A&QT-R 2002 (THETA 13)
International Conference on Automation, Quality and Testing, Robotics
May 23-25, 2002, Cluj-Napoca, Romania

NUMERICAL KINETIC CHEMISTRY

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Abstract. Mathematics and computer programming have a major contribution to chemistry. Two directions can be identified: one that searches and tries (rich) to explain the structural binding and shape of the chemical compounds [1] with major applications in QSPR/QSAR studies [2], and applied sciences such as engineering of materials or agriculture [3]; the second direction is to models the kinetic processes that are involved in chemical reactions [4]. Many such models are available here. The present paper describes three variants of well the known kinetic models and presents the mathematical equations associated with them. The differential equations are numerically solved and fitted with MathCad program.

Keywords: numerical methods, kinetics, oscillating reactions

1. Introduction

The oscillating reactions are the most spectacular and essential for life. All live processes are based on one or more oscillating reactions.

The possibility of periodically altering the concentrations of the reactants, the agents and the product, in space and time, is a result of the autocatalysis. Fig. 1 represents two temporary aspects of the space distribution (distribution in space) of the reaction products through the concentration wave front in the proximity of the electron participates in the reaction as a reactant.

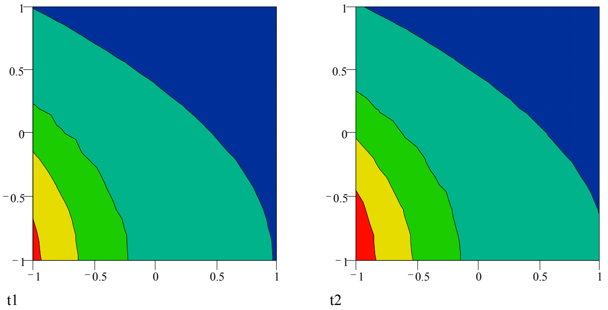

Fig. 1 Concentration gradient in an oscillating reaction (a) at the t, (b) at the t + Δt moments

The oscillating reactions are more than a laboratory curiosity. If in the industrial processes they appear in few cases, in biochemical systems there are numerous examples of oscillating reactions. For instance, the oscillating reactions maintain the rhythm.

A general characteristic of the oscillating reactions in that, under the same conditions, all the participants from the reaction chain oscillate with the same frequency but a different displacement (lagging) shift.

2. Lotka – Volterra autocatalytic oscillator model

For the first time Lotka [5] suggested a mechanism of a complex reaction, în homogeneous phase (stage), which shows damped oscillations. Ten years later, in his paper, [6] Lotka modified the mechanism suggested in 1910 in order to generate undamped oscillations.

The mechanism is named Lotka-Volterra and it is further presented. The following pattern of reactions is considered:

$$\begin{array}{lll} R + X \rightarrow 2X, & \upsilon = \kappa_1\cdot[R]\cdot[X] & (a) \\ X + Y \rightarrow 2Y, & \upsilon = \kappa_2\cdot[X]\cdot[Y] & (b) \\ Y \rightarrow P, \upsilon = \kappa_3\cdot[Y] & & (c) \\ P \rightarrow, & \upsilon = \kappa_4\cdot[P] & (d) \end{array} \qquad (1)$$

The last equation (1d), represents an extraction process of the reaction product P, while the stages (1a) and (1b) are autocatalytic. In Lotka–Volterra model of the reaction mechanism, concentration of the reactant R is maintained constant, (for example either by an addition in the reaction vessel or by an equilibrium between two non-miscible phases when necessary). These restrictions cause the concentrations of X and Y intermediaries/agents to be variable/changeable/unsteady:

$$\frac{d[X]}{dt} = \upsilon_{(29a)} - \upsilon_{(29b)} = \kappa_1\cdot[R]\cdot[X] - \kappa_2\cdot[X]\cdot[Y] \qquad (2)$$

$$\frac{d[Y]}{dt} = \upsilon_{(29b)} - \upsilon_{(29c)} = \kappa_2\cdot[X]\cdot[Y] - \kappa_3\cdot[Y] \qquad (3)$$

