Delta_x \varphi \, dx + \frac{d_5}{2} \int_\Omega m^\varepsilon \, \Delta_x \varphi \, dx \\
&\quad + \frac{1}{2} \int_\Omega (c^\varepsilon d^\varepsilon - a^\varepsilon b^\varepsilon) \, \varphi \, dx \;\; .
\end{aligned}$$

Therefore

$$\begin{aligned}
\int_0^T \left| \partial_t \int_\Omega \left(a^\varepsilon + \frac{1}{2} m^\varepsilon \right) \varphi \, dx \right| dt \;\; &\leq \;\; d_1 \, \| \, a^\varepsilon \|_{L^1} \, \| \, \Delta_x \varphi \|_{L^\infty} \\
&\quad + \;\; \frac{d_5}{2} \, \| \, m^\varepsilon \|_{L^1} \, \| \, \Delta_x \varphi \|_{L^\infty} \\
&\quad + \;\; \frac{1}{2} \Big(\| c^\varepsilon \|_{L^2} \, \| d^\varepsilon \|_{L^2} + \| a^\varepsilon \|_{L^2} \, \| b^\varepsilon \|_{L^2} \Big) \, \| \varphi \|_{L^\infty} \\
&\leq \;\; C_T \, \| \, \varphi \|_{W^{2,\infty}} \; .
\end{aligned}$$

Fourth step: We introduce $\nu > 0$ and a mollifying sequence $\varphi_\delta(x) = \delta^{-N} \, \varphi(x/\delta)$ of smooth functions with compact support $B(0, \delta)$, so that $B(0, \delta) + \omega_\nu \subset \Omega$

when $\delta < \nu$. Then, for any $t \in [\mu, T-\mu] \subset [0,T]$ $(0 < \mu < T/2)$, and for any $h \in \mathbb{R}$, $|h| \leq \mu$, we get

$$
\begin{aligned}
&\int_{\mu}^{T-\mu} \int_{\omega_\nu} |\, a^\varepsilon(t+h,x) - a^\varepsilon(t,x)|\; dxdt \\
&\quad \leq \int_{\mu}^{T-\mu} \int_{\omega_\nu} |\,(a^\varepsilon *_x \varphi_\delta)(t+h,x) - (a^\varepsilon *_x \varphi_\delta)(t,x)|\; dxdt \\
&\qquad + 2\int_{0}^{T} \int_{\omega_\nu} |\,(a^\varepsilon *_x \varphi_\delta)(t,x) - a^\varepsilon(t,x)|\; dxdt \\
&\quad \leq \int_{\mu}^{T-\mu} \int_{\omega_\nu} \left| \left[(a^\varepsilon + \frac{1}{2} m^\varepsilon) *_x \varphi_\delta\right](t+h,x) - \left[(a^\varepsilon + \frac{1}{2} m^\varepsilon) *_x \varphi_\delta\right](t,x) \right| dxdt \\
&\qquad + \frac{1}{2}\int_{\mu}^{T-\mu} \int_{\omega_\nu} |\,(m^\varepsilon *_x \varphi_\delta)(t+h,x) - (m^\varepsilon *_x \varphi_\delta)(t,x)|\; dxdt + C_T\,\delta
\end{aligned}
$$

according to the second step.

Then, thanks to the first step (i.e. to the fact that m^ε is of order ε in L^1) and to the third step, we have

$$
\begin{aligned}
&\int_{\mu}^{T-\mu} \int_{\omega_\nu} |\, a^\varepsilon(t+h,x) - a^\varepsilon(t,x)|\; dxdt \\
&\leq \int_{t=\mu}^{T-\mu} \int_{x\in\omega_\nu} |h| \left| \int_{u=0}^{1} \left[\int_{y\in\Omega} \left(a^\varepsilon + \frac{1}{2} m^\varepsilon\right)(\cdot, y)\, \varphi_\delta(x-y)\, dy \right]'(t+uh) du \right| dxdt \\
&\qquad\qquad + C_T\,\varepsilon + C_T\,\delta \\
&\leq |\,h|\, \int_{x\in\omega_\nu} \int_{u=0}^{1} \int_{t=0}^{T} \left| \partial_t \int_{y\in\Omega} \left(a^\varepsilon + \frac{1}{2} m^\varepsilon\right)(t,y)\, \varphi_\delta(x-y)\, dy \right| dtdudx \\
&\qquad\qquad + C_T\,\varepsilon + C_T\,\delta \\
&\leq C_T\; |\,h|\, \int_{x\in\omega_\nu} ||\varphi_\delta(x-\cdot)||_{W^{2,+\infty}}\; dx + C_T\,\varepsilon + C_T\,\delta\;.
\end{aligned}
$$

