

Modelisation and Numerical Simulation of a Class of Reaction-Diffusion System Resulting from Chemical Kinetics

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Abstract: In this work, we are interested in modeling the evolution of chemical reactions in the form of reaction-diffusion system. Our interest relates to quantitative of formal chemical kinetics. The key quantity is that of the reaction rate. A numerical code has been produced allowing to take into account the various non-linearities.

Key words: Chemical kinetics, mathematical modeling, reaction rate, reaction-diffusion system, finite element method.

1. Introduction

Mathematics always has the benefit of participating in the development of several scientific fields: physics, biology, biomedical, engineering ... For the mathematician, these domains offer new and exciting branches of research, while for the specialist, Mathematical modeling offers another suitable research tool with new laboratory techniques (see [1]-[3]...).

Chemical kinetics is one of the most important domains in which mathematical modeling is used. This branch of science groups together works aimed at describing qualitatively and quantitatively the evolution of chemical systems and the different processes appearing in Chemical reactions (see [4]).

One of the aims of chemical kinetics is qualitative: for example, it is a question of describing the modes of activation of a chemical reaction which, of course, requires adequate conditions for its triggering. Another object of qualitative chemical kinetics is to study the different chemical species which may appear in the reactions. We distinguish other major types of active forms: activated molecules, radicals, ions, complexes (combinations of chemical species).

We are mainly interested in quantitative or formal chemical kinetics. The key quantity is that of the reaction rate. Knowing the nature of the constituents, it is necessary to specify the quantitative influence of all the measurable factors on the reaction rates. These factors are, for example: concentration of constituents, products, reagents, catalysts, temperature, pressure, ect ...

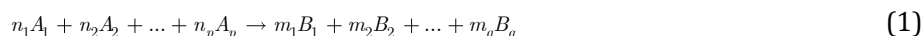
We found it expedient to explain in the first place the modeling of chemical reactions. This leads to so-called reaction-diffusion systems. It should be noted that during these last decades the interest in the study of this type of system has grown steadily and an abundant literature has been developed on this subject (see [5], [6] ...).

The second part was devoted to the numerical simulation of the reaction diffusion systems obtained in

the first part of the modeling by the finite element method. We present the general method of finite elements to solve the problems of evolutions, we also present the variational formulation of the continuous problem and that of the approximated problem. A numerical code has been created in Matlab language which allows to take into account the various nonlinearities and the numerical results are given here in graphical form.

2. The Model Problem

To explain the model, we consider the equation in equilibrium, in the following general form



where $p, q, n_i, m_j \in \mathbb{N}^*$, for all $i = 1 \dots p, j = 1 \dots q$

Assuming the system is closed, we obtain

$$v = \frac{1}{m_j} \frac{d[B_j]}{dt} = -\frac{1}{n_i} \frac{d[A_i]}{dt}, \quad i = 1 \dots p, j = 1 \dots q$$

where $[A]$ and v denote simultaneously the concentration of component A and the instantaneous rate of reaction (1).

In general, an equilibrium reaction consists not only of an elementary reaction but of several parallel or successive reactions.

For example like :



or



or again



For simplicity, we note $a = [A]; b = [B] \dots$

For these equations, the law of conservation of matter is expressed by

$$b'(t) = -a'(t) - c'(t)$$

that is to say $a(t) + b(t) + c(t) = cste$ for (2)

$$a'(t) + b'(t) = 0 \quad \text{for (3)}$$

and $x'(t) = 2 - a'(t) - c'(t) ; a'(t) = b'(t); c'(t) = d'(t)$ for (4).

For the reaction rates, we have

$$v_1 = -a'(t); v_2 = c'(t) \quad \text{for (2)}$$

$$v = -a'(t) = b'(t) \quad \text{for (3)}$$

and $v_1 = -a'(t) = -b'(t); v_2 = c'(t) = d'(t)$ for (4).

