

# MODELS OF OSCILLATING CHEMICAL REACTIONS. PARTICULARITIES OF SOME PROPOSED MODELS FOR THE CHARACTERIZATION OF CHEMICAL OSCILLATIONS

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**abstract:** Some models proposed for the characterisation of the oscillatory behaviour of certain systems will be presented. One of them will be used for the explanation of Belousov-Zhabotinsky reaction, one of the most famous oscillating chemical reactions.

## Introduction

In order to explain an oscillating behaviour of a chemical reaction there were proposed several models. A model for a chemical reaction should consist the following parts:

- A mechanism  
This is a set of elementary chemical reactions necessary for the description how reactants form intermediates, intermediates combine with one another and reactants, and finally the products are formed.
- A set of rate equations  
These are differential equations corresponding to the reaction mechanism and giving the rates of change of all reactants, intermediates and products.
- A set of integrated rate equations  
These equations show the concentrations as functions of time for reactants, intermediates and products. They are obtained by integrating the rate (differential) equations.

The criterion for an acceptable theoretical model is that it agrees with experimental observations of measured time variation of concentrations. If the model is acceptable one can say that we have got a better understanding of the studied reaction.

Analytical and computational methods have proven to be useful mathematical tools for the elucidation of mechanisms of oscillating chemical reactions. The ordinary of partial differential equations which describe the oscillating system are parameterized by rate constants, initial conditions, boundary conditions etc. the successful modelling of an oscillating system depends on:

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1. An appropriate choice of the form of differential equation;
2. An appropriate choice of values for each of the parameters.

The usual mathematical methods for studying the properties of models of oscillating reactions are: linear stability analysis, bifurcation theory, numerical simulation [1].

The most representative models for the simulation oscillations will be presented. For the simplification the next notations were made: A, B, C, D – are the reactants, P, Q, R – are the reaction products and U, V, W, X, Y, Z – are the intermediates. The concentrations of the respective species were noted by: a, b, c, d, p, q, r, u, v, w, x, y, z (were it was necessary).

## 1. The Lotka Model

In 1910, Lotka showed that a set of consecutive reactions can give rise to damped oscillations on the way to equilibrium. The model consists of three irreversible steps with one autocatalytic reaction:



Considering that the concentration of A is constant, the model contains only two variables: x and y. The system of differential equations attached to the model is:

$$\begin{array}{l}
 \frac{dx}{dt} = k_1 a - k_2 xy \\
 \frac{dy}{dt} = k_2 xy - k_3 y
 \end{array} \tag{1.2}$$

At stationary state:

$$\frac{dx}{dt} = \frac{dy}{dt} = 0 \tag{1.3}$$

$$\begin{cases}
 k_1 a - k_2 xy = 0 = f_1 \\
 k_2 xy - k_3 y = 0 = f_2
 \end{cases} \tag{1.4}$$

The solution of stationary state obtained from equation (4) is:

$$\begin{cases}
 x_0 = \frac{k_3}{k_2} \\
 y_0 = \frac{k_1 a}{k_3}
 \end{cases} \tag{1.5}$$

The Jacobian attached to the system (4) is:

$$\begin{aligned}
 a_{11} &= \frac{\partial f_1}{\partial x} = -k_2 y & a_{21} &= \frac{\partial f_2}{\partial x} = k_2 y \\
 a_{12} &= \frac{\partial f_1}{\partial y} = -k_2 x & a_{22} &= \frac{\partial f_2}{\partial y} = k_2 x - k_3
 \end{aligned}
 \tag{1.6}$$

At stationary state, the Jacobian is:

$$J = \begin{vmatrix} \frac{k_1 k_2 a}{k_3} & -k_3 \\ \frac{k_1 k_2 a}{k_3} & 0 \end{vmatrix}
 \tag{1.7}$$

From equation (7) one can obtain:

$$\text{tr} J = T = -\frac{k_1 k_2 a}{k_3} < 0
 \tag{1.8}$$

$$\det J = \Delta = k_1 k_2 a > 0
 \tag{1.9}$$

One can observe that the expressions (8, 9) fulfil the stability conditions ( $T < 0$ ,  $\Delta > 0$ ) for any values of the fourth parameters. Therefore the solution of the model is stable. Analyzing the difference:

$$T^2 - 4\Delta = k_1 k_2 a \left[ \frac{k_1 k_2 a}{k_3^2} - 4 \right]
 \tag{1.10}$$

One can observe that there is a threshold when  $(T^2 - 4\Delta)$  passes from positive to negative value (in the case when the amount from the brackets is smaller than zero). In this situation the solution of the system passes from a stable node (A class behaviour) in stable focus (B class behaviour) and the trajectory of the system in  $(x, t)$  or  $(y, t)$  coordinates presents damped oscillations.