Finally, optimizing in δ, we get

$$
\begin{aligned}
\int_{\mu}^{T-\mu} \int_{\omega_\nu} |\, a^\varepsilon(t+h,x) - a^\varepsilon(t,x)|\; dxdt \;&\leq\; C_T\; |\,h|\; \delta^{-N-2} + C_T\,\varepsilon + C_T\,\delta \\
&\leq\; C_T\, \left(|h|^{1/(N+3)} + \varepsilon\right)\;.
\end{aligned}
$$

Fifth step: We use (only in this step) the notation a^n instead of a^ε in order to insist on the fact that we consider a sequence ($n = 1/\varepsilon$). Using the second step and the fourth step, we get (for $|h| < \mu$, $|k| < \nu$):

$$\int_{\mu}^{T-\mu} \int_{\omega_\nu} |\, a^n(t+h, x+k) - a^n(t,x)|\, dxdt \leq C_T \left(|h|^{1/(N+3)} + |k| + \frac{1}{n} \right) . \tag{73}$$

We introduce a mollifying sequence $\psi_\delta(t,x) = \delta^{-(N+1)}\, \psi(t/\delta, x/\delta)$.

Let $\mu \in \,]0, \min\{T/2, 1\}\,[$ and $\eta > 0$ be fixed. We first introduce $\delta > 0$ such that $C_T\,(\delta^{1/(N+3)} + \delta) \leq \eta/3$, and such that $\delta < \mu$. Then, we take $m \in \mathbb{N}$ such that $C_T/m \leq \eta/3$.

Since a^n is a bounded sequence of L^1, the sequence $a^n *_{t,x} \psi_\delta$ is compact in $L^1(]\mu, T-\mu[\times\omega_\nu)$. Then, it is possible (compact $\Longrightarrow$ uniformly bounded) to find $f_1, .., f_P \in L^1$, such that $a^n *_{t,x} \psi_\delta \in \bigcup_{i=1}^{P} B(f_i, \eta/3)$, where B denotes the ball $B_{\|\cdot\|_{L^1(]\mu,T-\mu[\times\omega_\nu)}}$. Thanks to (73), we see that when $n \geq m$,

$$\|\, a^n *_{t,x} \psi_\delta - a^n\|_{L^1(]\mu,T-\mu[\times\omega_\nu)} \leq C_T \left(\delta^{1/(N+3)} + \delta + \frac{1}{m} \right) \leq \frac{2}{3}\,\eta\, .$$

Then, when $n \geq m$, we obtain $a^n \in \bigcup_{i=1}^{P} B(f_i, \eta)$. Finally, for all n, $a^n \in \bigcup_{i=1}^{P} B(f_i, \eta) \cup \bigcup_{i=1}^{m} B(a^i, \eta)$.

Conclusion: We deduce that the sequence a^n is uniformly bounded in $L^1(]\mu, T-\mu[\times\omega_\nu)$. Since $L^1(]\mu, T-\mu[\times\omega_\nu)$ is complete, we obtain the compactness in $L^1(]\mu, T-\mu[\times\omega_\nu)$ of this sequence. Since μ, ν can be taken arbitrarily close to 0, we see that a^n is compact in $L^1_{loc}(]0, T[\times\Omega)$. Therefore it converges (up to a subsequence) a.e. to some function a. The same holds for b^n since it satisfies the same equation as a^n. For c^n and d^n, the proof is also exactly the same. $\square$

2.3 Passing to the limit

We begin by writing down the equations satisfied by $a_i^\varepsilon + \frac{1}{2}\, m^\varepsilon$. This gives

$$\partial_t \left(a_i^\varepsilon + \frac{1}{2} m^\varepsilon \right) - d_i\, \Delta_x a_i^\varepsilon - \frac{d_5}{2}\, \Delta_x m^\varepsilon = \frac{1}{2}\, (-1)^{k_i} (c^\varepsilon\, d^\varepsilon - a^\varepsilon\, b^\varepsilon), \tag{74}$$

with $k_i = 0$ for $i = 1, 2$ and $k_i = 1$ for $i = 3, 4$.

We recall that the weak form associated to (74) (together with initial data and boundary conditions) is the following : for any smooth (C^2) test function $\varphi \equiv \varphi(t,x)$ with compact support in $[0,+\infty[\times\bar{\Omega}$ and such that $n(x)\cdot\nabla_x\varphi(t,x)=0$ for $x\in\partial\Omega$,

$$\int_0^{+\infty}\int_\Omega \left(a_i^\varepsilon + \frac{1}{2}m^\varepsilon\right)\partial_t\varphi\,dxdt + \int_\Omega a_{i0}(x)\,\varphi(0,x)\,dx$$
$$+\int_0^{+\infty}\int_\Omega \left(d_i\,a_i^\varepsilon + \frac{d_5}{2}\,m^\varepsilon\right)\Delta_x\varphi\,dxdt = \frac{1}{2}(-1)^{k_i}\int_0^{+\infty}\int_\Omega (a^\varepsilon\,b^\varepsilon - c^\varepsilon\,d^\varepsilon)\,\varphi\;dxdt\,. \tag{75}$$

