Master de Chemoinformatique et Modélisation M1S1
Examen de mathématiques pour la chimie *

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Résumé

Documents autorisés. Durée : 2h. La copie de l'étudiant sera constituée d'un support papier traditionnel et d'un ou plusieurs fichiers de calcul pour Maple. ***Toute réponse doit être motivée ou sera considérée comme nulle.***

Exercise 1

Question 1.1

Explain briefly the meaning of the following notions :
— Analytic function,
— Jacobian Matrix,
— Differential equation.

The Brusselator is an hypothetical oscillating reaction inspired by the Belousov-Zhabotinsky reaction [1]. In this case, the Cerium III is converted to Cerium IV during a reaction catalyzed by bromate ions but inhibited by bromide ions. In the mean time, the Cerium IV is converted to Cerium III by a bromide ions generating reaction. Thus, independently of the total reaction balance, during the reaction, the Cerium III and IV concentrations are oscillating : the presence of bromate ions catalyze the production of Cerium IV that are converted back to Cerium III faster when the bromide ions reach a sufficient concentration ; while the Cerium IV is consumed, the bromide concentration become insufficient to inhibit the conversion of Cerium III, then becoming preponderant and the cycle continues. This process is modeled by the 4 following chemical reactions implying 6 species, with the kinetic reaction rates k_1 to k_4 :

$$\begin{aligned} A &\xrightarrow{k_1} X \\ 2X + Y &\xrightarrow{k_2} 3X \\ B + X &\xrightarrow{k_3} Y + C \\ X &\xrightarrow{k_4} D \end{aligned}$$

Each reaction step is considered irreversible.

Question 1.2

Using the symbols A, B ,C, D, X and Y for the concentrations and k_1 to k_4 for reaction rates, complete the table 1 resuming the kinetics of each reaction steps.

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TABLE 1 – reaction steps and rate laws contributions

Step	Reaction	Step contribution to rate law
1	?	`eq1A=diff(A(t),t)=-k1*A(t)` `eq1X=diff(A(t),t)=k1*A(t)`
2	$2X + Y \xrightarrow{k_2} 3X$	`eq2X=`? `eq1Y=`?
3	$B + X \xrightarrow{k_3} Y + C$	`eq3B=`? `eq3X=`? `eq3Y=`? `eq3C=`?
4	$X \xrightarrow{k_4} D$	`eq4X=`? `eq4D=`?

Question 1.3

Using the table 1 above, demonstrate that the sum of the species concentrations A, D, X and Y is time independent and the sum of the species concentrations B and C is also time independent. To do so it is sufficient to show that the time derivative of these sums is nul.

From this we conclude on the following conservation laws, where M and N are constants fixed by the initial conditions :

$$A(t) + X(t) + Y(t) + D(t) = M \tag{1}$$

$$B(t) + C(t) = N \tag{2}$$

Question 1.4

Use the table 1 to deduce the kinetic equations for A, B, X et Y.

Question 1.5

Substituting $\alpha = k1A(t)$, $\beta = k3B(t)$ and $k_2 = k_4 = 1$ demonstrate that

$$\frac{dx(t)}{dt} = \alpha - (1+\beta)x(t) + x(t)^2 y(t) \tag{3}$$

$$\frac{dy(t)}{dt} = \beta x(t) - x(t)^2 y(t) \tag{4}$$

The usage of lowercase notation $x(t)$ and $y(t)$ instead of $X(t)$ and $Y(t)$ simply emphasizes that the same system of equation can be obtained by a more general change of variable that do not make any assumption about k_2 et k_4. However, they shall be interpreted as a reference to the concentrations of species X and Y.

These equations (3 and 4) constitute the system refered as the *Brusselator* when α and β are time independent. For instance, when A and B are in excess and C and D are extracted from the reactor.

Question 1.6

Numerically, solve the Brusselator system with $\alpha = 1$ and $\beta = 3$ and the initial conditions $x(0) = y(0) = 1$.

Question 1.7

Plot on the same graph, the evolution with time of $x(t)$ and $y(t)$ between 0 and 50 time units. Then plot $y(t)$ as a function of $x(t)$.

Question 1.8

Use the tool `DEplot` of the library `DEtools` to animate the solution of the Brusselator system with $\alpha = 1$, $\beta = 3$ and the initial conditions $x(0) = y(0) = 1$, in the phase space ($y(t)$ vs $x(t)$). Plot the evolution between 0 et 50 time units, $x(t)$ between 0 and 5, $y(t)$ between 0 and 6.

This system admits periodic solutions for a careful choice of the parameteres α and β.

Question 1.9

Search for a fix point such that $\frac{dx(t)}{dt} = \frac{dy(t)}{dt} = 0$. To this end, find the values x_0 and y_0 simultaneously cancelling the right member of the Brusselator system, referred to as $f(x, y)$ and $g(x, y)$.

Question 1.10

Linearize the Brusselator in the neighboring of the fix point. To this end, compute the Taylor series of $f(x, y)$ and $g(x, y)$ in the neighborhood of the fix point (x_0, y_0) and use it to define the new differential equation system. Solve the system symbolically.

The behavior of the solutions is exclusively exponential. The exponentials are controlled by the eigenvalues of the jacobian matrix of the vector field $|f(x, y), g(x, y)\rangle$ in the neighborhood of the fix point.

Question 1.11

Compute the jacobian matrix of the Brusselator in the neighborhood of the fix point and compute its eigenvalues.

There are five scenarios for the solutions of the Brusselator system depending of the signs of the real parts of the eigenvalue and whether or not they have an imaginary component.

1. If the eigenvalues are positive reals, the fix point is unstable.
2. If the eigenvalues are negative reals, the fix point is stable.
3. If the eigenvalues are real number of opposite signs, the fix point is a saddle.
4. If the eigenvalues are complex numbers with a positive real part, the fix point is a spiral source.
5. If the eigenvalues are complex numbers with a negative real part, the fix point is a spiral sink.

Question 1.12

Give your conclusions

Marking scheme

— Question 1.1 : 3 points
— Question 1.2 : 2 points
— Question 1.3 : 1 points
— Question 1.4 : 2 points
— Question 1.5 : 1 points
— Question 1.6 : 2 points
— Question 1.7 : 2 points
— Question 1.8 : 2 points
— Question 1.9 : 2 points
— Question 1.10 : 2 points
— Question 1.11 : 2 points
— Question 1.12 : 1 points

Références

[1] Ilya Prigogine and René Lefever. Symmetry breaking instabilities in dissipative systems. ii. *The Journal of Chemical Physics*, 48(4) :1695–1700, 1968.