Note that in the previous systems, there are always fewer equations than unknowns. The laws of behavior will make it possible to close these systems. On the other hand, it is assumed that the elementary reactions satisfy the law of mass action. Thus, considering the following simple form the reaction



If this reaction is elementary, the reaction rate is proportional to the concentration $[A]$, such as

$$a'(t) = -ka(t) = -b'(t) \tag{5}$$

Integrating (5), we obtain $a(t) = a_0 e^{-kt}$

where $a_0 = a(0)$ is the initial value of a and k the constant of rate.

For the following reaction $A + B \rightarrow C$

assumed to be elementary, we obtain $c'(t) = ka(t)b(t)$

so

$$\begin{cases} \frac{a(t)}{a(t) - a_0 + b_0} = \frac{a_0}{b_0} e^{-k(b_0 - a_0)t}; & \text{if } b_0 \neq a_0 \\ a(t) = \frac{a_0}{1 + a_0 kt}; & \text{if not.} \end{cases}$$

Now, for the next reaction



Assuming that each reaction (6) is elementary of order 1, we obtain

$$\begin{cases} a' = -k_1 ab + k_{-1} x = b' \\ x' = k_1 ab - k_{-1} x - k_2 x \\ c' = k_2 x = d' \end{cases} \tag{7}$$

2.1. Principle of Stationary States

It consists to consider brutally that $x'(t) = 0$ in the system (7), which gives

$$k_1 ab = k_{-1} + k_2 x$$

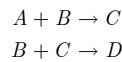
that is to say $x = \frac{k_1}{k_{-1} + k_2} ab$

then, we obtain

$$\begin{cases} a' = \frac{k_{-1} k_2}{k_{-1} + k_2} ab \\ b = a + b_0 - a_0 \\ c' = \frac{k_1 k_2}{k_{-1} + k_2} ab = d'. \end{cases}$$

2.2. Reaction-Diffusion System

Now, we place ourselves in a more realistic situation, where the reactions take place in an ambient environment and the concentrations also depend on the space variable. For example, we take the following reaction



Assuming that each of the reactions is elementary and follows a law of order 2, we would have

$$\begin{cases} a' = -k_1 ab \\ b' = -k_1 ab - k_2 bc \\ c' = k_1 ab - k_2 bc \\ d' = k_2 bc \end{cases}$$

then, the conservation of matter is expressed by

$$c' = -a' - d', b' = a' - d'$$

To take account of the dependence of concentrations of the variable of space x , we can assimilate each constituent to a continuous medium animated by a Eulerian rate $\vec{v}(x, t)$.

The quantity of a constituent A contained in the volume $w(t)$ is given by

$$m_a(w(t)) = \int_{w(t)} a(x, t) dx$$

from where

$$\frac{dm_a(w(t))}{dt} = \int_{w(t)} \frac{\partial a}{\partial t} + \operatorname{div} a(x, t) \vec{v} \, dx$$

Assuming that the rate of the reactions follows a law of order 2, we obtain

$$\frac{\partial a}{\partial t} + \operatorname{div} a(x, t) \vec{v} = -k_1 ab$$

To complete the system, we use the law of Fick $\vec{av} = -d_a \nabla \vec{a}$, where d_a is the diffusivity constant of component A.

Applying the same procedure for the other constituents, we obtain the following system

$$\begin{cases} \frac{\partial a}{\partial t} - d_a \Delta a = -k_1 ab \\ \frac{\partial b}{\partial t} - d_b \Delta b = -k_1 ab - k_2 bc \\ \frac{\partial c}{\partial t} - d_c \Delta c = -k_1 ab - k_2 bc \\ \frac{\partial d}{\partial t} - d_d \Delta d = k_2 bc \end{cases}$$

It is a system of reaction diffusion, terminology that refers to the two phenomena appearing in the diffusion equation of each constituent with its own rate of diffusion and non-linear interaction between the different constituents.

To close the system, it is necessary to add conditions to the edge of Ω which must reflect the possible exchanges of matter with the external environment.