(2) and (3) equations form a system of differential equations with the functions $[X] = [X](t)$ and $[Y] = [Y](t)$. This system can be simply solved by a numerical method [7]. Thus the equations (2) and (3) became:

$$x_{n+1} = x_n + (t_{n+1}-t_n)\cdot x_n\cdot(\kappa_1\cdot[R]-\kappa_2\cdot y_n) \qquad (4)$$

$$y_{n+1} = y_n+(t_{n+1}-t_n)\cdot y_n\cdot(\kappa_2\cdot x_n-\kappa_3) \qquad (5)$$

With numerical values:

$$x_0 = [X]_0 = 1, y_0 = [Y]_0 = 1, \kappa_1 = 3, \kappa_2 = 4, \kappa_3 = 5, [R] = 2 \qquad (6)$$

there can be produced/generated the numerical series/systems $(x_n)_{n\geq 0}$ şi $(y_n)_{n\geq 0}$ corresponding to the temporal series $(t_n)_{n\geq 0}$.

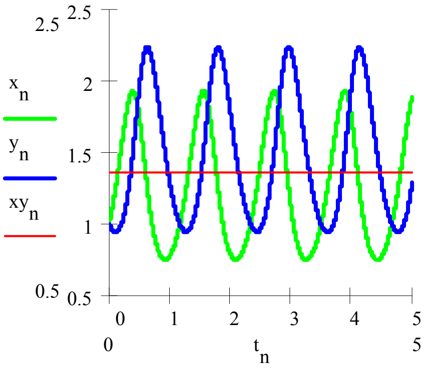

Fig. 2 The oscillation of the intermediaries in L-V mechanism

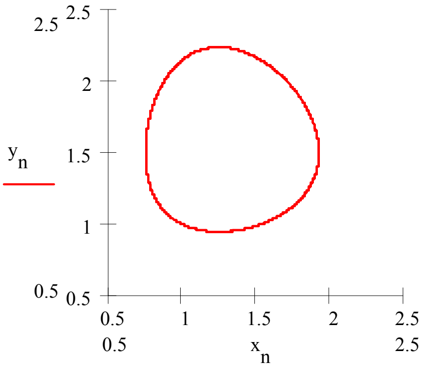

Fig. 3 The variation path ([X],[Y]) in the L-V mechanism

In order to obtain an as faithful representation of the mechanism as possible a very fine/careful division of the temporal coordinate in the numerical simulation is required. Thus, considering the series $t_n = n/10^5$ with $n = 0,1..5\cdot 10^5$ there are obtained the representations from fig. 2 and 3 for the concentration of the intermediaries $[X] = (x_n)_{n\geq 0}$ şi $[Y] = (y_n)_{n\geq 0}$.

In the fig. 4 the concentration of the reaction product [P] develops/grows in the time through P_n (the equations 1c and 1d, taking $\kappa_4 = 3$). Carrying out/performing the regression resulted from the equation (1c) and represented in fig. 5, by p_n , according to the concentration [P] and depending on time, the regression slope gives the average rate of formation equal to 1.481.

There are a few remarks to be made, namely: the sum of average concentrations of the agents is maintained in time as the regression equation xy_n also shows (the slope of the regression equation is null). This average sum M([X]) + M([Y]) = 1.365; hence it results that the average concentrations of the agents also remain constant in time; the values of the average concentrations are M([Y]) = 1.468 şi M([Y]) = 1.263.

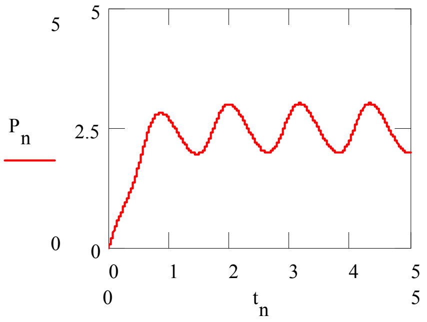

Fig. 4 The variation of the product concentration in L-V mechanism

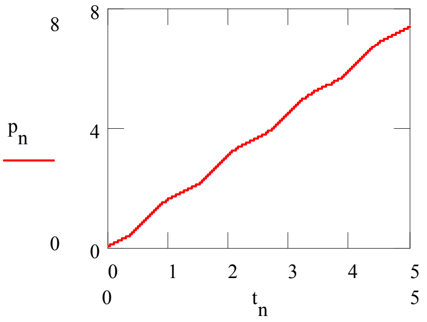

Fig. 5 Product storage in L-V mechanism

3. A model of damped oscillations

Let it be a chemical process that takes place according to the following model of a reaction mechanism:

