NEW APPROACH OF WELL KNOWN OSCILATING REACTION MODELS

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SUMMARY

The oscillating reactions are the most spectacular and essential for life [1]. All live processes are bases on one or more oscillating reactions [2, 3]. 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. The heartbeat is controlled by an oscillating electrical signal; which is generated by chemical reactions that should be also oscillatory. [4-6]. Other direction is to models the kinetic processes that are involved in chemical reactions [7]. The present paper describes three variants of well the known oscillating reaction models and presents the mathematical equations associated with them. The differential equations are numerically solves and fit with MathCad program.

Keywords: numerical methods, kinetics, oscillating reactions

INTRODUCTION

The first characteristic feature of oscillatory reactions is non-linearity. Many reactions display non-linear behavior when far from equilibrium, most of them do not exhibit oscillatory behavior. Non-linearity of the system is necessary but not suffices to provide oscillations. A condition for oscillatory behavior is the existence of an

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autocatalysis. One consequence of autocatalysis is the possibility that concentration of reactants, intermediates or products will vary periodically either in space or in time.
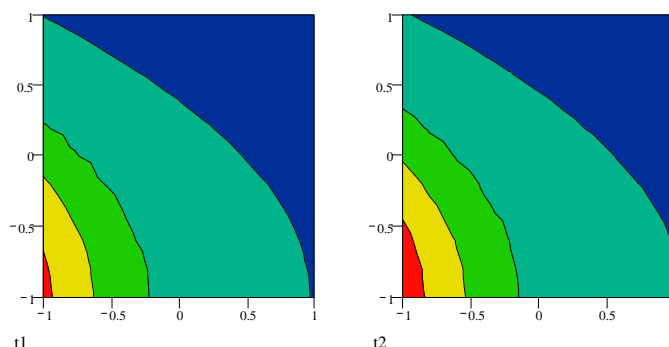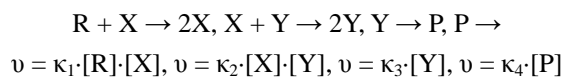

Figure 1. Concentration gradient in an oscillating reaction at the t, and at the t + Δt moments;
Avi animation: http://lori.academicdirect.ro/free/RO.avi

Figure 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. 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.

LOTKA – VOLTERRA AUTOCATALYTIC OSCILLATOR MODEL

For the first time Lotka [8] suggested a mechanism of a complex reaction, in homogeneous phase (stage), which shows damped oscillations. Ten years later, in his paper, [9] Lotka modified the mechanism suggested in 1910 in order to generate undamped oscillations. The mechanism is names Lotka-Volterra and it is further present. The following pattern of reactions is considered (equation 1 and 2):

$$R + X \rightarrow 2X, X + Y \rightarrow 2Y, Y \rightarrow P, P \rightarrow$$
$$\upsilon = \kappa_1 \cdot [R] \cdot [X], \upsilon = \kappa_2 \cdot [X] \cdot [Y], \upsilon = \kappa_3 \cdot [Y], \upsilon = \kappa_4 \cdot [P]$$

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

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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 (equations 3):

$$\frac{d[X]}{dt} = \upsilon_{(29a)} - \upsilon_{(29b)} = \kappa_1 \cdot [R] \cdot [X] - \kappa_2 \cdot [X] \cdot [Y], \quad \frac{d[Y]}{dt} = \upsilon_{(29b)} - \upsilon_{(29c)} = \kappa_2 \cdot [X] \cdot [Y] - \kappa_3 \cdot [Y]$$

Equations (3) form a system of differential equations with the functions $[X] = [X](t)$ and $[Y] = [Y](t)$. This system can be simply solves by a numerical method [10]. Thus, the equations (3) became (equation 4):

$$x_{n+1} = x_n + (t_{n+1}-t_n) \cdot x_n \cdot (\kappa_1 \cdot [R]-\kappa_2 \cdot y_n), \quad y_{n+1} = y_n+(t_{n+1}-t_n) \cdot y_n \cdot (\kappa_2 \cdot x_n-\kappa_3)$$

With numerical values $x_0 = [X]_0 = 1$, $y_0 = [Y]_0 = 1$, $\kappa_1 = 3$, $\kappa_2 = 4$, $\kappa_3 = 5$, $[R] = 2$ 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 $(t_n)_{n \geq 0}$.
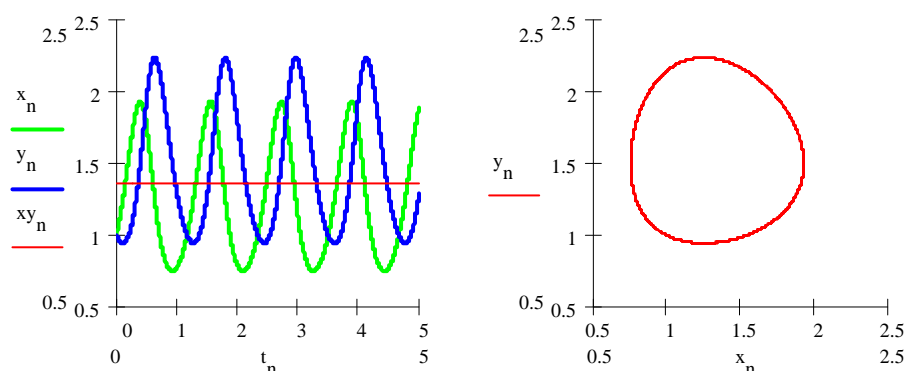

