

**SERBIAN ACADEMY OF  
NONLINEAR SCIENCE**



**2nd CONFERENCE  
ON NONLINEARITY**

**Editors**

**B. Dragovich, Ž. Čupić**

Belgrade, 2022

SERBIA

**P r o c e e d i n g s**  
of the  
**2nd CONFERENCE ON NONLINEARITY**

(October 18 – 22, 2021, Belgrade, Serbia)

**Editors**  
**B. Dragovich, Ž. Čupić**

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# **2nd Conference on Nonlinearity**

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# PREFACE

This book contains some papers related to the talks presented at the *2nd Conference on Nonlinearity*, held online on October 18–22, 2021. The conference is organized by the Serbian Academy of Nonlinear Sciences (SANS) in cooperation with the Mathematical Institute (Serbian Academy of Sciences and Arts), Faculty of Mathematics (University of Belgrade), Institute of Chemistry, Technology and Metallurgy (University of Belgrade), and Faculty of Sciences and Mathematics (University of Niš).

It is well known that nonlinear phenomena and processes are present everywhere in nature – from fundamental interactions between elementary particles, via various terrestrial processes in fluids and optics, to the dynamics of celestial objects and the evolution the universe as a whole. Nonlinear methods, in particular nonlinear differential equations, are used in research of all sciences – from fundamental to applied. Contemporary comfortable human life largely depends on technological achievements based on nonlinear processes.

*Serbian Academy of Nonlinear Sciences* is a scientific society whose members are scientists that significantly contributed to developments of nonlinear sciences in Serbia. The main goal of SANS is a strong fruitful support to versatile developments of nonlinear sciences, particularly in Serbia. Organization of scientific meetings – colloquiums and conferences on nonlinearity – are among principal activities of SANS. SANS strives to connect as much as possible with scientists and related scientific activities throughout the world. More information on the Serbian Academy on Nonlinear Sciences is available at its website <http://www.sann.kg.ac.rs/en/sans/>.

About 70 scientists from 19 countries participated in this conference (Australia, Austria, France, Germany, Hungary, India, Israel, Japan, Poland, Qatar, Romania, Russia, Serbia, Slovenia, Spain,

UAE, UK, Ukraine, USA). Lectures were given by 4 keynote speakers (45 min.), 9 invited speakers (35 min.) and 35 other participants (25 min.). Some details can be seen on the conference website <http://www.nonlinearity2021.matf.bg.ac.rs/>.

On behalf of the Serbian Academy of Nonlinear Sciences, we would like to express our gratitude to the Ministry of Education, Science and Technological Development of the Republic of Serbia for a financial support to publish these Proceedings. We are also thank the Coorganizers and the management of the journal Symmetry for a support of this conference. In particular, we are thankful to all speakers and the authors of contributions to the Proceedings. We hope very much that this collection of papers will be useful not only to participants of this conference but also to all others who are interested in nonlinearity.

The Serbian Academy of Nonlinear Sciences plans to continue with the organization of Conferences on Nonlinearity regularly with a period of two years. It is our great wish that next year there will be no problem with the Corona virus epidemic and that the third conference will be held in person. We will be happy to see all participants of the first two conferences again, as well as many new ones.

Belgrade, Summer 2022

E d i t o r s

Branko Dragovich  
(President of SANS)

Zeljko Cupic  
(General secretary of SANS)

## CONTENTS

M. P. Cartmell	
<b>On the terrestrial measurement of frame-dragging</b>	1
I. D. Atanasovska, D. B. Momcilovic	
<b>Analysis of contact fatigue coupled with geometry and material nonlinearities by Theory of critical distances</b>	27
M. M. Filipovic, Lj. B. Kevac	
<b>The procedure of generating trajectory of motion of carrier conveyor for granular material in dependance of pod systems characteristics</b>	48
F. Geogriades	
<b>Design of a mechanical system to admit similar rigid body nonlinear modes and the correlation with perpetual mechanics</b>	63
K.-Y. Huang, Y. Zhao, L. Xue, J.-R. He, K.-W. Wang, S.-L. Xu, M. R. Belić, B. A. Malomed	
<b>Supporting quantum squeezing in two component solitons by means of electromagnetically-induced transparency</b>	79
A. Obradović	
<b>Mass minimization of an AFG Timoshenko beam with coupled axial and bending vibrations</b>	96
V. Skarka, M. Lekić	
<b>Self-organized bridge connecting THEORY to EXPERIMENTS</b>	109
S. Zdravković, D. Ranković	
<b>W-potentials in nonlinear biophysics of microtubules</b>	136
S. Paunović,	
<b>Modelling the Steel Fibre Reinforced Concrete material nonlinearity with ANSYS</b>	150
Ž. Čupić, A. Ivanović-Šašić	
<b>Bray-Liebhavsky reaction: From monotonous to chaotic evolution</b>	170
C. N. Babalic, R. Constantinescu	
<b>Auxiliary equations for solving nonlinear evolutionary equations</b>	200