$$\begin{array}{lll} R_1 \rightarrow X, & \upsilon = \kappa_1\cdot[R_1] & (a) \\ 2X + Y \rightarrow 3Y, & \upsilon = \kappa_2\cdot[X]^2\cdot[Y] & (b) \\ R_2 + X \rightarrow Y + P_1, & \upsilon = \kappa_3\cdot[R_2]\cdot[X] & (c) \\ Y \rightarrow P_2, & \upsilon = \kappa_4\cdot[Y] & (d) \end{array} \tag{7}$$

As in Lotka – Volterra, model, the concentrations of the R_1 şi R_2 reacting substances remain constant during the process.

The solving of the model begins by writing the variation equation for the intermediaries:

$$\frac{d[X]}{dt} = \upsilon_{(34a)} - 2\cdot\upsilon_{(34b)} - \upsilon_{(34c)} = \kappa_1\cdot[R_1] - 2\cdot\kappa_2\cdot[X]^2\cdot[Y] - \kappa_3\cdot[R_2]\cdot[X] \tag{8}$$

$$\frac{d[Y]}{dt} = 2\cdot\upsilon_{(34b)} + \upsilon_{(34c)} - \upsilon_{(34d)} = 2\cdot\kappa_2\cdot[X]^2\cdot[Y] + \kappa_3\cdot[R_2]\cdot[X] - \kappa_4\cdot[Y] \tag{9}$$

The equations (8) and (9) form a system of differential equations having the functions [X] = [X](t) şi [Y] = [Y](t). This system may also be easily solved by a numerical method. The equations (8, 9) are written thus:

$$x_{n+1} = x_n+(t_{n+1}-t_n)\cdot(\kappa_1\cdot[R_1]-x_n\cdot(2\cdot\kappa_2\cdot x_n\cdot y_n+\kappa_3\cdot[R_2])) \tag{10}$$

$$y_{n+1} = y_n+(t_{n+1}-t_n)\cdot(x_n\cdot(2\cdot\kappa_2\cdot x_n\cdot y_n+\kappa_3\cdot[R_2])-\kappa_4\cdot y_n) \tag{11}$$

Having the numerical value:

$$x_0 = 0,\ y_0 = 1,\ \kappa_1 = 3,\ \kappa_2 = 4,\ \kappa_3 = 5,\ \kappa_4 = 7,\ [R_1] = 2,\ [R_2] = 2 \tag{12}$$

there can be generated the numerical series $(x_n)_{n\geq 0}$ şi $(y_n)_{n\geq 0}$ corresponding to the temporal series $(t_n)_{n\geq 0}$. Taking into account the series $t_n = n/100000$ cu $n = 0,1..300000$ there are obtained the representation from fig. 6 for the concentrations of the intermediaries $[X] = (x_n)_{n\geq 0}$ şi $[Y] = (y_n)_{n\geq 0}$.

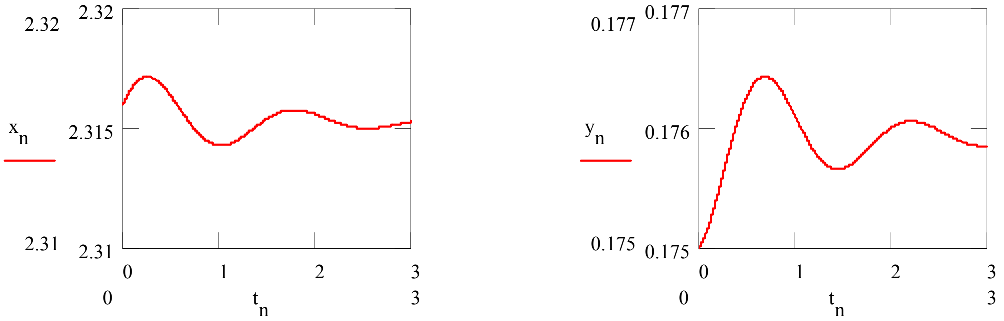

Fig. 6 The damped oscillations in chem. reactions (a) the conc. of the intermediaries X, (b) the concentration of the intermediaries Y

Fig. 6 shows that the system tends towards a state of equilibrium state characterized a ratio of the concentrations of the two intermediaries. The system of the agents practically causes damped oscillations around of the equilibrium ratio for two intermediaries.