At this point, let us recall that according to Lemma 2.4, a_i^ε converges a.e. (up to a subsequence) to a_i; moreover, the sequence a_i^ε is bounded in $L^2\ln L([0,T]\times\Omega)$ (see Lemma 2.3), and consequently there exists a subsequence which converges in $L^2_{loc}(\mathbb{R}^+;L^2(\Omega))$ strong (toward a_i). Bearing also in mind the fact that m^ε converges to 0 in $L^1_{loc}(\mathbb{R}^+;L^1(\Omega))$ strong (first step of Lemma 2.4), we can pass to the limit $\varepsilon\to 0$ in the left-hand side of (75), obtaining

$$\int_0^{+\infty}\int_\Omega a_i\;\;\partial_t\varphi\,dxdt + \int_\Omega a_{i0}\;\varphi(0,\cdot)\;dx + \int_0^{+\infty}\int_\Omega d_i\,a_i\;\;\Delta_x\varphi\,dxdt. \tag{76}$$

As concerns the right-hand side of (75), the following estimate holds

$$\int_0^T\int_\Omega a^\varepsilon b^\varepsilon\sqrt{|\ln(a^\varepsilon b^\varepsilon)|} \le \int_0^T\int_\Omega a^\varepsilon b^\varepsilon\sqrt{|\ln a^\varepsilon|} + \int_0^T\int_\Omega a^\varepsilon b^\varepsilon\sqrt{|\ln b^\varepsilon|}$$
$$\le \left\|a^\varepsilon\sqrt{|\ln a^\varepsilon|}\right\|_{L^2}\left\|b^\varepsilon\right\|_{L^2} + \left\|b^\varepsilon\sqrt{|\ln b^\varepsilon|}\right\|_{L^2}\left\|a^\varepsilon\right\|_{L^2} \le C_T$$

thanks to Lemma 2.3. We can bound in the same way the quantity $\int_0^T\int_\Omega c^\varepsilon d^\varepsilon\sqrt{|\ln(c^\varepsilon d^\varepsilon)|}$. Thus, the sequence $a^\varepsilon b^\varepsilon$ (or $c^\varepsilon d^\varepsilon$) is equiintegrable. Combining this result with the fact that $a_i^\varepsilon\to a_i$ a.e. implies $a_i^\varepsilon a_j^\varepsilon\to a_i a_j$ a.e., we see that

$$\int_0^{+\infty}\int_\Omega (a^\varepsilon\,b^\varepsilon - c^\varepsilon\,d^\varepsilon)\,\varphi\;dxdt$$

converges to

$$\int_0^{+\infty}\int_\Omega (a\,b - c\,d)\,\varphi\;dxdt\;.$$

Finally, we can pass to the limit in the weak form of system (74), ending up with

$$\begin{aligned}\int_0^{+\infty}\int_\Omega a_i\;\;\partial_t\varphi\,dxdt + \int_\Omega a_{i0}\;\varphi(0,\cdot)\;dx +\; d_i\int_0^{+\infty}\int_\Omega a_i\;\;\Delta_x\varphi\,dxdt =\\ = \frac{1}{2}(-1)^{k_i}\int_0^{+\infty}\int_\Omega (a\,b - c\,d)\,\varphi\;dxdt\,,\end{aligned} \tag{77}$$

which is exactly the weak form of system (11) – (16).

In order to conclude the proof of theorem 1.1, it remains to prove point 3. For this, we recall that when $N = 1$, since (for a given $\varepsilon \geq 0$, and with the convention $a_i^0 = a_i$) $\partial_t a_i^\varepsilon - d_i\, \partial_{xx} a_i^\varepsilon \in L^1([0,T] \times \Omega)$ for all $T > 0$, standard estimates for the heat equation (Cf. for example [8]) ensure that $a_i^\varepsilon \in L^{3-\delta}([0,T] \times \Omega)$ for all $\delta > 0$. As a consequence, $\partial_t a_i^\varepsilon - d_i\, \partial_{xx} a_i^\varepsilon \in L^{3/2-\delta/2}([0,T] \times \Omega)$, and by bootstrapping, it is possible to get that a_i^ε are smooth (in $C^2([0,+\infty[\times\bar{\Omega}))$, provided that the initial data are in $C^2(\bar{\Omega})$ and compatible with the Neumann boundary condition (Cf. for example [13]). Any weak solution is therefore a strong solution, and uniqueness (of a weak solution) for systems (4)-(10) and (11)-(16) is then easily obtained. As a consequence, any subsequence of $(a^\varepsilon, ..., m^\varepsilon)_{\varepsilon>0}$ converges to the unique solution of system (11)-(16), and therefore the whole sequence converges.

Remark.