D. Jovanović, O. Alexandrova, M. Maksimović, M. Belić <b>Fluid theory of coherent magnetic vortices in high-<math>\beta</math> space plasmas</b>	212
P. Jovanović, V. Borka Jovanović, D. Borka, A. F. Zakharov <b>Graviton mass and Yukawa-like nonlinear correction to the gravitational potential: constraints from stellar orbits around the Galactic Center</b>	232
A. Maluckov, D. Leykam, S. Flach, A. Mančić, E. Smolina, D. Smirnova <b>Scanning band topology by the modulation instability</b>	246
Nikola Petrović <b>Exact traveling and solitary wave solutions to the generalized Gross-Pitaevskii equation with cylindrical potential</b>	259
R. Cimpoiasu, R. Constantinescu, G. Florian, A. Pauna <b>Reduction methods and travelling wave solutions for nonlinear evolutionary phenomena</b>	268
B. Dragovich <b>On <math>p</math>-adic scalar matter</b>	280
<b>Talks not presented to the Proceedings</b>	297
<b>List of participants</b>	299

## **Bray-Liebhafsky reaction: From monotonous to chaotic evolution**

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### ABSTRACT

Many physicochemical processes can exhibit various forms of non-linear dynamics, which have been widely investigated in the oscillatory reaction Bray-Liebhafsky, too. The stoichiometry of this reaction corresponds to the hydrogen peroxide decomposition to water and oxygen in an acidic environment, in the presence of iodate ions as a catalyst. During this reaction an oscillatory change of the intermediate species concentration, along with a cascade change in the hydrogen peroxide concentration and oxygen removal can be obtained. By selecting the experimental conditions, the simple periodic or complex chaotic concentration changes can be generated. Concentration oscillations are a consequence of alternating dominance of different reaction pathways present in the reaction mechanism. Large extent of the phenomena experimentally observed in the oscillatory reaction Bray-Liebhafsky is well explained by the mechanistic model, investigated by the Belgrade group over a many years.

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## 1. Introduction

In everyday practice of the whole of human activity, including physical chemistry, the nonlinear dynamics is represented at least equally as well as linear; actually, linear dynamics is only a limit case of the nonlinear one. [1] Probably, the human tendency toward simplification and limited capacity of the human brain to perceive and predict the nonlinear dynamics, are the only ones responsible for the long-standing dominance of linear models of natural processes. This statement is supported by the fact that the processes of nonlinear dynamics are observed in all areas that are the subject of scientific considerations, among which are the typical examples in elementary particle physics, [2] in chemical kinetics, [3]-[7] in electrochemistry [8]-[10] in cell biochemical processes [11] and at the level of multicellular organisms, [12],[13] in population processes at the level of ecosystems, [14] in the economy [15] and astrophysics. [16]

The study of homogeneous oscillatory reactions (such as: the Bray-Liebhafsky one [17]-[30] – first reported homogeneous oscillatory chemical reaction, the Belousov-Zhabotinsky [31]-[38] – the most popular one, and the Briggs-Rauscher [39]-[43] oscillatory reaction) is one of the most important contributions from physical chemistry to development of the nonlinear dynamics. In this area, oscillatory reaction Bray-Liebhafsky (BL) has a particular importance because it was first discovered homogeneous oscillatory chemical reaction, furthermore, because it is probably the simplest studied chemical oscillator, but also, because the study of this system allow the experimental and numerical analysis of a wide range of dynamic phenomena.

Multiple-time-scale behavior of the BL reaction is explored here to explain mechanistic sources of dynamic transitions. Different levels of understanding oscillatory process are described here by models with varying complexity. Hence, present paper presents results about modeling BL reaction at different levels.

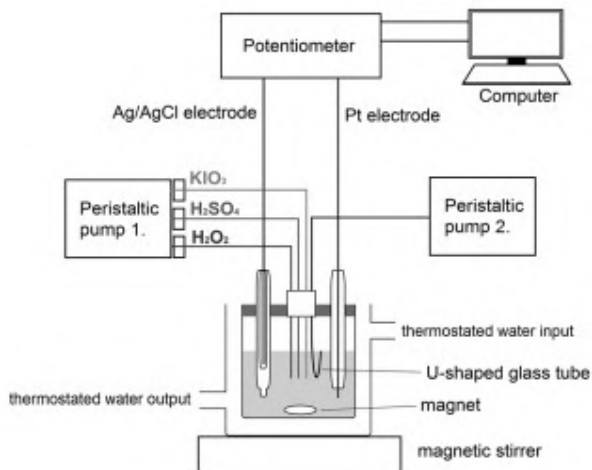
## 2. Multi-level modeling of the BL reaction

The Bray-Liebhafsky reaction is the hydrogen peroxide decomposition in the presence of iodate and hydrogen ions, as catalysts. This, apparently simple oscillatory reaction, known as the Bray-Liebhafsky one, consists of a complex homogeneous catalytic oscillatory processes involving periodic changes in concentrations of numerous iodine intermediates such as  $I_2$ ,  $I^-$ ,  $HIO$ ,  $HIO_2$  and  $I_2O$ , that all oscillates in the same time-scale, but in different phases and relative intensities. [25] Periodic changes of the solution color, oxygen removal and indicator electrode potential were detected in this system, at temperatures between 20°C and 65°C. Periodicity in this system is a consequence of complex reaction mechanism which consists of a series of reaction steps with multiple feedbacks. Just like any complex process, the BL reaction may be modeled at several levels of understanding. Here, it will be described starting from the most

rudimentary, system level, where system components are defined, and then, with gradually increasing complexity, details of the process will be added to the model, making it, finally, convenient to describe even the strangest dynamic states of chaos.