The chart representing the agent concentration [Y] depending on the agent concentration [X] from fig. 7 shows the same thing.

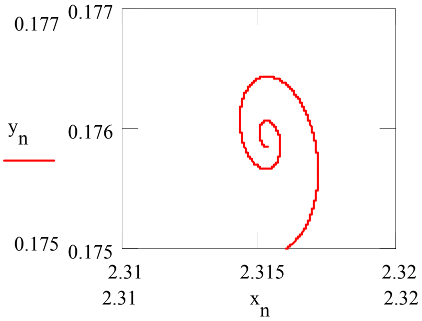

Fig. 7 The damped oscillation path ([X],[Y])

The values obtained for the equilibrium concentration are [X] = 2.315 and [Y] = 0.176 and the equilibrium ratio are [X]/[Y] = 13.53.

The dependence on time $(t_n)_{n\geq 0}$ of the accumulation of the reaction products $[P_1] = (p1_n)_{n\geq 0}$ şi $[P_2] = (p2_n)_{n\geq 0}$ is given in fig. 8.

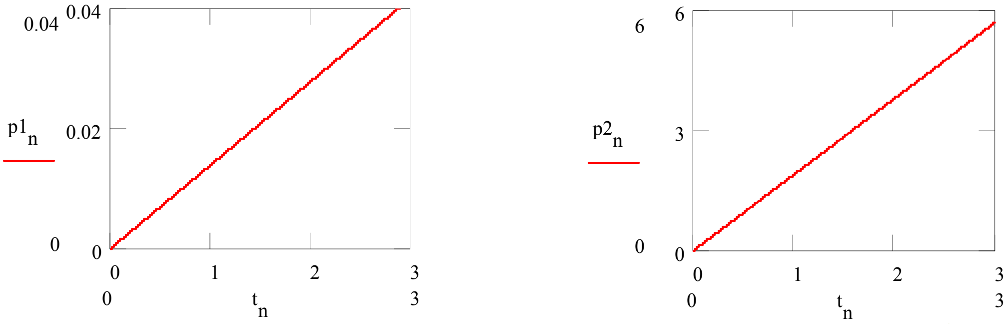

Fig. 8 The linear variation of the amount of products in damped oscillating reactions

Fig. 8 shows that this time the concentration of the reaction products changes linearity even if the concentrations of the agents X şi Y oscillate towards the equilibrium value.

4. The brussel model of autocatalytic oscillation

The brussel model was initiated by a group from Bruxelles directed by Ilya Prigogine it introduce for the first time, mechanism of a reaction whose scheme of evolution converged on an attractor [8]. More authors have changed this variant and have studied the systems running according to this mechanism [9,10]. Further, a simplified variant is presented:

$$\begin{array}{lll} R \rightarrow X, & \upsilon = \kappa_1 \cdot [R] & (a) \\ X + 2Y \rightarrow 3Y, & \upsilon = \kappa_2 \cdot [X] \cdot [Y]^2 & (b) \\ Y \rightarrow P, & \upsilon = \kappa_3 \cdot [Y] & (c) \end{array} \tag{13}$$

As in the previous situations it is supposed that the concentration of the reacting substance R remains constant and the product P may be extracted from the system by a reaction of the type (7d).

X and Y are the intermediaries again. Their speed equations written on the basis of the mechanism (13) are:

$$\frac{d[X]}{dt} = \upsilon_{(39a)} - \upsilon_{(39b)} = \kappa_1 \cdot [R_1] - \kappa_2 \cdot [X] \cdot [Y]^2 \tag{14}$$

$$\frac{d[Y]}{dt} = \upsilon_{(39b)} - \upsilon_{(39c)} = \kappa_2 \cdot [X] \cdot [Y]^2 - \kappa_3 \cdot [Y] \tag{15}$$

Though the equations (14) and (15) seem simpler, at first sight, they are even more difficult to be solved by integration than (2-3) or (8-9). Moreover, the literature has not recorded their integration into the general case described by (14-15). Besides, the equations (14-15) do not lead to an attractor model not matter by values of the constants of speed and of the concentrations

[R], $[X]_0$ and $[Y]_0$. The attempt of solving (14-15) is full of surprises. For most of the values a system which develops towards a position of equilibrium is obtained; there are values for which damped oscillations to equilibrium are found again; the undamped periodical oscillations have also an important role, which is confirmed by the majority of the organisms in which the cellular biochemical processes are based on such oscillations. The processes taking place within the heart are a conclusive example; the periodical heart beats are due to processes of this type. The importance of these processes is great. This was the reason for which Ilya Prigogine was awarded the Nobel Prize for chemistry in 1977, namely for his theories on the dissipative systems.