Figure 2. The oscillation of the intermediaries and the variation path ([X],[Y]) in L-V mechanism

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 figure 2 for the concentration of the intermediaries $[X] = (x_n)_{n \geq 0}$ şi $[Y] = (y_n)_{n \geq 0}$. In the figure 3, the concentration of the reaction product $[P]$ develops/grows in the time through P_n (the equations 2c and 2d, taking $\kappa_4 = 3$).
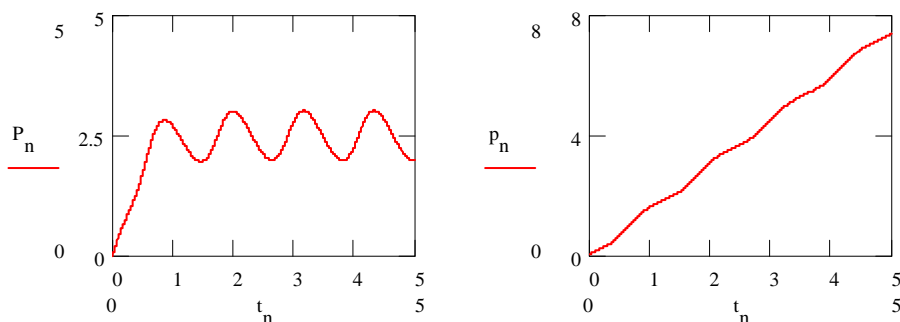
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Figure 3. The variation of the product concentration and storage in L-V mechanism

Carrying out/performing the regression resulted from the equation (2c) and represented in fig. 3, 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.
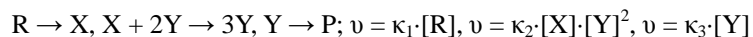
There are a few remarks to be made, namely: the sum of average concentrations of the agents is maintained in time, as the regression equation xy_n also is shows (the slope of the regression equation is null).

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 and M([Y]) = 1.263.

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 [11].

More authors have changed this variant and have studied the systems running according to this mechanism [12,13]. Further, a simplified variant is presented (equation 5):

$R \rightarrow X$, $X + 2Y \rightarrow 3Y$, $Y \rightarrow P$; $\upsilon = \kappa_1 \cdot [R]$, $\upsilon = \kappa_2 \cdot [X] \cdot [Y]^2$, $\upsilon = \kappa_3 \cdot [Y]$

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

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reaction of the type (5). X and Y are the intermediaries again. Their rate equations written based on the mechanism (5) are (equation 6):

$$\frac{d[X]}{dt} = \upsilon_{(39a)} - \upsilon_{(39b)} = \kappa_1 \cdot [R_1] - \kappa_2 \cdot [X] \cdot [Y]^2, \quad \frac{d[Y]}{dt} = \upsilon_{(39b)} - \upsilon_{(39c)} = \kappa_2 \cdot [X] \cdot [Y]^2 - \kappa_3 \cdot [Y]$$

Though the equations (6) seem simpler, at first sight, they are even more difficult to be solved by integration than (6). Moreover, the literature has not recorded their integration into the general case described by (6).

Besides, the equations (6) do not lead to an attractor model not matter by values of the constants of rate and of the concentrations [R], $[X]_0$ and $[Y]_0$. The attempt of solving (6) is full of surprises. For most of the values, a system that develops towards a position of equilibrium is obtain; there are values for which damped oscillations to equilibrium are found again; the un-damped 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 heartbeats 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 (6) are simplified [14] if [R] = 1, $\kappa_1 = 1$ şi $\kappa_3 = 1$, are chosen and when the differential system of equations becomes (equation 7):

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

where the derivate related to the time of the x variable was $\dot{x}$. This system of the differential equation (13) 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 (13) is writes (equation 8):

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

Now let us chouse $\kappa_2 = 0.88$. 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 one with $x2_0 = [X]_{2,0} = 2$ şi $y2_0 = [Y]_{2,0} = 2.5$. Using 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 (figure 4).
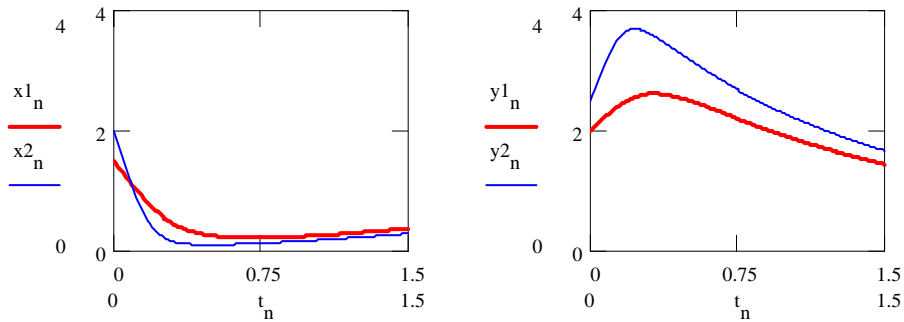
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Figure 4. The concentrations of the intermediaries up to the attractor
for two cases with different initial conditions

The variation diagram of [Y] depending on [X] and the variation in time of the storage of reaction product are depicting in figure 5.