### 2.1. System-level – components

Investigation of the BL reaction is often performed in either open or closed reactor, usually in the form of thermostated bath with some mixing device (Fig 1.). Although the system has finite phase boundary, reaction goes on within the liquid phase. The advantage of open systems over the closed ones is in the presence of inlets/outlets for continuous inflow/outflow of reactants/reaction mixture, which is the external force used to maintain this dissipative system in vicinity of the unstable steady state, far from equilibrium.



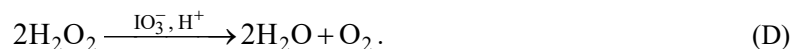
**Figure 1.** *Continuous Stirred Tank Reactor (CSTR)*. If pumps are removed, the batch reactor is obtained.

Flow rate in open oscillating BL systems is always small against the fast reaction rates in oscillations, and mixing makes the liquid system macroscopically homogeneous. Thermostated coat ensures that rate constants have really constant values independent on extent of the reaction and its heat effects. Hence, usual approach in modeling BL reaction assumes deterministic, mean field approximation, where state of the system is represented by mean concentrations of all species. Thus, the BL reaction is described by the system of *Ordinary Differential Equations* (ODE) which depicts the changes in concentration of reaction species in time (see below).

Moreover, the first approximation of the BL reaction system would have to be nothing else, but liquid water (H<sub>2</sub>O), since it is by far the most abundant component in the system. The water concentration is about 55 M and concentrations of other macro-components (H<sub>2</sub>O<sub>2</sub>, H<sup>+</sup>, IO<sub>3</sub><sup>-</sup>, K<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>) are for about three orders of magnitude lower. Besides, ionic species K<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> are not involved in any significant reaction, and will not be considered further. Thus, typical concentration of hydrogen peroxide (as well as H<sup>+</sup> and IO<sub>3</sub><sup>-</sup>) during the oscillatory state of the system is between 10<sup>-2</sup> and 10<sup>-1</sup> M, the concentration of iodine, I<sub>2</sub>, is between 10<sup>-5</sup> and 10<sup>-4</sup> M, whereas the concentrations of other intermediary species are even much lower, between 10<sup>-9</sup> and 10<sup>-6</sup> M. Nonetheless, the role of water in the BL system is often neglected and underestimated, since it is not directly involved in reduction - oxidation processes. There is no doubt that water plays important role in solvation, changing all reaction rates and dynamics of the oscillating process. There is also increasing number of evidences that water is even more important, taking part in redirecting energy transfer during the delicate oxidation phase of the BL reaction. [44]-[48] However, we are still far away from clear understanding of water structure and its dynamics, and therefore, this level of modeling will here, again, be neglected. All effects of water will here be considered as included in rate constants of particular reactions.

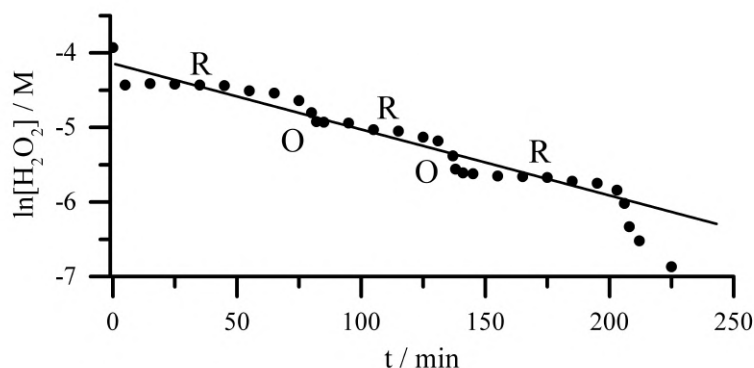
## 2.2. Process-level – reaction

The most intensive effect of the BL reaction is the decomposition of the hydrogen peroxide with production of oxygen.



Process is followed by the stoichiometrically equivalent production of water, which has no noticeable effect on overall composition, since it is already present in large excess. Concentrations of two other macrocomponents (iodate and hydrogen ions) are changed during reaction, but in so small extent that we can consider them as constant, and equal to initial values during the whole process. Thus, their role is mainly catalytic. Hence, corresponding reaction (D) represents the next level model of the BL reaction. The process (D) is irreversible, since oxygen leaves liquid phase and goes to the gas phase. Consequently, the equilibrium is never reached and reaction goes until complete exhaust of the hydrogen peroxide as the only reactant. Since hydrogen peroxide decays in time, and oxygen, as the only product besides water, leaves the mixture through the phase boundary, concentrations of all species in liquid mixture are much less than the water content in all times, and hence, new model is consistent with previous one.