Example 1

For the Ammonia reaction $N_2 + 3H_2 \rightarrow NH_3 + NH_3$

the mechanism of which can be explained by the introduction of an intermediate state, we obtain

$$\begin{cases} \frac{\partial [N_2]}{\partial t} - d_1 \Delta [N_2] = -\frac{k_1 k_2}{k_{-1} + k_2} [N_2] [H_2]^3 & \text{for } x, t \in \Omega \times [0, \infty \\ \frac{\partial [H_2]}{\partial t} - d_2 \Delta [H_2] = -\frac{3k_1 k_2}{k_{-1} + k_2} [N_2] [H_2]^3 & \text{for } x, t \in \Omega \times [0, \infty \\ \frac{\partial [NH_3]}{\partial t} - d_3 \Delta [NH_3] = \frac{2k_1 k_2}{k_{-1} + k_2} [N_2] [H_2]^3 & \text{for } x, t \in \Omega \times [0, \infty \\ \frac{\partial [N_2]}{\partial t} = \frac{\partial [H_2]}{\partial t} = \frac{\partial [NH_3]}{\partial t} = 0 & \text{for } (x, t) \in \Omega \times [0, \infty) \\ \frac{\partial v}{\partial t}(x, 0) = n_0, [H_2](x, 0) = h_0, [NH_3](x, 0) = 0 & \text{for } x \in \Omega \end{cases} \quad (8)$$

Example 2

For the Enzymatic reaction $E + S \rightarrow E + P$

where the molecules of the substituent S react with the enzyme E to give a product P via the formation of an intermediate complex. Then, we obtain

$$\begin{cases} \frac{\partial [E]}{\partial t} - d_1 \Delta [E] = 0 & \text{in } \Omega \times [0, \infty \\ \frac{\partial [S]}{\partial t} - d_2 \Delta [S] = -\frac{k_2}{k_M + [S]} [E]_0 [S] & \text{in } \Omega \times [0, \infty \\ \frac{\partial [P]}{\partial t} - d_3 \Delta [P] = \frac{k_2}{k_M + [S]} [E]_0 [S] & \text{in } \Omega \times [0, \infty \\ \frac{\partial [E]}{\partial t} = \frac{\partial [S]}{\partial t} = \frac{\partial [P]}{\partial t} = 0 & \text{on } \partial \Omega \times [0, \infty \\ [E](x, 0) = E_0, [S](x, 0) = S_0, [P](x, 0) = 0 & \text{for } x \in \Omega \end{cases} \quad (9)$$

Example 3

for the reaction of Hydrogen-Bromine $Br_2 + H_2 \rightarrow 2HBr$

We obtain

$$\begin{cases} \frac{\partial [Br_2]}{\partial t} - d_1 \Delta [Br_2] = \frac{-L [H_2] \cdot [Br_2]^{\frac{1}{2}}}{1 + m [H Br] / [Br_2]} & \text{in } \Omega \times [0, \infty \\ \frac{\partial [H_2]}{\partial t} - d_2 \Delta [H_2] = \frac{-L [H_2] \cdot [Br_2]^{\frac{1}{2}}}{1 + m [H Br] / [Br_2]} & \text{in } \Omega \times [0, \infty \\ \frac{\partial [H Br]}{\partial t} - d_3 \Delta [H Br] = \frac{2L [H_2] \cdot [Br_2]^{\frac{1}{2}}}{1 + m [H Br] / [Br_2]} & \text{in } \Omega \times [0, \infty) \\ \frac{\partial [Br_2]}{\partial t} = \frac{\partial [H_2]}{\partial t} = \frac{\partial [H Br]}{\partial t} = 0 & \text{on } \partial \Omega \times [0, \infty) \\ \frac{\partial v}{\partial t}(x, 0) = n_0, [H_2](x, 0) = h_0, [H Br](x, 0) = 0 & \text{For } x \in \Omega \end{cases} \quad (10)$$

where $L = k_2 \sqrt{\frac{k_1}{k_5}}$ and $m = \frac{k_4}{k_3}$.