## 2 Lotka – Volterra Model

In 1920 Lotka proposed the following reaction mechanism (with corresponding rate equations). Each reaction step refers to the molecular mechanism by which the reactant molecules combine to produce intermediates or products. For example, in step 1 a molecule of species A combines with a molecule of species X to yield two molecules of species X. this step depletes molecules A (and adds molecules X) at a rate proportional to the product of the concentrations of A and X.

A key feature of this system, and of most chemical systems that exhibit oscillations, is autocatalysis, which means that the rate of growth of species increases with the concentration of the species. Step 1 is autocatalytic because X accelerates its own production. Likewise step 2 is autocatalytic. Lotka obtained oscillating concentrations for both intermediates X and Y when the concentration of reactant A is constant.



As indicated, each step is irreversible. We can write down a system of differential equation to describe the behaviour of the species:

$$\begin{cases} \frac{dx}{dt} = k_1ax - k_2xy \\ \frac{dy}{dt} = k_2xy - k_3y \end{cases}
 \tag{2.1}$$

Similarly with the treatment at Lotka model we can obtain:

$$\begin{cases} T = 0 \\ \Delta = k_1k_3a > 0 \end{cases}
 \tag{2.2}$$

The solution of the system is a conservative center (C class behaviour). Lotka's mechanism can be re-interpreted as a model for oscillating populations of predators and preys as was done by Volterra. In this, A represents the ecosystem in which prey X and predator Y live. Step 1 represents pre procreation: prey population doubles (typical exponential growth). Then Y is the population of predators that consume the prey in order to sustain (and expand) their population. Step 2 represents the inclination of predators to reproduce in proportion to the availability of prey. Finally (step 3), predators die at a certain natural rate (also exponential) so that they are removed from the ecosystem.

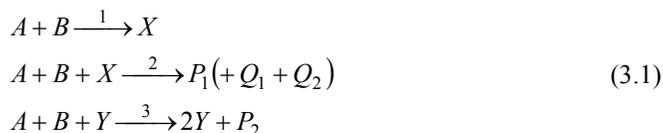
Despite the fact that it generates sustained oscillatory behaviour from simple "chemical reactions" with mass action kinetics, the Lotka – Volterra model is not an appropriate description of any actual chemical, as opposed to ecological, system. It is possible to prove that the model has an oscillatory solution for any values of the rate constant and initial values of a, x and y, and the amplitude and period of the oscillations obtained depend upon all of these quantities; there is an infinite array of oscillatory solutions. If the system is perturbed (for example by adding a bit more a or x or y) it continues to oscillate, but with a new period or amplitude until it is perturbed again. In the presence of any significant of noise, the behaviour would hardly be recognizable as periodic, since it would constantly be jumping from one oscillatory behaviour to another. Real chemical systems do not behave this way. They oscillate only within a finite range of parameters, and they have a single mode (amplitude and frequency) of oscillation, to which they return if the system is perturbed.

### 3. Models Derived from Lotka Model

Beginning with 1990 a series of models derived from Lotka AND Lotka-Volterra models was proposed.

### **3.1 Alternator**

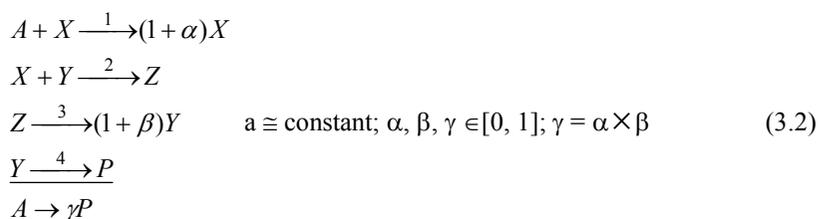
This model [1] consists from three steps and two variables:



Any of these three steps can be reversible. Because steps 2 and 3 are trimolecular the non-linearity degree is increased and complex behaviour can appear. The model is not complete; the overall chemical reaction couldn't be written because the Y species doesn't disappear from the system.

### **3.2 Explodator**

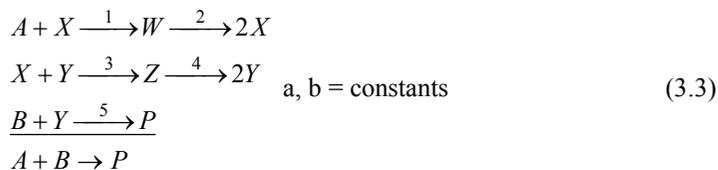
Explodator model [2] has four steps and three variables:



This model have one non-stable solution which tends to infinite (explode).