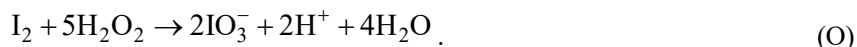
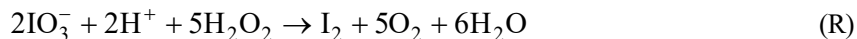
The BL reaction rate depends on several control parameters, such as the temperature in both reactors (closed and open) and flow rate in open reactor, or also the initial concentrations of the above mentioned reaction species ( $H^+$  and  $IO_3^-$ ) which are approximately constant during reaction. Finally, reaction rate in BL reaction depends also on hydrogen peroxide concentration. Usually, decomposition reactions correspond to the first order reaction kinetics. In fact, within a very wide region of concentration values of the BL system constituents, hydrogen peroxide concentration really monotonously decays in time with first order kinetics. Even, during the periodic changes of iodine species concentrations, while hydrogen peroxide decays in cascades, small steps in its concentration curve could be neglected, and overall change fits well the first order kinetics (Fig. 2).



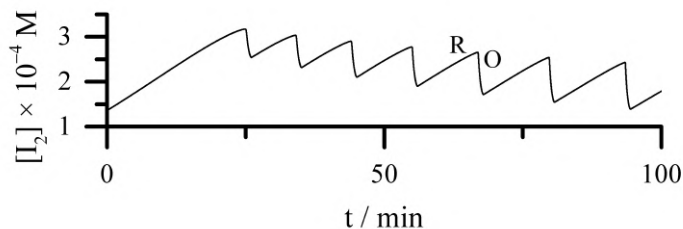
**Figure 2.** Changes of the hydrogen peroxide concentration with time, during oscillatory reaction BL. Solid circles designate experimentally measured values and line approximates the first order decay. The R and O branches are indicated. Results from ref. [49].

### 2.3. Alternate-pathways-level of modelling

Periodic changes of the solution color (connected with hydrogen peroxide concentration changes, Fig. 2) observed in the BL system are not explained either by the stoichiometry of the reaction (D) or by the simple first order reaction kinetics. The first attempt to explain these phenomena was already in the first report about the BL oscillatory reaction, [17] where Bray analyzed dual role of hydrogen peroxide as an oxidizing and reducing agent. There, he noticed that the hydrogen peroxide decomposition to water and oxygen in the presence of iodate and hydrogen ions is the result of the reduction (R) of iodate to iodine and the oxidation (O) of iodine to iodate by the following reaction scheme:



Rates of the two processes are in such ratio that only small extent of the iodate is converted to iodine and *vice versa* in any moment of time. Their rates tend to become equal, and, when the two processes achieve balance, the overall process is represented by the sum of these two reactions (R) and (O), which is identical to the smooth decomposition reaction (D). Then, we usually observe only a smooth decomposition described by reaction (D) where iodine, as intermediate species, does not appear in corresponding net stoichiometric relation. Hence, the model is at present level in consistency with the previous one. However, concentration of iodine, produced in reaction pathway (R), and removed in reaction pathway (O), gives coloration to the BL system solution. Periodic changes of the color are induced by periodic changes in the domination of the processes (R) and (O). Namely, in a narrow range of initial concentrations values, the alternating domination of processes (R) and (O) occurs, resulting in alterations between periods of slower increase (R branch) and faster decrease (O branch) of the iodine concentration during stepwise decrease of the hydrogen peroxide and increase of the oxygen concentrations.



**Figure 3.** Changes of the iodine concentration with time, during oscillatory reaction BL. The R and O branches are indicated. The concentrations of iodate and hydrogen ions were:  $[\text{IO}_3^-] = 0.0474 \text{ M}$ ,  $[\text{H}^+] = 0.0958 \text{ M}$ . Rate constants are taken from the ref. [50].

Nevertheless, it is obvious that the two reactions cannot be elementary processes. Their kinetics was investigated in many years and complex kinetic rates were established indicating several reaction steps with many intermediary species involved in each of the two. At the end, no rate law identified in two of the processes could successfully simulate periodic changes. Thus, stoichiometry of periodic processes was well described at the present level of model, but not the reaction kinetics. More precisely, the necessary feedback needs to be included in the model of the reaction mechanism.

#### **2.4. Kinetic level – model capable to simulate oscillatory dynamics**

In attempts to construct appropriate model able to simulate oscillating reaction, several reaction networks were synthesized with all possible reaction steps and intermediary species. However, reaction rates mainly remained unknown. Therefore, modeling based on such detailed description was still unsuccessful. Further development led to several approximations and model reductions, based on excluding very slow or less probable reaction pathways and condensing details of complex branches from detailed reaction network into simplified representations by single steps with empirically evaluated rate constants. This phase in the frame of modeling process is not uniquely defined and, consequently, several models occurred attempting to explain the BL system. [17]-[19],[21],[22],[50]-[60] Among the most successful results, there is a model M(1-8) represented by eight reactions or reaction steps (R1-R8 in Table 1), where three of them are reversible. It will be used in the following analysis of the process.

Summation of all reactions in model M(1-8) gives again reaction (D), making system inherently consistent with its lower level representation. Reaction (D) represents smooth decomposition steady state of the model M(1-8), in which, all reactions run with equal rate. Reactions (R) and (O) are also incorporated in the reaction network of the model M(1-8), but in less obvious way. They are manifested only as partial sums of certain reaction pathways alternately dominating during the reduction and oxidation phase in oscillations (Table 2).