- We explain why we think that the assumption that the chemistry is reversible and that at most two species appear on each side of the reaction is mandatory for our analysis. Note first the crucial role played by the entropy (67), which allows to prove the bounds stated in Lemma 2.2. Since the entropy plays a key-role there, we think that our method of proof cannot be easily adapted to non reversible mechanisms of reaction. Note also that the duality argument gives a bound in $L^2\,(\ln L)^2$ (and not in L^3), so that our method is also not adapted to reaction mechanisms involving three (or more) species on one side of a reaction. In this last situation, one can hope however that renormalized solutions (Cf. [9]) could be the right concept in order to prove the validity of the QSSA.

- We now discuss the initial and boundary conditions. We think that our analysis still holds if $m^\varepsilon(0,x) = O(\varepsilon)$. It fails however if ε is negligible in front of m^ε: in such a situation, an initial layer appears and it has to be taken into account in the analysis. We also point out the fact that non bounded domains (or homogeneous Dirichlet conditions) could be considered by our method without changing much the results. However, if a non homogeneous Dirichlet condition is imposed at the boundary for m^ε, then some boundary layer should appear.

- Finally, we discuss the type of diffusion operator that can be considered. Note first that if the constant diffusion coefficients are replaced by smooth x-dependent matrices leading to a non degenerate diffusion for each equation, our analysis is still valid. We think in fact that as long as the sum of the diffusion matrices of the (non vanishing) species is non-degenerate, the validity of our analysis is preserved (Cf. [9] for such a situation). Finally, adding an advection term involving a drift velocity (the velocity of the background for example, if the species that we are considering are traces) of the kind $\nabla_x \cdot (u\, a_i)$ should lead to no difficulty, provided that u is smooth enough.

3 Proof of Theorem 1.2

We now turn to the rigorous proof of the QSSA for a system of ODEs taking into account the temperature of the mixture.

3.1 Proof of points 1. to 6. of Theorem 1.2

We begin with the proof that (48)-(50) holds on $[0, T_\varepsilon[$, where T_ε is the largest possible time of existence of a solution of the Cauchy problem (33)-(38) whose components are all strictly positive.

More precisely, we define first τ_ε as the largest possible time of existence of a solution of the Cauchy problem (33)-(38). This quantity is well-defined and strictly positive thanks to Cauchy-Lipschitz' theorem, which can be used since all the functions in the system are assumed to be of class C^1 at least in a neighborhood of the initial datum.

Then, we define $T_\varepsilon = \sup\{T \in [0, \tau_\varepsilon[\,:\, \forall t \in]0, T], \quad n^\varepsilon_{A,B,C,D,M}(t) > 0, \Theta^\varepsilon(t) > 0\}$. It is obvious that $T_\varepsilon > 0$ if all initial data are strictly positive. Then, if $n_{C0} = 0$, one can verify that $(n^\varepsilon_C)'(0) = 0$ and $(n^\varepsilon_C)''(0) > 0$. The same is true when C is replaced by D. As a consequence, $T_\varepsilon > 0$ also in this case.

At this point, it can be easily proven that no one of the field variables can vanish at a time $T^* < \tau_\varepsilon$. In fact, if we consider the first time when at least one of the field variables vanishes, all possible cases lead to one of the following two contradictions :

1. in some cases, we get that one of the vanishing quantities has strictly positive prime derivative at time T^*, and this is in contradiction with the fact that it is strictly positive before T^*,

2. in other cases, we get that the unique solution is the constant one, and this leads to the contradiction that some of the variables vanishing at T^* are supposed to have strictly positive initial values.

Therefore, we must have $T_\varepsilon = \tau_\varepsilon$.

Remember that the chemical bond energies $E_A, \ldots, E_D$ are assumed to be all positive. The independent conserved quantities on $[0, T_\varepsilon]$ are:

$$
\begin{aligned}
& n_A^\varepsilon + n_C^\varepsilon + n_M^\varepsilon := \bar{n}_1 > 0 \ , && (78)\\
& n_A^\varepsilon + n_D^\varepsilon + n_M^\varepsilon := \bar{n}_2 > 0 \ , && (79)\\
& n_B^\varepsilon + n_C^\varepsilon + n_M^\varepsilon := \bar{n}_3 > 0 \ , && (80)\\
& E_A n_A^\varepsilon + E_B n_B^\varepsilon + E_C n_C^\varepsilon + E_D n_D^\varepsilon + \left(E_A + E_B + \frac{1}{\varepsilon} \right) n_M^\varepsilon \\
& \qquad + \frac{3}{2} n^\varepsilon \Theta^\varepsilon := \bar{W} > 0 \ . && (81)
\end{aligned}
$$