3. Numerical Simulation

In this section we are interested to the numerical resolution of the reaction-diffusion system (8), (9) and (10). We have adopted the finite element method for the spatial approximation and that of Newton-Raphson to treat the non-linear part. We note that the numerical processing of the three reaction-diffusion (8), (9) and (10), is of the same nature and presents the same difficulties of solving a parabolic problem of the form

$$\begin{cases} \frac{\partial u}{\partial t} - d\Delta u = f(x,t,u) & \text{in } \Omega \times]0, T[\\ \frac{\partial u}{\partial \nu} = 0 & \text{on } \partial\Omega \times]0, T[\\ u(x,0) = u_0(x) & \text{in } \Omega \end{cases} \quad (11)$$

where $f : \Omega \times]0, T[\times \mathbb{R} \rightarrow \mathbb{R}$ is a measurable function such that

$$u \mapsto f(t, x, u) \text{ is of class } \mathbb{C}^1 \quad (12)$$

$$f(t, x, u) \in L^\infty(\Omega \times]0, T[) \text{ for } \forall u \in \mathbb{R} \quad (13)$$

$$\frac{\partial f(t, x, u)}{\partial u} \leq 0 \text{ for almost all } x, t \in \Omega \times]0, T[\text{ and } \forall u \in \mathbb{R} \quad (14)$$

where $\frac{\partial f}{\partial u}$ denotes the partial derivative of f compared to u .

Consider then the following spaces $X = L^2(\Omega)$ and $V = W^{1,r}(\Omega)$, where $r > 2$.

The variational formulation of problem (11) is then written as follows

$$\begin{aligned} &\text{Find } u \in V \text{ such that} \\ &\frac{d}{dt} \langle u(t), v \rangle + d \int_{\Omega} \nabla u \nabla v \, dx = \int_{\Omega} f(t, x, u) v \, dx \quad \forall v \in W^{1,r'}(\Omega) \\ &u(0) = u_0 \in X \end{aligned} \quad (15)$$

where $\langle \cdot, \cdot \rangle$ denotes the product of duality between $L^2(\Omega)$ and $L^{r'}(\Omega)$ where $\frac{1}{r} + \frac{1}{r'} = 1$.

3.1. Remark

The variational formulation (15) has a meaning. Indeed, since $r > 2, V \subset L^\infty(\Omega)$ and according to hypothesis (13), we have $f \in L^\infty(\Omega)$. Consequently $\int_{\Omega} f(t, x, u) v \, dx$ has a meaning for all $v \in W^{1,r'}(\Omega)$.

For the approximate variational problem, we consider the space $V_h^1 = \{v \in W^{1,\infty}(\Omega), v|_{T_{\text{cél}}} \in \tau_h\}$

where τ_h denotes the triangulation of Ω .

Let $m = \dim V_h^1, \Phi_i, 1 \leq i \leq m$ base of V_h^1 and z_i be the vertices of the mesh such as

$$\Phi_i(z_j) = \delta_{ij}, 1 \leq i, j \leq m$$

Consider the following approximate problem :

given $u_{0,h} \in V_h^1$, find the function $u_h : t \in]0, T[\rightarrow u_h(t) \in V_h^1$ solution of the following ordinary differential system

$$\begin{cases} \frac{d}{dt} \langle u_h(t), v_h \rangle + d \int_{\Omega} \nabla u_h \nabla v_h \, dx = \int_{\Omega} f(t, x, u_h) v_h \, dx \quad \forall v_h \in V_h^1 \\ u_h(0) = u_{0,h}. \end{cases} \quad (16)$$

We put
$$u_h(t) = \sum_{j=1}^m \xi_j(t) \Phi_j; u_{0,h} = \sum_{j=1}^m \xi_{0,j} \Phi_j$$

The approximate variational problem (16) is then written

$$\left\{ \begin{array}{l} \text{Find } \xi_j(t) \quad 1 \leq j \leq m \text{ such that} \\ \sum_{j=1}^m \frac{d}{dt} \xi_j(t) \langle \Phi_j, \Phi_i \rangle + d \sum_{j=1}^m \xi_j(t) \int_{\Omega} \nabla \Phi_j \nabla \Phi_i dx = \int_{\Omega} f(t, x, \sum_{j=1}^m \frac{d}{dt} \xi_j(t) \Phi_j) \Phi_i dx \\ \xi_j(0) = \xi_{0,j} \quad 1 \leq j \leq m \end{array} \right.$$