**Table 1.** Model M(1-8) of the BL reaction used in numerical simulations under batch conditions. [57]

Reaction or Reaction step	Reaction rate <sup>a</sup>	No.
$\text{IO}_3^- + \text{I}^- + 2\text{H}^+ \rightleftharpoons \text{HIO} + \text{HIO}_2$	$r_1 = k_1 [\text{I}^-]$ $r_{-1} = k_{-1} [\text{HIO}] [\text{HIO}_2]$	(R1) (R-1)
$\text{HIO}_2 + \text{I}^- + \text{H}^+ \longrightarrow \text{I}_2\text{O} + \text{H}_2\text{O}$	$r_2 = k_2 [\text{HIO}_2] [\text{I}^-]$	(R2)
$\text{I}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HIO}$	$r_3 = k_3 [\text{I}_2\text{O}]$ $r_{-3} = k_{-3} [\text{HIO}]^2$	(R3) (R-3)
$\text{HIO} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2 + \text{H}_2\text{O}$	$r_4 = k_4 [\text{HIO}] [\text{I}^-]$ $r_{-4} = k_{-4} [\text{I}_2]$	(R4) (R-4)
$\text{HIO} + \text{H}_2\text{O}_2 \longrightarrow \text{I}^- + \text{H}^+ + \text{O}_2 + \text{H}_2\text{O}$	$r_5 = k_5 [\text{HIO}]$	(R5)
$\text{I}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{HIO} + \text{HIO}_2$	$r_6 = k_6 [\text{I}_2\text{O}]$	(R6)
$\text{HIO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	$r_7 = k_7 [\text{HIO}_2]$	(R7)
$\text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}_2 \longrightarrow \text{HIO}_2 + \text{O}_2 + \text{H}_2\text{O}$	$r_8 = k_8$	(R8)

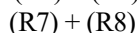
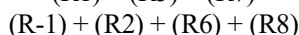
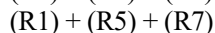
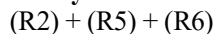
<sup>a</sup> Reaction rate constants at 60°C:  $k_1 = 1.383 \times 10^2 \text{ min}^{-1}$ ;  $k_{-1} = 7.91 \times 10^7 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_2 = 4.79 \times 10^{10} \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_3 = 5.00 \times 10^3 \text{ min}^{-1}$ ;  $k_{-3} = 3.15 \times 10^8 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_4 = 3.00 \times 10^{11} \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_{-4} = 46.97 \text{ min}^{-1}$ ;  $k_5 = 2.974 \times 10^2 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_6 = 1.00 \times 10^4 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_7 = 4.00 \times 10^1 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_8 = 4.4606 \times 10^{-6} \text{ min}^{-1}$ . The concentrations of iodate and hydrogen ions, taken as constant in simulations ( $[\text{IO}_3^-] = 0.0474 \text{ mol} \times \text{dm}^{-3}$  and  $[\text{H}^+] = 0.0958 \text{ mol} \times \text{dm}^{-3}$ ) are included in corresponding rate constants. Unlike the models presented in the literature, here, the concentration of hydrogen peroxide is taken as constant in simulations, too ( $[\text{H}_2\text{O}_2] = 0.0200 \text{ mol} \times \text{dm}^{-3}$ ) and also included in corresponding rate constants.

Hence, reactions (R) and (O) and corresponding reaction pathways represent some new kind of steady states, other than smooth decomposition one. Corresponding steady states must be connected with balanced production and consumption of selected intermediary species, only. The hydrogen peroxide is always only consumed and therefore it cannot be balanced in present model. Besides, the iodine is also produced from iodate in process (R) and it is spent in process (O) to regenerate iodate. Hence, production and consumption are not balanced for these two species in corresponding (R) and (O) steady states. Other iodine species do not appear in the observed stoichiometry, and thus, seem to be

balanced. Similar differentiation between reaction species is usually connected with slow-fast dynamics.

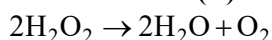
**Table 2.** The reaction pathways derived from the model M(1-8)

**1.Reaction pathways:**

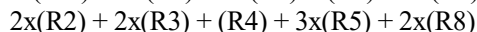
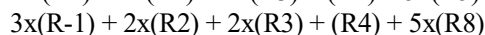
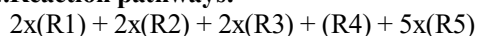



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**Net reaction (D)**

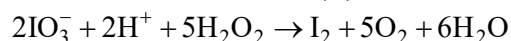


**2.Reaction pathways:**

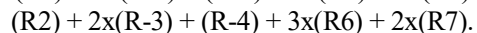
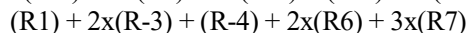
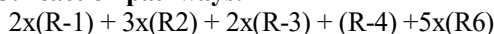