Therefore, it is possible to obtain (up to time T_ε) estimates (48), (49) and the upper bound in (50) :

$$\Theta^\varepsilon(t) \leq c_5.$$

Finally, in order to get a lower bound for Θ^ε, we introduce the entropy

$$e^\varepsilon = n_A^\varepsilon \ln n_A^\varepsilon + n_B^\varepsilon \ln n_B^\varepsilon + n_C^\varepsilon \ln n_C^\varepsilon + n_D^\varepsilon \ln n_D^\varepsilon + n_M^\varepsilon \ln n_M^\varepsilon - \frac{3}{2} n^\varepsilon \ln \Theta^\varepsilon,$$

which is easily seen to be a decreasing function of time. In fact, one can check that

$$
\begin{aligned}
(e^\varepsilon)' \quad = \quad & -\varphi^\varepsilon S_1^\varepsilon \left\{ \ln \left(n_A^\varepsilon n_B^\varepsilon \right) - \ln \left(n_M^\varepsilon e^{\frac{1}{\varepsilon \Theta^\varepsilon} + \frac{3}{2} \ln \Theta^\varepsilon - \frac{5}{2}} \right) \right\} \\
& -\psi^\varepsilon S_2^\varepsilon \left\{ \ln \left(n_C^\varepsilon n_D^\varepsilon \right) - \ln \left(n_M^\varepsilon e^{\frac{1}{\varepsilon \Theta^\varepsilon} - \frac{\Delta E}{\Theta^\varepsilon} + \frac{3}{2} \ln \Theta^\varepsilon - \frac{5}{2}} \right) \right\} \leq 0,
\end{aligned}
$$

thanks to the standard inequality $(x - y)(\ln x - \ln y) \geq 0$, $\forall\, x, y > 0$.

So, using the lower bound for n^ε and the inequality $x \ln x > -1$, $\forall\, x > 0$, the lower bound for Θ^ε in (50) (on $[0, T_\varepsilon[$) follows from the estimate

$$e^\varepsilon(t) \leq e(0) \qquad \forall\, t \in [0, T^\varepsilon[.$$

According to standard theorems for ODEs, we deduce from the previous properties of boundedness that $T_\varepsilon (= \tau_\varepsilon) = +\infty$.

Notice also that the properties of existence and uniqueness of solutions (together with boundedness and strict positivity of the components of the solution) for the limiting system can be proven following the same lines as above. The fact that the constants in (52)-(54) are the same as those in (48)-(50) is a consequence of point 7. proven below.

3.2 Estimate for n_M^ε

At this point, we are able to prove the statement (55) of theorem 1.2. Note first that eq. (41) can be rewritten under the form

$$\left(n_M^\varepsilon e^{\int_0^\cdot \zeta^\varepsilon(s)\,ds}\right)' = e^{\int_0^\cdot \zeta^\varepsilon(s)\,ds}\left(\varphi^\varepsilon n_A^\varepsilon n_B^\varepsilon + \psi^\varepsilon n_C^\varepsilon n_D^\varepsilon\right) ,$$

and then, integrating on $[0,t]$, we get

$$n_M^\varepsilon(t) e^{\int_0^t \zeta^\varepsilon(\sigma)\,d\sigma} - n_M^\varepsilon(0) = \int_0^t e^{\int_0^s \zeta^\varepsilon(\sigma)\,d\sigma}\left(\varphi^\varepsilon n_A^\varepsilon n_B^\varepsilon + \psi^\varepsilon n_C^\varepsilon n_D^\varepsilon\right)(s)\,ds ,$$

from which, recalling that $n_M^\varepsilon(0)=0$, we obtain that

$$n_M^\varepsilon(t) = \int_0^t e^{-\int_s^t \zeta^\varepsilon(\sigma)\,d\sigma}\left(\varphi^\varepsilon n_A^\varepsilon n_B^\varepsilon + \psi^\varepsilon n_C^\varepsilon n_D^\varepsilon\right)(s)\,ds .$$

Since Θ^ε is bounded (from above and below), then φ^ε and ψ^ε are bounded too (both being sufficiently smooth functions of Θ^ε). So, thanks to the upper bounds for n_A^ε, n_B^ε, n_C^ε and n_D^ε, we get

$$n_M^\varepsilon(t) \le \bar{C}\int_0^t e^{-\int_s^t \zeta^\varepsilon(\sigma)\,d\sigma}\,ds , \tag{82}$$

where $\bar{C} = c_1^2 \sup_{c_4\le\Theta\le c_5}(\varphi^\varepsilon(\Theta)+\psi^\varepsilon(\Theta))$. Moreover, again from the boundedness of Θ^ε, the following inequality holds for all $\sigma\in[0,t]$:

$$\zeta^\varepsilon(\sigma) \ge \tilde{C}\,e^{\frac{1}{c_4\,\varepsilon}} ,$$

where $\tilde{C} = \inf_{c_4\le\Theta\le c_5}(\varphi^\varepsilon(\Theta)+\psi^\varepsilon(\Theta)\,e^{-\Delta E/c_5})\,c_5^{3/2}\,e^{-5/2}$. Thus, estimate (82) yields

$$n_M^\varepsilon(t) \le \bar{C}\int_0^t e^{-\tilde{C}\,(t-s)\,e^{\frac{1}{c_4\,\varepsilon}}}\,ds = \bar{C}\,\frac{1-e^{-\tilde{C}\,t\,e^{\frac{1}{c_4\,\varepsilon}}}}{\tilde{C}\,e^{\frac{1}{c_4\,\varepsilon}}} \le \frac{\bar{C}}{\tilde{C}}\,e^{-\frac{1}{c_4\,\varepsilon}} \tag{83}$$

for all $t\ge0$ and $\varepsilon>0$.