We introduce the Rigidity matrix $R = a_{ij}$ and the mass matrix $M = b_{ij}$ defined by

$$a_{ij} = \int_{\Omega} \nabla \Phi_j \nabla \Phi_i dx \text{ et } b_{ij} = \int_{\Omega} \Phi_j \Phi_i dx.$$

The approximate variational problem (16) finally takes the form

$$\left\{ \begin{array}{l} M \frac{d\xi}{dt} + dR\xi = F(t, \xi) \\ \xi(0) = \xi_0 \end{array} \right. \tag{17}$$

where $\xi(t) = \xi_j(t)$, $\xi(0) = \xi_{0,j}$ and $F(t, \xi) = F_i(t, \xi)$ defined by

$$F_i(t, \xi) = \int_{\Omega} f(t, x, \sum_{j=1}^m \frac{d}{dt} \xi_j(t) \Phi_j) \Phi_i dx \quad 1 \leq i \leq m.$$

We then apply the θ – method to solve our problem (16). It consists in replacing an ordinary differential equation by the finite difference diagram

$$\frac{1}{\Delta t} y_{n+1} - y_n + \theta \varphi(t_{n+1}, y_{n+1}) + 1 - \theta \varphi(t_n, y_n) = 0, \quad 1 \leq n \leq N \tag{18}$$

Therefore, to solve the differential system (17), we put $\xi^n = \xi(t_n)$ and $\xi^0 = \xi_0$. We are getting

$$\left\{ \begin{array}{l} M + d\theta\Delta t R \xi^{n+1} - \theta\Delta t F(t_{n+1}, \xi^{n+1}) = M - d(1 - \theta)\Delta t R \xi^n + 1 - \theta \Delta t F(t_n, \xi^n) \\ \xi^0 = \xi_0 \end{array} \right. \tag{19}$$

Transition algorithm from t_1 to t_{L+1}

- a) We start from $y_0 = \xi(t_1)$
- b) for $n = 1$ à L make

$$y_1 = \xi(t_n) ; \quad y_0 = y_1;$$

Repeat until Newton's convergence

$$\left\{ \begin{array}{l} M + d\theta\Delta t R - \theta\Delta t D_{\xi} F(y_1, t_{n+1}) V = M(y_0 - y_1) - d\theta\Delta t R y_1 \\ + \theta\Delta t F(y_1, t_{n+1}) + 1 - \theta \Delta t F(y_0, t_n) \\ y_1 = y_1 + V \end{array} \right.$$

End of the Newton loop

$$\xi_{t_{n+1}} = y_1;$$

end.

3.2. Numerical Results

We present the numerical results for the reaction-diffusion systems that we obtained after modelisation of the three examples studied. The initial state $t_1 = 0$ and the instant $t_{L+1} = 10$.