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**Net reaction (R)**



**3.Reaction pathways:**




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**Net reaction (O)**



**Slow and fast subsystem**

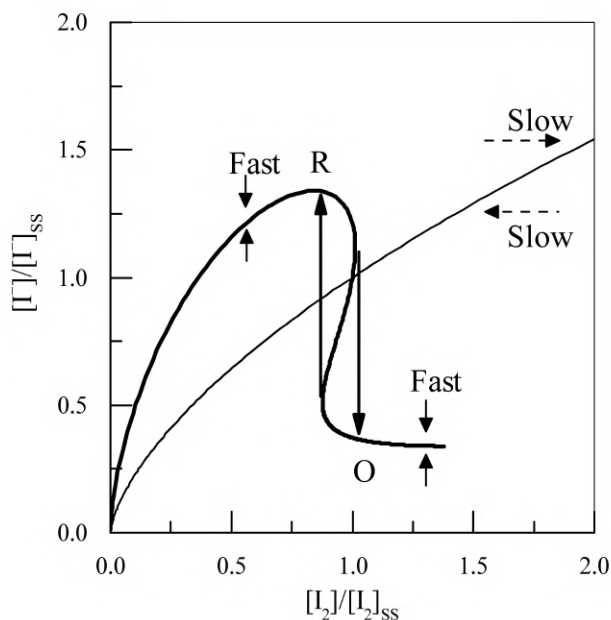
Obvious difference between reaction species included in the model, is in the concentration levels. The concentrations of reaction species in the considered process differ for several orders of magnitudes among themselves. Thus, in oscillatory dynamic state of the BL system, typical concentration of hydrogen peroxide is between  $10^{-2}$  and  $10^{-1}$  M, concentration of iodine is between  $10^{-5}$  and  $10^{-4}$  M, whereas the concentrations of other species are much lower, between  $10^{-9}$  and  $10^{-6}$  M.

In systems, where concentrations of crucial species differ significantly, the *relaxation oscillations* are common. Such oscillations are generated by alternating relatively long periods of slow changes, eventually interrupted by short and sudden jumps to another state of relatively slow changes. These oscillations are connected with slow-fast dynamical systems where dynamical variables are divided in slow and fast ones, according to time scale at which they are changed. There, fast variables always quickly adjust to any change in

slow variables, which act as the parameters for the fast subsystem. Dynamics of such systems is reduced to lower dimensional subspace of the phase space.

Hydrogen peroxide, hydrogen ion and iodate concentrations are much higher than those of other species and one can approximate that they are constant. Thus, in a case where these concentrations are considered as a fixed parameters, iodine concentration is the only slow variable and concentrations of other four iodine species ( $I^-$ , HIO, HIO<sub>2</sub>, I<sub>2</sub>O) from the Model(1-8) are fast variables. The stationary values of fast variables are positioned on the one-dimensional curve in five-dimensional space. This curve, known as *slow nullcline*, represents steady states of the fast subsystem, which are functionally dependent on instantaneous values of the slow variable, iodine concentration. There are other nullclines too, and they correspond to various combinations of four variables, among complete set of five ones. However, only the one that correspond to the set of fast variables only, attracts the trajectories from the whole phase space and it represents one form of the so-called slow manifold of the dynamical system. Starting from an arbitrary point in the phase space, the system follows its fast component dynamics and jumps to the nearest point on the slow nullcline. Once after the system reaches it, fast variables are balanced and only slow component of the dynamics governs further propagation over the nullcline, ending usually in the special point on the nullcline representing stable steady state. Therefore, this specific nullcline is named the slow nullcline, while all others are fast ones. The direction of propagation over the slow nullcline is governed by relative position of the dynamic system with respect to the fast nullclines. The steady state is positioned in the crosspoint of slow and fast nullclines.

In the domain where relaxation oscillations are present slow nullcline is folded having at least two stable and one unstable branch in one interval of slow variable values. Slow nullcline calculated for the studied model is folded, as can be seen in Fig. 4. The steady state is in that case positioned on the unstable middle branch of the slow nullcline, and this steady state is also unstable. In that case, the fast variables often alternate between two stable branches resulting in relaxation oscillatory evolution of considered dynamical system.



**Figure 4.** Slow (thick) and fast (thin) nullclines of the Model(1-8). R and O branches of the folded slow nullcline are designated. Arrows indicate directions of fast (solid line) and slow (dashed line) components of the dynamics in areas divided by nullclines.

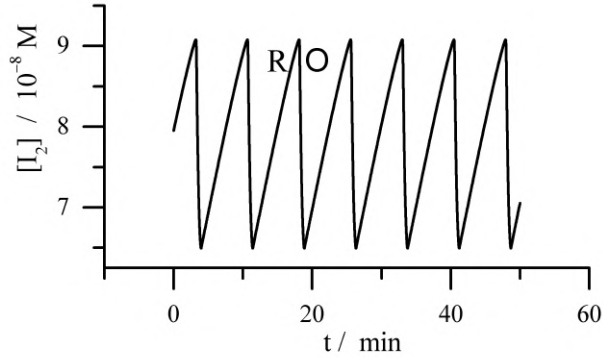
Described two stable branches of the slow nullcline correspond to reaction pathways (R) and (O). System represented by the point on the upper branch (high iodide concentration) evolves according to (R) stoichiometry. It means that iodine concentration is increased and point is moved to right until it eventually reaches fold point delimiting stable and unstable branch. At this special point, system tends to continue increasing iodine concentration but for new higher values only lower branch values of the fast variables could satisfy fast subsystem steady state conditions. Hence, the system jumps to lower branch of the nullcline. There, it moves toward lower values of the iodine concentration according to the stoichiometry of (O) process until it comes to the other fold point. From this point, the only way is the new jump to the upper branch where cycle is closed. According to calculated nullclines Model(1-8) should be able to simulate oscillations. However, it must be confirmed by direct numerical experiment.

