**Exercises on numerical methods for chemical kinetics**

# 1 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 $Y$.*

$$
\begin{aligned}
A &\xrightarrow{k_1} X, && (1)\\
B + X &\xrightarrow{k_2} Y + D, && (2)\\
2X + Y &\xrightarrow{k_3} 3X, && (3)\\
X &\xrightarrow{k_4} E. && (4)
\end{aligned}
$$

*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 $[Y]$.*

The concentrations $[A]$ and $[B]$ are kept constant, so their evolution is not to be computed through a differential equation. Following the rules presented in the introduction, the other concentrations obey the following differential equations :

$$
\begin{aligned}
\frac{d[D]}{dt} &= -k_2[B][X],\\
\frac{d[E]}{dt} &= -k_4[X],\\
\frac{d[X]}{dt} &= k_1[A] - k_2[B][X] - 2k_3[X]^2[Y] + 3k_3[X]^2[Y] - k_4[X],\\
\frac{d[Y]}{dt} &= k_2[B][X] - 2k_3[X]^2[Y].
\end{aligned}
$$

**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.*

The evolution of the concentrations $[D]$ and $[E]$ depend only on the concentration $[X]$, while the evolution of $[X]$ does not depend on $[D]$ and $[E]$. Therefore, it is possible to compute in a first time the evolutions of $[X]$ and $[Y]$ alone, and then deduce the evolution of $[D]$ and $[E]$, through classical integration formulas. In the following, we thus only consider the following system :

$$
\begin{aligned}
\frac{d[X]}{dt} &= k_1[A] - k_2[B][X] - 2k_3[X]^2[Y] + 3k_3[X]^2[Y] - k_4[X], && (5)\\
\frac{d[Y]}{dt} &= k_2[B][X] - 2k_3[X]^2[Y]. && (6)
\end{aligned}
$$

**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 $\alpha$, $\beta$ and $\gamma$ are real parameters and $x$ and $y$ are the new unknown functions to be determined.*

*Prove that we can choose $\alpha$, $\beta$ and $\gamma$ such that the functions $x$ and $y$ satisfy*

$$x' = a + x^2 y - (b+1)x \tag{7}$$
$$y' = bx - x^2 y. \tag{8}$$

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

From the definition of $x$ and $y$ we can write

$$[X]'(t) = \gamma\alpha x'(\gamma t) \text{ and } [Y]'(t) = \gamma\beta y'(\gamma t).$$

If we express the equations (11) and (12) using the functions $x$ and $y$ we get

$$\begin{aligned}\gamma\,\alpha\,x'(\gamma t) &= k_1[A] - k_2[B]\alpha\,x(\gamma t) - 2k_3\alpha^2\,\beta\,x^2(\gamma t)\,y(\gamma t) + 3k_3\alpha^2\,\beta\,x^2(\gamma t)\,y(\gamma t)\\ &\quad -k_4\alpha\,x(\gamma t), \qquad (9)\\ \gamma\,\beta\,y'(\gamma t) &= k_2[B]\alpha\,x(\gamma t) - 2k_3\alpha^2\,\beta\,x^2(\gamma t)\,y(\gamma t). \qquad (10)\end{aligned}$$

or equivalently, if we note $s = \gamma t$

$$x'(s) = \frac{k_1[A]}{\gamma\,\alpha} - \frac{(k_2[B]+k_4)}{\gamma}x(s) + \frac{k_3\alpha\,\beta}{\gamma}x^2(s)\,y(s), \tag{11}$$
$$y'(s) = \frac{\alpha k_2[B]}{\gamma\,\beta}x(s) - \frac{2k_3\alpha^2}{\gamma}x^2(s)\,y(s). \tag{12}$$

We deduce the following relationships :

$$\begin{aligned}\frac{k_1[A]}{\gamma\,\alpha} &= a,\\ \frac{(k_2[B]+k_4)}{\gamma} &= b+1,\\ \frac{k_3\alpha\,\beta}{\gamma} &= 1,\\ \frac{\alpha k_2[B]}{\gamma\,\beta} &= b,\\ \frac{2k_3\alpha^2}{\gamma} &= 1.\end{aligned}$$

We solve this system and obtain :

$$\begin{aligned}
\gamma &= \frac{k_2[B]+2k_4}{2}, \\
\alpha &= \sqrt{\frac{k_2[B]+2k_4}{4k_3}}, \\
\beta &= 2\alpha = \sqrt{\frac{k_2[B]+2k_4}{k_3}}, \\
b &= \frac{k_2[B]}{k_2[B]+2k_4}, \\
a &= \frac{k_1[A]}{\gamma\,\alpha} = \frac{4k_1\sqrt{k_3}\,[A]}{(k_2[B]+2k_4)^{3/2}}.
\end{aligned}$$