### **3.3 Model with Four Intermediates**

This model [27] has five (or six) steps and four variables:



The six step could be the formation of X. the model is used at the simulation of complex behaviour in systems with many intermediates.

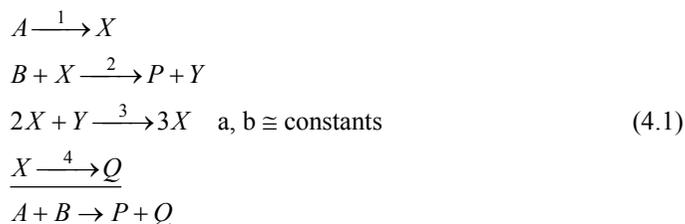
### **3.4 Model with Dimmer**

This model [4] was created for open isothermal systems (CSTR) which have uniform spatial concentrations. The reaction mechanism where intermediate X is a dimmer of P.



#### 4. Brusselator

The Brusselator model was proposed by Prigogine and his collaborators in 1967 [5, 6]. The reaction mechanism is:



This model was created for the explanation of the mechanism of Bray – Liebhafsky. In the case of the Bray reaction A, Q would correspond to  $\text{HIO}_3$ ; Y corresponds to  $\text{H}_2\text{O}_2$ , and P to  $\text{O}_2$ . Because  $A = Q$  the overall balance is:



The autocatalytic step (3) of the Brusselator and of the reaction model of the Bray reaction is trimolecular. This is the most problematic step of this model because trimolecular reactions are extremely improbable, especially in a reaction mixture like that of Bray – Liebhafsky reaction for which 16 possible reactions of 11 reactants have to be considered and in which two bimolecular reactions are in competition.

The variables of the model are the concentrations of X and Y species. The differential equations system is:

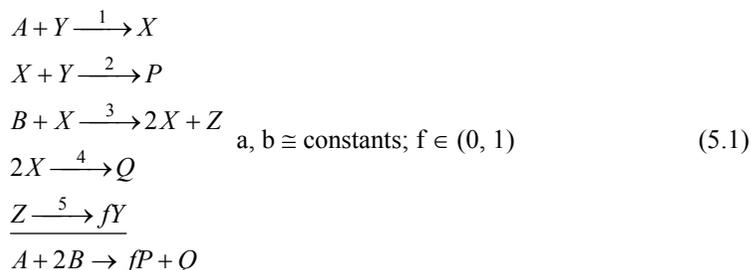
$$\begin{cases} \frac{dx}{dt} = k_1 a - k_2 b x + k_3 x^2 y - k_4 x \\ \frac{dy}{dt} = k_2 b x - k_3 x^2 y \end{cases} \tag{4.2}$$

Brusselator is a complex model, which can describe different behaviours including limit cycles that appear around the non-stable focus. This model with small modifications can describe chemical waves and spatial structures. This model presents certain insufficiencies. Several authors like Edelstein [7], Schlogl [8], Escher and Vidal [9, 10] proposed changing or addition of some steps of Brusselator in order to improve it.

#### 5. Oregonator

The mechanism of the Belousov – Zhabotinsky reaction is well understood. The basic framework was suggested by Field, Koros and Noyes in 1972 and elaborated on by Edelson et al. Parameterization of the mechanism is thermodynamically internally and externally consistent and in agreement with all known direct kinetic measurements of the rates of component reactions. It and various simplifications have been very successful modelling, all known experimental behaviours of the BZ reaction, except aperiodicity [7, 11-17].

Model contains five steps and three variables:



The usual variable identifications are:  $A = \text{BrO}_3^-$ ,  $X = \text{HBrO}_2$ ,  $Y = \text{Br}^-$ ,  $Z = \text{Ce}^{4+}$ ,  $P = \text{BrCH}(\text{COOH})_2$ ,  $B = \text{CH}_2(\text{COOH})_2$ .

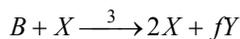
The quantities X, Y and Z are dynamic variables corresponding to intermediates, while A and P are reactants and products whose concentrations are usually assumed to be constant. The quantity f is an expandable stoichiometric factor that can be eliminated in more complex models than three dynamic variables. In order to respect the thermodynamic constrain on the entire domain of variables is necessary a reversibility of step 1 or a supplementary slow step as:



The system of differential equation of the model is:

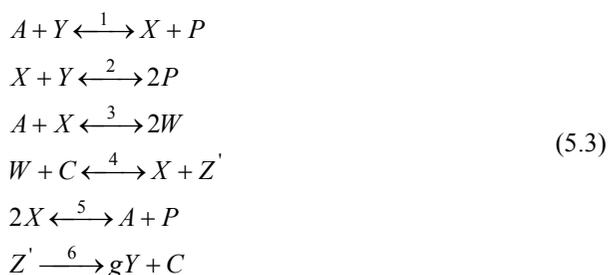
$$\begin{cases}
 \frac{dx}{dt} = k_1ay - k_2xy - k_3bx - 2k_4x^2 \\
 \frac{dy}{dt} = -k_1ay - k_2xy + fk_5z \\
 \frac{dz}{dt} = k_3bz - k_5z
 \end{cases}
 \quad (5.2)$$

The model has eight parameters and the solutions can be limit cycles in tridimension phase space. The weak point of the model is step 5, because of the presence of  $f$ : the Z species doesn't have a great importance and for the simplification of the model, step 3 was re-written, and Z was eliminated:



In that form the oscillations disappeared, it means that Z species introduce a delay in producing Y [18].

In 1978, Showalter and coworkers [19,20,13] proposed an amplification of Oregonator. The model consists in the following steps:

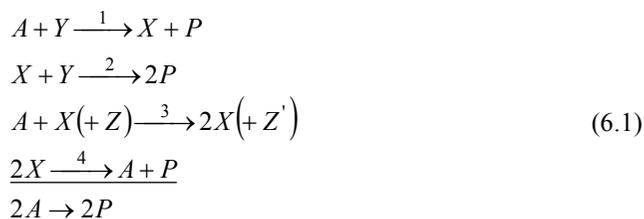


The identification of the variables with the components of BZ reaction is:  $A = \text{BrO}_3^-$ ,  $W = \text{BrO}_2^\bullet$ ,  $Y = \text{HBrO}_2$ ,  $Y = \text{Br}^-$ ,  $C = \text{Ce (IV)}$ ,  $P =$  species with bromine in oxidation state (+1) as  $\text{HOBr}$  or bromurated organic substrate.

By analogy with Oregonator we can see that is appeared a new step and a new intermediate, five steps are reversible, and  $A$  and  $C$  are re-formed. This model can lead to the reducing of very complex models.

## 6. Berlinator

The elimination of  $Z$  species and step 5 from Oregonator and introducing a feedback created this model in 1982 [21]. The Berlinator contains four steps (bimolecular) and three variables:



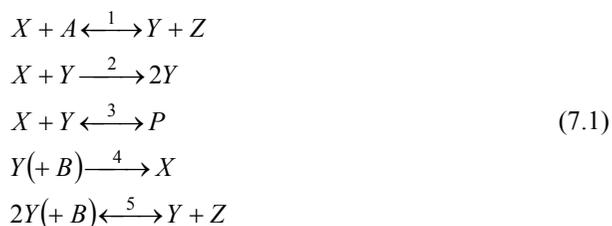
This model is used for the explanation of BZ reaction behaviours. The usual variable identifications are:  $A = \text{BrO}_3^-$ ,  $P = \text{HOBr}$ ,  $X = \text{HBrO}_2$ ,  $Y = \text{Br}^-$ ,  $Z = 2\text{Ce}^{3+}$ ,  $Z' = 2\text{Ce}^{4+}$ . We can observe that reactant  $A$  is reformed in step 4, so we cannot consider that the concentration of  $A$  is constant. Berlinator model has four parameters and leads to the following kinetic equations:

$$\begin{cases}
 \frac{da}{dt} = -k_1ay - k_3ax + k_4x^2 \\
 \frac{dx}{dt} = k_1ay - k_2xy + k_3ax - 2k_4x^2 \\
 \frac{dy}{dt} = -k_1ay + k_2xy
 \end{cases} \tag{6.2}$$

The system (6.2) has three solutions: two stable nodes and a saddle point.

## 7. Braylator

In order to understand the behaviour of Bray – Liebhafsky reaction several models have been proposed. By the neglect of oxygen effect and elimination of hypothetical species  $I_2O$ , the Braylator have been obtained [22, 23]. The model has five steps, two of them being reversible (steps 1 and 3):



In the case of Bray – Liebhafsky reaction:  $X = I^-$ ,  $Y = HIO$ ,  $Z = HIO_2$ ,  $A = IO_3^-$ ,  $B = H_2O_2$ . This model has not any reaction of the type  $Y \rightarrow 2Y$  (direct autocatalysis) like models presented before (Brusselator, Oregonator, Explodator). The Braylator contains an indirect autocatalytic reaction:  $2Y \rightarrow Y$ . For the stability study the concentrations of species A and B are considered constant. If the stationary state is stable, the regular decomposition of hydrogen peroxide is obtained. If the stationary state is not stable, the Braylator produces oscillations similar with those obtained by experiment.

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