### Numerical simulations

For final tests of oscillatory properties, the Model(1-8) must be used to generate periodic changes of concentrations. Hence, the system of ODE-s must be formed in accordance with the model. Each concentration is changed with rate which is sum of individual reaction rates multiplied by corresponding stoichiometric coefficients. Rates of individual reaction steps are given in Table 2, according to reaction stoichiometry and mass action law. Relative significance of these steps is given by rate constants multiplying concentrations of reacting species in particular step. The same rules could be used to form rate equations for each one reaction species, no matter if it is reactant, product, or intermediary species. However, some of reaction species are dynamically unimportant. Since the concentrations of iodate and hydrogen ions are significantly larger than the concentrations of other reaction species, they can be considered as constant without affecting qualitatively the results. Extending the model with two differential equations to account for the temporal evolution of these two species does not alter the dynamic structure of the system, including the highly sensitive mixed mode oscillation range, but only shifts a little the bifurcation points with respect to any control parameter values. [61] Hence the calculations presented here use  $[\text{IO}_3^-] = 0.0474$  and  $[\text{H}^+] = 0.0958 \text{ mol/dm}^3$ . [62],[63] Furthermore, in model M(1-8) hydrogen peroxide is the only reactant. The reaction kinetics depends on its concentration only parametrically. Its changes in oscillations are much slower than others, and we consider that it is not essential for occurrence of oscillations and it will be taken as constant in the first approximation. Hence, in the model under consideration, there are five independent intermediary species:  $\text{I}_2$ ,  $\text{I}^-$ ,  $\text{HIO}$ ,  $\text{HIO}_2$  and  $\text{I}_2\text{O}$  and only they are dynamically important.

$$\begin{aligned}
 d[\text{I}_2]/dt &= r_{+4} - r_{-4} \\
 d[\text{I}^-]/dt &= -r_{+1} + r_{-1} - r_2 - r_{+4} + r_{-4} + r_5 \\
 d[\text{HIO}]/dt &= r_{+1} - r_{-1} + 2r_{+3} - 2r_{-3} - r_{+4} + r_{-4} - r_5 + r_6 \\
 d[\text{HIO}_2]/dt &= r_{+1} - r_{-1} - r_2 + r_6 - r_7 + r_8 \\
 d[\text{I}_2\text{O}]/dt &= r_2 - r_{+3} + r_{-3} - r_6.
 \end{aligned} \tag{1}$$

The  $r_i$ ,  $r_{+i}$  and  $r_{-i}$  denote respectively the rates of whole reactions  $i$ , its forward part and its reverse part. The values given in Table 1 are taken from ref. [64],[65] and include fixed concentrations of iodate, hydrogen ions and hydrogen peroxide.



**Figure 5.** Numerical simulations of the Model(1-8).  $[\text{H}_2\text{O}_2] = 0.02 \text{ M}$ .

Results in Fig. 5 confirm ability of the Model(1-8) to simulate sustained oscillations of iodine, maintaining the same type of relaxation oscillations as they are observed in experiments.

### 2.5. Dynamic level – model capable to simulate chaotic dynamics

In numerical simulations of batch reactor experiments, changes of hydrogen peroxide concentrations are also important, just because its parametrical influence on changes in the form of oscillograms. Hence, additional differential equation has to be added for new variable:

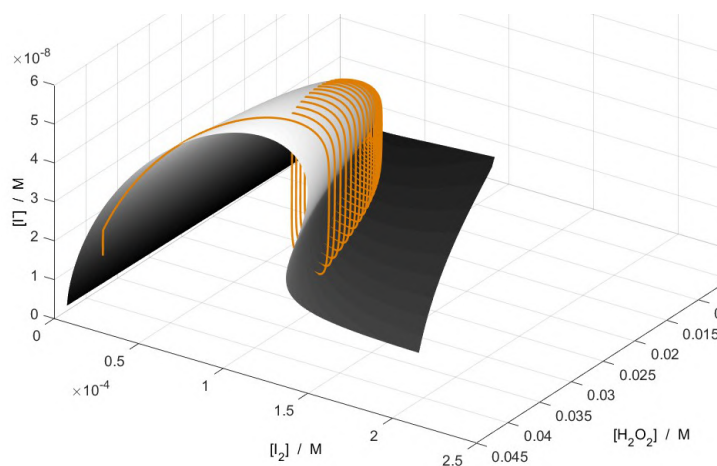
$$d[\text{H}_2\text{O}_2]/dt = -r_5 - r_6 - r_7 - r_8. \quad (2)$$

Moreover, some rate equations need to be adapted since hydrogen peroxide concentration is not included in rate constants any more:  $k_5 = 1.487 \times 10^4 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_6 = 5.00 \times 10^5 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_7 = 2.00 \times 10^3 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_8 = 2.2303 \times 10^{-4} \text{ min}^{-1}$ . Appropriate rate expressions are now:

$$\begin{aligned} r_5 &= k_5 [\text{HIO}] [\text{H}_2\text{O}_2] \\ r_6 &= k_6 [\text{I}_2\text{O}] [\text{H}_2\text{O}_2] \\ r_7 &= k_7 [\text{HIO}_2] [\text{H}_2\text{O}_2] \\ r_8 &= k_8 [\text{H}_2\text{O}_2]. \end{aligned} \quad (3)$$