Now, increasing the time interval by choosing another $n = 0,1..,3000$ the following concentrations of the agents are obtained $[X]_1 = (x1_n)_{n\geq0}$, $[X]_2 = (x2_n)_{n\geq0}$, $[Y]_2 = (y2_n)_{n\geq0}$ și $[Y]_2 = (y2_n)_{n\geq0}$ for the two cases 1 and 2 of the chosen system (fig. 6). It is notice that, even if they do not evolve according the same values, same period and amplitude of the oscillations are record.

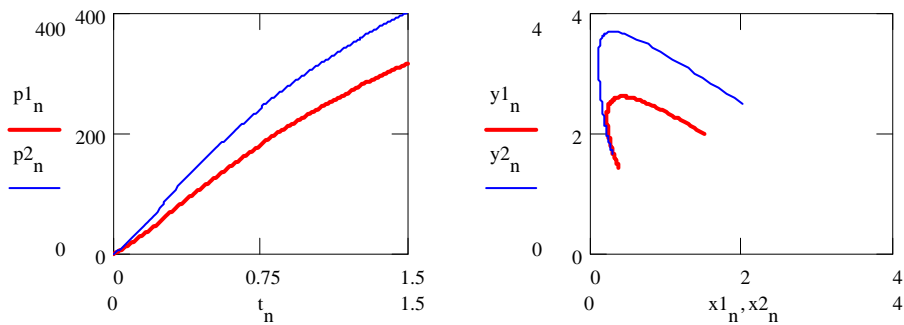Figure 7 gives the dependence of [Y] under [X] for the cases as well as the accumulation of the product.

Figure 5. The ([Y], [X]) hodograph (the entrance of [Y] related to [X] on the same gravitational orbit for both cases) and the product – time dependence two for cases having different initial conditions.
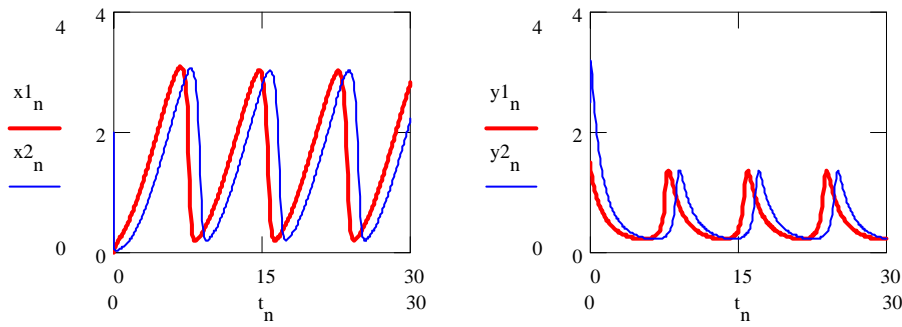
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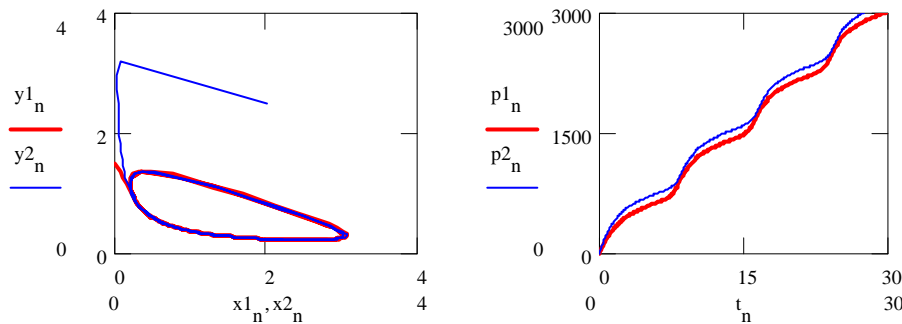Figure 6. The periodical evolution with same oscillation period T = 0.226 and different initial conditions

Figure 7. Convergence at atractor of brusselator system independent from initial conditions and different quantities of resulted product for brusselator system

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 k2 there are minimum y0,min şi x0,min values from which the periodical oscillations arise and the system tends towards the curve given in figure 7. 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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CONCLUSIONS

There exist a many models of biochemical processes reactions, and every process has some characteristics, as we described below. The importance of every mechanism is give by his applications. It exist much more kinetic models, unexplained in this paper, such as Oregonator model [3], one of them implying tens of substances and reactions. As we mentioned before, most spectacular and important because is most frequent in nature is the brusselator model, every alive organism has one. The symbolic calculations of reaction rate for biochemical processes are, in most of cases, impossible. In opposite, the numerical modeling of biochemical kinetics proves that it is a very good instrument for mechanism understanding, comparative studies and model validation.

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