# 2 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*

$$\begin{aligned}
\frac{x^{n+1}-x^n}{\Delta t} &= a + (x^n)^2\,y^{n+1} - (b+1)x^{n+1} \\
\frac{y^{n+1}-y^n}{\Delta t} &= bx^{n+1} - (x^n)^2\,y^{n+1}.
\end{aligned} \tag{13}$$

*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 (13) 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 $2 \times 2$ matrix that is to be written explicitly.*

The numerical scheme can be re-written

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

or equivalently

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

or equivalently

$$\begin{pmatrix} 1+\Delta t(b+1) & -(x^n)^2\Delta t \\ -\Delta t b & 1+\Delta t(x^n)^2 \end{pmatrix} \begin{pmatrix} x^{n+1} \\ y^{n+1} \end{pmatrix} = \begin{pmatrix} x^n + \Delta t a \\ y^n \end{pmatrix}$$

Thus the matrix $A_n$ is defined by :

$$A_n = \begin{pmatrix} 1+\Delta t(b+1) & -(x^n)^2\Delta t \\ -\Delta t\, b & 1+\Delta t(x^n)^2 \end{pmatrix}$$

**2.** *Prove that for all $n \geq 0$ $A_n$ is invertible, and deduce from this result that the numerical scheme is well-defined.*

We compute the discriminant $\delta$ of $A_n$.

$$\begin{aligned} \delta &= (1+\Delta t(b+1)) \times (1+\Delta t(x^n)^2) - \Delta t^2 b(x^n)^2 \\ &= 1+\Delta t(b+1) + \Delta t(x^n)^2 + \Delta t^2(b+1)(x^n)^2 - \Delta t^2 b(x^n)^2 \\ &= 1+\Delta t(b+1) + \Delta t(x^n)^2 + \Delta t^2(x^n)^2 > 0 \end{aligned}$$

Thus $A_n$ is invertible for all $n \geq 0$.

**3.** *Prove that all coefficients of $A_n^{-1}$ are positive, and that $x^n$ and $y^n$ are positive for all $n \geq 0$.*

$$A_n^{-1} = \frac{1}{\delta}\begin{pmatrix} 1+\Delta t(x^n)^2 & (x^n)^2\Delta t \\ \Delta t\, b & 1+\Delta t(b+1) \end{pmatrix}$$

We know that $\delta > 0$ thus all coefficients of $A_n^{-1}$ are positive. Consequently, because $x_0$ and $y_0$ are positive, we can prove with a reasoning by recurrence that $x^n$ and $y^n$ are positive for all $n \geq 0$.

**4.** *Prove that*

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

$$\begin{aligned} \begin{pmatrix} x^{n+1} \\ y^{n+1} \end{pmatrix} &= A_n^{-1} \begin{pmatrix} x^n + \Delta t a \\ y^n \end{pmatrix} \\ &= \frac{1}{\delta}\begin{pmatrix} 1+\Delta t(x^n)^2 & (x^n)^2\Delta t \\ \Delta t\, b & 1+\Delta t(b+1) \end{pmatrix} \begin{pmatrix} x^n + \Delta t a \\ y^n \end{pmatrix} \end{aligned}$$

$$x^{n+1} + y^{n+1} = \frac{1}{\delta}\Big((1+\Delta t(x^n)^2)(x^n+\Delta t a) + y^n(x^n)^2\Delta t + \Delta t\, b(x^n+\Delta t a) + (1+\Delta t(b+1))y^n\Big)$$

Instead of computing explicitly $x^{n+1} + y^{n+1}$, which can be tedious, we want to prove that

$$\delta(x^{n+1} + y^{n+1}) \leq \delta(x^n + y^n + a\Delta t)$$

which is equivalent to :

$$\begin{aligned} &(1+\Delta t(x^n)^2)(x^n+\Delta t a) + y^n(x^n)^2\Delta t \\ &+\Delta t\, b(x^n+\Delta t a) + (1+\Delta t(b+1))y^n \leq \Big(1+\Delta t(b+1) + \Delta t(x^n)^2 + \Delta t^2(x^n)^2\Big)(x^n + y^n + a\Delta t\Big) \end{aligned}$$

We develop the right-hand side and check that it is superior to the left-hand side.