Then, let us compute the quantity

$$\begin{aligned} e^{-\frac{1}{\varepsilon\,\Theta^\varepsilon}}\left(n_M^\varepsilon\,e^{\frac{1}{\varepsilon\,\Theta^\varepsilon}}\right)' &= \varphi^\varepsilon\left[1-\left(\frac{1}{\varepsilon\,\Theta^\varepsilon}-\frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon}\right]n_A^\varepsilon n_B^\varepsilon \\ &+ \psi^\varepsilon\left[1-\left(\frac{1}{\varepsilon\,\Theta^\varepsilon}+\frac{2\,\Delta E}{3\varepsilon\,(\Theta^\varepsilon)^2}-\frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon}\right]n_C^\varepsilon n_D^\varepsilon \\ &- n_M^\varepsilon\,e^{\frac{1}{\varepsilon\,\Theta^\varepsilon}}(\Theta^\varepsilon)^{3/2}\,e^{-5/2}\left\{\varphi^\varepsilon\left[1-\left(\frac{1}{\varepsilon\,\Theta^\varepsilon}-\frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon}\right]\right. \\ &\left.+ \psi^\varepsilon\,e^{-\frac{\Delta E}{\Theta^\varepsilon}}\left[1-\left(\frac{1}{\varepsilon\,\Theta^\varepsilon}+\frac{2\,\Delta E}{3\varepsilon\,(\Theta^\varepsilon)^2}-\frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon}\right]\right\}, \end{aligned}$$

namely

$$e^{-\frac{1}{\varepsilon\,\Theta^\varepsilon}}\left(n_M^\varepsilon\, e^{\frac{1}{\varepsilon\,\Theta^\varepsilon}}\right)' = \varphi^\varepsilon\,\alpha^\varepsilon\, n_A^\varepsilon n_B^\varepsilon + \psi^\varepsilon\beta^\varepsilon\, n_C^\varepsilon n_D^\varepsilon - \left(n_M^\varepsilon\, e^{\frac{1}{\varepsilon\,\Theta^\varepsilon}}\right)(\Theta^\varepsilon)^{3/2}\, e^{-5/2}\left[\varphi^\varepsilon\,\alpha^\varepsilon + \psi^\varepsilon\beta^\varepsilon\, e^{-\frac{\Delta E}{\Theta^\varepsilon}}\right] \tag{84}$$

where

$$\alpha^\varepsilon = 1 - \left(\frac{1}{\varepsilon\,\Theta^\varepsilon} - \frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon}$$

$$\beta^\varepsilon = 1 - \left(\frac{1}{\varepsilon\,\Theta^\varepsilon} + \frac{2\,\Delta E}{3\varepsilon\,(\Theta^\varepsilon)^2} - \frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon}.$$

As a consequence, by applying Duhamel's formula to (84) (remembering that $n_M^\varepsilon(0) = 0$), we get, for any $t \ge 0$,

$$|n_M^\varepsilon\, e^{\frac{1}{\varepsilon\,\Theta^\varepsilon}}(t)| \le \frac{\sup_{s\in[0,t]}\{|\varphi^\varepsilon\,\alpha^\varepsilon\, n_A^\varepsilon n_B^\varepsilon + \psi^\varepsilon\beta^\varepsilon\, n_C^\varepsilon n_D^\varepsilon|(s)\}}{\inf_{s\in[0,t]}\{(\Theta^\varepsilon)^{3/2}\, e^{-5/2}|\varphi^\varepsilon\,\alpha^\varepsilon + \psi^\varepsilon\beta^\varepsilon\, e^{-\frac{\Delta E}{\Theta^\varepsilon}}|(s)\}}.$$

Thanks to estimates (49), (50) and (83), we have

$$\beta^\varepsilon \le 1 + \frac{2}{3\varepsilon^2\,(\Theta^\varepsilon)^2}\frac{n_M^\varepsilon}{n^\varepsilon} \le 1 + \frac{2}{3\,c_4^2\,\varepsilon^2}\frac{\bar{C}}{c_2}\, e^{-\frac{1}{c_4\,\varepsilon}},$$

$$\beta^\varepsilon \ge 1 - \left(\frac{1}{\varepsilon\,\Theta^\varepsilon} + \frac{2\,\Delta E}{3\varepsilon\,(\Theta^\varepsilon)^2}\right)\frac{n_M^\varepsilon}{n^\varepsilon} \ge 1 - \left(\frac{1}{c_4\,\varepsilon} + \frac{2\,\Delta E}{3\,c_4^2\,\varepsilon}\right)\frac{\bar{C}}{c_2\,\tilde{C}} e^{-\frac{1}{c_4\,\varepsilon}}.$$