The equations (14-15) are simplified [11] if $[R] = 1$, $\kappa_1 = 1$ şi $\kappa_3 = 1$, are chosen and when the differential system of equations becomes:

$$\dot{x} = 1 - \kappa_2 \cdot x \cdot y^2;\ \dot{y} = \kappa_2 \cdot x \cdot y^2 - y \tag{16}$$

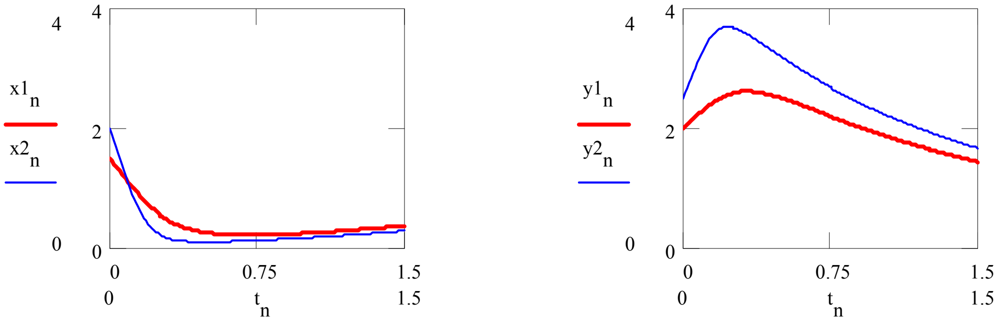

Fig. 9 The concentrations of the intermediaries up to the attractor for two cases with different I.C.

where the derivate related to the time of the x variable was $\dot{x}$. This system of the differential equation (16) does not offer more chances for an exact resolution either. However, the numerical simulation is made in the same way. Thus the iteration equation of variation for (16) is written:

$$x_{n+1} = x_n + (t_{n+1} - t_n) \cdot (1 - \kappa_2 \cdot x_n \cdot y_n^2);\ y_{n+1} = y_n + (t_{n+1} - t_n) \cdot (\kappa_2 \cdot x_n \cdot y_n^2 - y_n) \tag{17}$$

Now choosing $\kappa_2 = 0.88$ and taking into consideration two cases, the first one in which the initial concentrations of the agents are $x1_0 = [X]_{1,0} = 1.5$ and $y1_0 = [Y]_{1,0} = 2$ and second case in which $x2_0 = [X]_{2,0} = 2$ şi $y2_0 = [Y]_{2,0} = 2.5$ and the series $t_n = n/100$ with $n = 0,1..150$ following representations for the concentrations of the agents $[X] = (x_n)_{n \geq 0}$ and $[Y] = (y_n)_{n \geq 0}$ are obtained (fig. 9). And the variation diagram of [Y] depending on [X] and the variation in time of the storage of reaction product is (fig. 10).

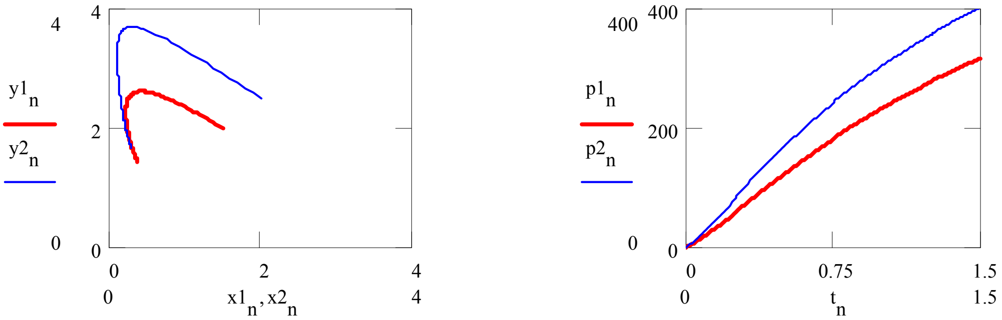

Fig. 10 (a) The entrance of [Y] related to [X] on the same gravitational orbit for
(b) different product quantities obtained in two cases having different initial conditions