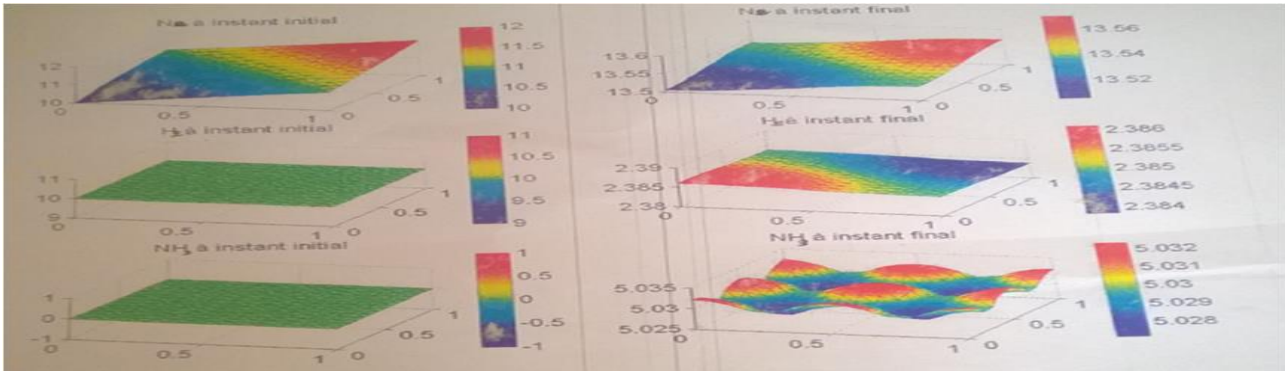


Fig. 1. Reaction of ammonia.

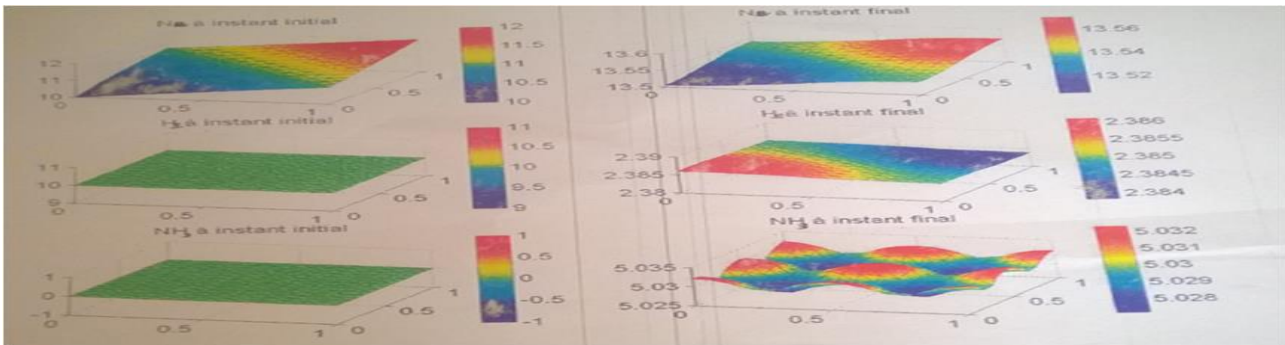


Fig. 2. Reaction of the enzyme.

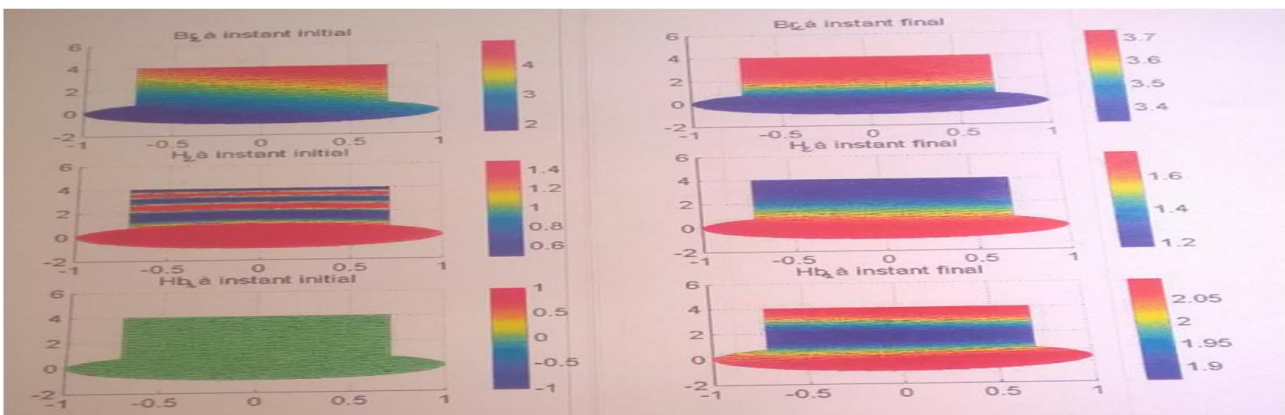


Fig. 3. Hydrogen-bromine reaction.

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