Hence, it can be checked that there exists $L \in]0,1[$ (depending on constants $c_1, ..., c_5$ but not on ε and t) such that $\beta^\varepsilon \in \left[\frac{1}{2}, \frac{3}{2}\right]$ (and, in the same way, $\alpha^\varepsilon \in \left[\frac{1}{2}, \frac{3}{2}\right]$) as soon as $\varepsilon \in]0, L[$. For the parameters ε in this interval, we get

$$\begin{aligned}|(n_M^\varepsilon\, e^{\frac{1}{\varepsilon\,\Theta^\varepsilon}})(t)| &\le \frac{c_1^2\,[\sup_{s\in[0,t]}\left(\varphi^\varepsilon\,\alpha^\varepsilon\right)(s) + \sup_{s\in[0,t]}\left(\psi^\varepsilon\,\beta^\varepsilon\right)(s)]}{c_4^{3/2}\, e^{-5/2}\,\inf_{s\in[0,t]}\left(\varphi^\varepsilon\,\alpha^\varepsilon\right)(s)} \\ &\le \frac{\frac{3}{2}\,c_1^2\,[\sup_{c_4\le\Theta\le c_5}\varphi(\Theta) + \sup_{c_4\le\Theta\le c_5}\psi(\Theta)]}{\frac{1}{2}\,c_4^{3/2}\, e^{-5/2}\,\inf_{c_4\le\Theta\le c_5}\varphi(\Theta)} := c_6.\end{aligned}$$

Therefore (up to increasing c_6 in order to treat $\varepsilon \in]L, 1[$), we obtain estimate (55).

As a consequence of (55), we see that

$$|S_1^\varepsilon| \le c_1^2 + c_6\, c_5^{3/2}\, e^{-5/2}, \qquad |S_2^\varepsilon| \le c_1^2 + c_6\, c_5^{3/2}\, e^{-5/2}\, e^{\frac{\Delta E}{c_4}}. \tag{85}$$

3.3 Conclusion of the proof of theorem 1.2

In order to prove (56), (57), we subtract from each equation (39), (40), (42) for the functions n^ε_A, n^ε_B, n^ε_C, n^ε_D and Θ^ε the corresponding ones (43)-(45) for n_A, n_B, n_C, n_D and Θ. We obtain, in matrix form, that

$$\begin{aligned}\begin{pmatrix} n^\varepsilon_{A,B}-n_{A,B} \\ n^\varepsilon_{C,D}-n_{C,D} \\ \frac{3}{2}n^\varepsilon\Theta^\varepsilon-\frac{3}{2}n\,\Theta \end{pmatrix}' \quad &= \quad \begin{pmatrix} 1 \\ -1 \\ \Delta E \end{pmatrix} (F^\varepsilon - F) \\ &+ \begin{pmatrix} -\frac{\varphi^\varepsilon}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \\ -\frac{\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \\ \frac{(E_A+E_B)\varphi^\varepsilon+(E_C+E_D)\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \end{pmatrix} n^{\varepsilon'}_M \\ &- \begin{pmatrix} 0 \\ 0 \\ E_A+E_B+\frac{1}{\varepsilon} \end{pmatrix} n^{\varepsilon'}_M .\end{aligned}$$

Integrating this identity on $[0,t]$, recalling that the initial values do not depend on ε, and that $n^\varepsilon_M(0)=n_M(0)=0$, we get :

$$\begin{aligned}\begin{pmatrix} n^\varepsilon_{A,B}-n_{A,B} \\ n^\varepsilon_{C,D}-n_{C,D} \\ \frac{3}{2}n^\varepsilon\Theta^\varepsilon-\frac{3}{2}n\,\Theta \end{pmatrix}(t) = &\int_0^t \begin{pmatrix} 1 \\ -1 \\ \Delta E \end{pmatrix} (F^\varepsilon - F)(s)ds \\ &+ \begin{pmatrix} -\frac{\varphi^\varepsilon}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \\ -\frac{\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \\ \frac{(E_A+E_B)\varphi^\varepsilon+(E_C+E_D)\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \end{pmatrix}(t)\, n^\varepsilon_M(t) \\ &- \int_0^t \begin{pmatrix} -\frac{\varphi^\varepsilon}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \\ -\frac{\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \\ \frac{(E_A+E_B)\varphi^\varepsilon+(E_C+E_D)\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}}{\varphi^\varepsilon+\psi^\varepsilon e^{-\Delta E/\Theta^\varepsilon}} \end{pmatrix}'(s) n^\varepsilon_M(s)ds \\ &- \begin{pmatrix} 0 \\ 0 \\ E_A+E_B+\frac{1}{\varepsilon} \end{pmatrix} n^\varepsilon_M(t) \ .\end{aligned}$$

The last term of the right-hand side of this equation is clearly bounded by $C\,\frac{e^{-\frac{1}{c_4\varepsilon}}}{\varepsilon}$.