If the fig. 9a and b are not very conclusive and fig. 10b seems to confirm this, fig. 10b shows that, though the two systems start from different values of the concentrations of the agents, in both cases the system comes to evolve rather early on the same trajectory. Now, increasing the time interval by choosing another $n = 0,1..3000$ the following concentrations of the agents are obtained $[X]_1 = (x1_n)_{n \geq 0}$, $[X]_2 = (x2_n)_{n \geq 0}$, $[Y]_2 = (y2_n)_{n \geq 0}$ şi $[Y]_2 = (y2_n)_{n \geq 0}$ for the two cases 1 and 2 of the chosen system (fig. 11). It is noticed that, even if they do not evolve according the same values, same period and amplitude of the oscillations are recorded. Fig. 12 gives the dependence of [Y] under [X] for the cases as well as the accumulation of the product.

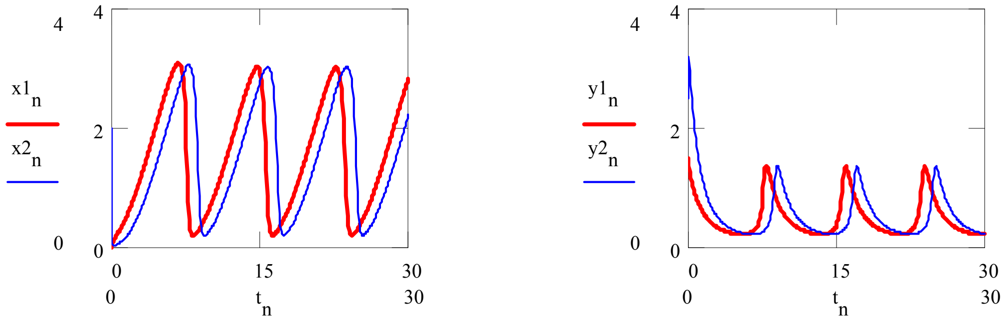

Fig. 11 The periodical evolution having the same oscillation period $T = 0.226$ of: (a) [X] and (b) [Y], for two cases having different initial conditions

The difference between the Lotka-Voltera model and Bruxelles model one is the following: The Lotka-Voltera model oscillates around the initial values of the concentrations of the agents, whereas the Bruxelles one converges, in time on the same variation equation irrespective of the initial values of the concentrations of the agents. In fact the attractor does not appear for any of their values; for a given k_2 there are minimum $y_{0,min}$ şi $x_{0,min}$ values from which the periodical oscillations arise and the system tends towards the curve given in fig. 12.

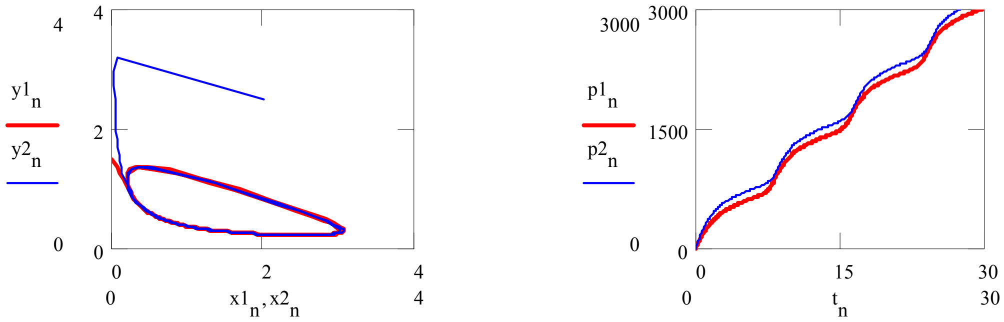

Fig. 12 (a) Convergence at atractor of brusselator system independent from initial conditions and (b) different quantities of resulted product

The convergence on the attractor of the brusselator system independent of the initial conditions and (b) different quantities of the product obtained.

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