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

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

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

$$R_x^n = \frac{x(t^{n+1}) - x(t^n)}{\Delta t} - a - (x(t^n))^2\, y(t^{n+1}) + (b+1)x(t^{n+1}) \qquad (14)$$

$$R_y^n = \frac{y(t^{n+1}) - y(t^n)}{\Delta t} - bx(t^{n+1}) + (x(t^n))^2\, y(t^{n+1}). \qquad (15)$$

***Be careful, there was a misspell in the original text of the exercise, for the definition of $R_y^n$. Here this misspell has been corrected.***

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

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

We deduce from the previous result, with a reasoning by recurrence, that :

$$x^n + y^n \le x^0 + y^0 + an\,\Delta t, \forall n \ge 0$$

Therefore,

$$\sup_{n\le M} || \begin{pmatrix} x^n \\ y^n \end{pmatrix} ||_1 = \sup_{n\le M} \{x^n + y^n\} \le x^0 + y^0 + aM\,\Delta t = C$$

Because in finite dimension all norms are equivalent, if we use another norm, we will find the same inequality with a different constant $C$.
We make Taylor series expansions of $x(t^{n+1})$ and $y(t^{n+1})$ with respect to $t^n$ :

$$\begin{aligned} x(t^{n+1}) &= x(t^n) + \Delta t x'(t^n) + O(\Delta t^2) \\ y(t^{n+1}) &= y(t^n) + \Delta t y'(t^n) + O(\Delta t^2). \end{aligned}$$

Because $x$ and $y$ are solutions of the differential system (7)-(8), they satisfy :

$$\begin{aligned} x'(t^n) &= a + x^2(t^n)y(t^n) - (b+1)x(t^n) \\ y'(t^n) &= bx(t^n) - x^2(t^n)y(t^n). \end{aligned}$$

We deduce from these four relationships that

$$\begin{aligned} R_x^n &= x'(t^n) + O(\Delta t) - a - (x(t^n))^2 \Big( y(t^n) + \Delta t y'(t^n) + O(\Delta t^2) \Big) \\ &\quad + (b+1)\Big( x(t^n) + \Delta t x'(t^n) + O(\Delta t^2) \Big) \\ &= x'(t^n) - a - (x(t^n))^2\, (y(t^n) + (b+1)x(t^n) + O(\Delta t) \\ &= O(\Delta t) \\ R_y^n &= y'(t^n) + O(\Delta t) - b\Big( x(t^n) + \Delta t x'(t^n) + O(\Delta t^2) \Big) \\ &\quad - (x(t^n))^2 \Big( y(t^n) + \Delta t y'(t^n) + O(\Delta t^2) \Big) \\ &= y'(t^n) + O(\Delta t) - b(x(t^n) + O(\Delta t)) - (x(t^n))^2\, y(t^n) + O(\Delta t) \\ &= O(\Delta t) \end{aligned}$$

Therefore 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*

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

*with* $C_4 > 0$ *a constant. Make a conclusion about the convergence of the numerical method.*
We start from the result of the previous question :

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

If we sum both equations we can write :

$$\begin{aligned} |e_x^{n+1}| + |e_y^{n+1}| &\leq |e_x^n| + |e_y^n| + 2C_3 \Delta t(|e_x^n| + |e_y^n|) + 2C_3 \Delta t(|R_x^n| + |R_y^n|) \\ &\leq (1 + 2C_3 \Delta t)(|e_x^n| + |e_y^n|) + 2C_2 C_3 \Delta t^2 \\ &\leq (1 + 2C_3 \Delta t)(|e_x^n| + |e_y^n|) + 2C_2 C_3 \Delta t^2 \end{aligned}$$

With a reasoning by recurrence we can prove that

$$\begin{aligned} |e_x^n| + |e_y^n| &\leq (1 + 2C_3 \Delta t)^n (\underbrace{|e_x^0|}_{=0} + \underbrace{|e_y^0|}_{=0}) + \sum_{i=0}^{n} (1 + 2C_3 \Delta t)^i 2C_2 C_3 \Delta t^2 \\ &\leq 2C_2 C_3 \Delta t^2 \sum_{i=0}^{n-1} (1 + 2C_3 \Delta t)^i \\ &\leq 2C_2 C_3 \Delta t^2 n (1 + 2C_3 \Delta t)^n \end{aligned}$$

Now we use the fact that $1 + u \leq e^u$ for all $u \geq 0$.

$$\begin{aligned} |e_x^n| + |e_y^n| &\leq 2C_2 C_3 \Delta t^2 n \, (e^{2C_3 \Delta t})^n \\ &\leq 2C_2 C_3 \Delta t^2 n \, e^{n 2C_3 \Delta t} \end{aligned}$$

If $n \leq M$ it means that $n\Delta t \leq T$. Thus for all $n \leq M$ we have :

$$|e_x^n| + |e_y^n| \leq 2C_2 C_3 \Delta t \, T \, e^{2C_3 \Delta T}$$

We have proved the expected result with $C_4 = 2C_2 C_3 e^{2C_3 \Delta T}$. This result means that the numerical method converges to the exact solution of the differential system when $\Delta t \to 0$.