Noticing that $\varphi^\varepsilon+\psi^\varepsilon\,e^{-\frac{\Delta E}{\Theta^\varepsilon}} \geq \inf_{c_4\leq\Theta\leq c_5}\varphi(\Theta)$, the second term of the right-hand side is bounded by $C\,e^{-\frac{1}{c_4\varepsilon}}$.

The third term can be written under the form $\int_0^t((\Theta^\varepsilon)'\,R(\Theta^\varepsilon)\,n^\varepsilon_M)(s)\,ds$, where (thanks to the assumption of smoothness of φ and ψ) $R(\Theta)\leq C$ for

$\Theta \in [c_4, c_5]$. Then, we notice that Θ^ε satisfies the equation

$$(\Theta^\varepsilon)' = \left(\Theta^\varepsilon - \frac{2}{3\varepsilon}\right) \frac{\varphi^\varepsilon}{n^\varepsilon} S_1^\varepsilon + \left(\Theta^\varepsilon + \frac{2}{3}(\Delta E - \frac{1}{\varepsilon})\right) \frac{\psi^\varepsilon}{n^\varepsilon} S_2^\varepsilon,$$

so that thanks to (85) and (49), (50),

$$|(\Theta^\varepsilon)'(t)| \le \frac{C}{\varepsilon}.$$

Finally, we see that the third term of the right-hand side is bounded by $C \, \frac{e^{-\frac{1}{c_4 \varepsilon}}}{\varepsilon} \, t$.

Now, thanks to the hypothesis of smoothness of φ and ψ, and hence of F, and thanks to estimates (49), etc., we can write that

$$\begin{aligned}
&\left(|n_A^\varepsilon - n_A| + \cdots + |n_D^\varepsilon - n_D| + \left|\frac{3}{2} n^\varepsilon \Theta^\varepsilon - \frac{3}{2} n\, \Theta\right|\right)(t) \\
&\le \sup(1, \Delta E) \int_0^t \left(\int_0^1 \left| \nabla F \left((1-u) n_A^\varepsilon + u n_A, \cdots, (1-u) \frac{3}{2} n^\varepsilon \Theta^\varepsilon + u \frac{3}{2} n \Theta \right) \right| du \right. \\
&\qquad \left. \times \left(|n_A^\varepsilon - n_A| + \cdots + \left|\frac{3}{2} n^\varepsilon \Theta^\varepsilon - \frac{3}{2} n\, \Theta\right| \right) \right)(s)\, ds + \frac{C}{\varepsilon}\, e^{-\frac{1}{c_4 \varepsilon}}\, (1+t) \\
&\le C \int_0^t \left(|n_A^\varepsilon - n_A| + \cdots + \left|\frac{3}{2} n^\varepsilon \Theta^\varepsilon - \frac{3}{2} n\, \Theta\right| \right)(s)\, ds + \frac{C}{\varepsilon}\, e^{-\frac{1}{c_4 \varepsilon}} (1+t).
\end{aligned}$$

Finally, using Gronwall's lemma, we deduce that (for $t \in [0, T]$)

$$\left(|n_A^\varepsilon - n_A| + \cdots + |n_D^\varepsilon - n_D| + \left|\frac{3}{2} n^\varepsilon \Theta^\varepsilon - \frac{3}{2} n\, \Theta\right| \right)(t) \le C\, \frac{1+T}{\varepsilon}\, e^{-\frac{1}{c_4 \varepsilon}}\, e^{C\,T}.$$

Theorem 1.2 is then easily deduced by noticing that n^ε and n are bounded below and above.

Remark.

- Note first that the restrictions on the sign of ΔE, or on the strict positivity of n_{A0} and n_{B0}, can easily be removed (up to very small changes in the statement of the theorem). Then, any reasonable energy law (for example the energy law of perfect polytropic gases) could be handled by our approach: the main modification is that one should write the correct entropy associated with the energy law under consideration. Finally, as in the case of reaction-diffusion, we think that our method (in which the entropy plays a crucial role) is not adapted to treat irreversible problems.

- As in the previous section, our analysis still holds if $m^\varepsilon(0,x) = O(\varepsilon)$, but it fails if ε is negligible in front of m^ε: in such a situation, an initial layer appears.

- Our estimates of convergence are uniform on any compact set (in time) of $\mathbb{R}$. If one wishes to obtain uniformity with respect to time on $\mathbb{R}$, one should study the large time behavior of the systems when $\varepsilon > 0$ and $\varepsilon = 0$, and use the fact that the mass action law defining the equilibrium when $\varepsilon = 0$ is a consequence of the mass action law for a given $\varepsilon > 0$, while the other constraints (conservation of the number of molecules and energy) at $\varepsilon = 0$ are the limit of the corresponding expression when $\varepsilon > 0$.

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