Exercises on numerical methods for chemical kinetics

1 Introduction

We denote an elementary irreversible chemical reaction under the form

$$\alpha_1 A_1 + \alpha_2 A_2 + \ldots \xrightarrow{k} \beta_1 B_1 + \beta_2 B_2 + \ldots \tag{1}$$

The reactants are the A_i and the products the B_i. The coefficients α_i and β_i are integers called stoichiometric coefficients, they measure the number of molecules of each reagent necessary for the reaction to happen, and the number of products molecules obtained. The number k is the kinetic constant of the chemical reaction and is used to establish its temporal dynamics.

More precisely, the temporal dynamics of the reaction is ruled by the law of mass action, which says that the rate of the reaction is proportional to the concentrations of all reactants. Assuming that the volume, temperature and pressure are kept constant in the experimental device considered, the average number of reactions taking place during a small time step $\Delta t > 0$ is

$$\Delta t\, k\, [A_1]^{\alpha_1}\, [A_2]^{\alpha_2}.$$

For instance, if we assume that the chemical reaction only involves 2 reactants A_1 and A_2 and 2 products B_1 and B_2, then the temporal evolution of the reaction is described by the following differential equations :

$$\begin{aligned}
\frac{d[A_1]}{dt} &= -\alpha_1\, k\, [A_1]^{\alpha_1}\, [A_2]^{\alpha_2}, \\
\frac{d[A_2]}{dt} &= -\alpha_2\, k\, [A_1]^{\alpha_1}\, [A_2]^{\alpha_2}, \\
\frac{d[B_1]}{dt} &= \beta_1\, k\, [A_1]^{\alpha_1}\, [A_2]^{\alpha_2}, \\
\frac{d[B_2]}{dt} &= \beta_2\, k\, [A_1]^{\alpha_1}\, [A_2]^{\alpha_2}.
\end{aligned}$$

2 Derivation of the model

In the following we consider a complex chemical reaction composed of 4 simultaneous elementary reactions involving 6 components A, B, D, E, X and Y.

$$A \xrightarrow{k_1} X, \tag{2}$$

$$B + X \xrightarrow{k_2} Y + D, \tag{3}$$

$$2X + Y \xrightarrow{k_3} 3X, \tag{4}$$

$$X \xrightarrow{k_4} E. \tag{5}$$

We assume that the concentrations $[A]$ and $[B]$ are kept constant all the time.

1. Write the system of differential equations describing the evolution of the concentrations $[D]$, $[E]$, $[X]$, and $[Y]$.
2. Explain why the study of this system can be simplified into the study of a system of two equations with two unknowns X and Y. Write this system.
3. The system obtained in the previous question depends on many parameters. To simplify its qualitative study, we want to identify the most relevant parameters by making linear changes of variables : we will look for $[X]$ and $[Y]$ under the form :

$$[X](t) = \alpha x(\gamma t) \text{ and } [Y](t) = \beta y(\gamma t).$$

where α, β and γ are real parameters and x and y are the new unknown functions to be determined.

Prove that we can choose α, β and γ such that the functions x and y satisfy

$$x' = a + x^2 y - (b+1)x \quad (6)$$
$$y' = bx - x^2 y. \quad (7)$$

where the only remaining parameters a and b have to be explicitly defined.

As a result of the above study, all the dynamics of the chemical reaction is described with a system containing only 2 parameters.

3 Numerical method

We define a final time T, and a time step $\delta t = \frac{T}{M}$. Thus M is the number of time steps that will be computed with the numerical method described in the following. For all $0 \leq n \leq M$ we define $t^n = n\Delta t$. The numerical method that we will study reads

$$\begin{aligned} \frac{x^{n+1} - x^n}{\Delta t} &= a + (x^n)^2 y^{n+1} - (b+1)x^{n+1} \\ \frac{y^{n+1} - y^n}{\Delta t} &= bx^{n+1} - (x^n)^2 y^{n+1}. \end{aligned} \quad (8)$$

with $x^0 = x_0 \geq 0$ and $y^0 = y_0 \geq 0$ the initial conditions of the system.

1. Prove that the numerical scheme (8) can be re-written

$$A_n \begin{pmatrix} x^{n+1} \\ y^{n+1} \end{pmatrix} = \begin{pmatrix} x^n + \Delta t a \\ y^n \end{pmatrix}$$

with A_n a 2×2 matrix that is to be written explicitly.
2. Prove that for all $n \geq 0$ A_n is invertible, and deduce from this result that the numerical scheme is well-defined.
3. Prove that all coefficients of A_n^{-1} are positive, and that x^n and y^n are positive for all $n \geq 0$.
4. Prove that

$$\forall n \geq 0, \;\; x^{n+1} + y^{n+1} \leq x^n + y^n + a\Delta t$$

5. Deduce from the previous result that there exists a constant $C > 0$ only depending of the date of the problem such that

$$\sup_{n\leq M} \left|\left| \begin{pmatrix} x^n \\ y^n \end{pmatrix} \right|\right| \leq C.$$

We define the consistency errors R_x^n and R_y^n by

$$R_x^n = \frac{x(t^{n+1}) - x(t^n)}{\Delta t} - a - (x(t^n))^2\, y(t^{n+1}) + (b+1)x(t^{n+1}) \tag{9}$$

$$R_y^n = \frac{y(t^{n+1}) - y(t^n)}{\Delta t} - bx(t^{n+1}) + (x(t^n))^2\, y(t^{n+1}). \tag{10}$$

Prove that there exists a constant $C_2 > 0$ only depending of the data of the problem such that

$$\sup_{n\leq M} (|R_x^n| + |R_y^n|) \leq C_2 \Delta t.$$

6. We define the approximation errors $e_x^n = x(t^n) - x^n$ and $e_y^n = y(t^n) - y^n$. We admit as a consequence of the results of the previous questions that there exists a constant $C_3 > 0$ only depending of the data of the problem such that

$$\begin{aligned} |e_x^{n+1}| &\leq |e_x^n| + C_3\Delta t(|e_x^n| + |e_y^n|) + C_3\Delta t(|R_x^n| + |R_y^n|) \\ |e_y^{n+1}| &\leq |e_y^n| + C_3\Delta t(|e_x^n| + |e_y^n|) + C_3\Delta t(|R_x^n| + |R_y^n|). \end{aligned}$$

Deduce from the previous inequalities the error estimation

$$\sup_{n\leq M} \Big(|e_x^n| + |e_y^n|\Big) \leq C_4 \Delta t$$

with $C_4 > 0$ a constant. Make a conclusion about the convergence of the numerical method.