The shape of the slow nullcline is dependent on parametrically changing hydrogen peroxide concentration. By merging slow nullclines for the range of hydrogen peroxide concentrations, one obtains folded surface that attracts all trajectories from the phase space. Since hydrogen peroxide concentration is slowly decaying in closed reactor, oscillations are evolving with time as system slowly glides over the surface (Fig. 6). After some time, system approaches the point where folded surface unfolds and oscillations disappear through the

sequence of damped, nearly harmonic oscillations. This transition corresponds to supercritical Andronov-Hopf bifurcation that occurs at critical value of hydrogen peroxide concentration.



**Figure 6.** Surface of slow nullclines for a sequence of  $[H_2O_2]$  values and trajectory of the BL reaction obtained for the Model(1-8) in the batch reactor.

Thus, at this level of modelling, damped oscillations of relaxation type, as well as nearly harmonic ones, are successfully described by model M(1-8). Even many other properties of the experimental oscillograms are simulated with given model, including pre-oscillatory period, and dependence on initial concentrations or temperature. However, complex oscillations are still not explained at this level of approximation.

Complex dynamic states like chaos, are better examined in open reactor where the selected dynamics can be sustained infinitely. Although, the first eight reactions in Table 1, are enough to describe well the mechanism of the process under batch conditions, additional ones must be taken into account in an open *continuous stirred tank reactor* (CSTR), where complex oscillations could be maintained for a very long time. Additional reactions represent only inflow and outflow of chemical species into the reaction mixture and out of it (Table 3). In this extended model only hydrogen peroxide is considered as the inflow species. (The reaction system can be open with respect to other species, too. However, in that case, the number of intermediate species and related reactions increases importantly resulting in large mathematical problems without essentially important results.) In the model under consideration, where hydrogen peroxide is taken as the only inflow species, there are now six independent species:  $H_2O_2$ ,

$I_2$ ,  $I^-$ ,  $HIO$ ,  $HIO_2$  and  $I_2O$  and again, they are all dynamically important. Concentrations of iodate and hydrogen ions are again considered as constant. Hence the calculations presented here use  $[IO_3^-] = 0.0474$  and  $[H^+] = 0.0958$  mol/dm<sup>3</sup> as before. [62],[63] The time evolutions of other species are described by the six following differential equations:

$$\begin{aligned}
 d[H_2O_2]/dt &= -r_5 - r_6 - r_7 - r_8 + j_0 ([H_2O_2]_{in} - [H_2O_2]) \\
 d[I_2]/dt &= r_{+4} - r_{-4} - j_0 [I_2] \\
 d[I^-]/dt &= -r_{+1} + r_{-1} - r_2 - r_{+4} + r_{-4} + r_5 - j_0 [I^-] \\
 d[HIO]/dt &= r_{+1} - r_{-1} + 2r_{+3} - 2r_{-3} - r_{+4} + r_{-4} - r_5 + r_6 - j_0 [HIO] \\
 d[HIO_2]/dt &= r_{+1} - r_{-1} - r_2 + r_6 - r_7 + r_8 - j_0 [HIO_2] \\
 d[I_2O]/dt &= r_2 - r_{+3} + r_{-3} - r_6 - j_0 [I_2O].
 \end{aligned} \tag{4}$$

The values given in Table 3 are taken from the already published model [64],[65] and include fixed concentrations of iodate and hydrogen ions.

Thus, mathematically speaking, we are dealing with six-dimensional problem. This model is able to describe almost all features of BL reaction, including regular simple oscillatory evolution, periodic mixed-modes with *large-amplitude oscillations* (LAO-s) and *small-amplitude oscillations* (SAO-s), as well as the chaotic occurrence of LAO-s and SAO-s and their combinations. [66]



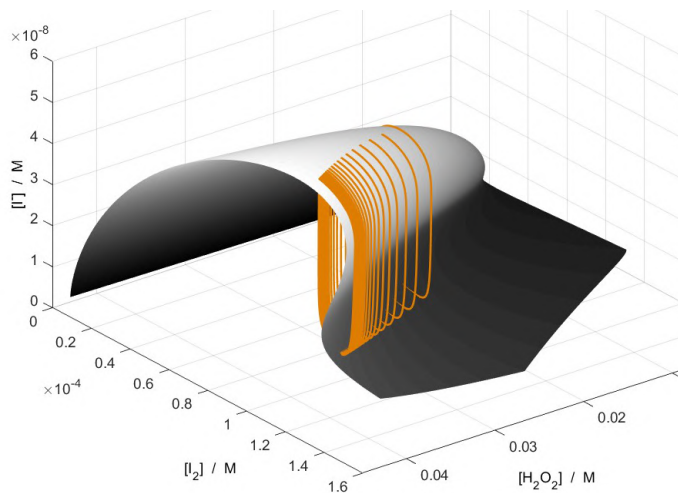
**Table 3.** Model M(1-15) of the BL reaction used in numerical simulations under CSTR conditions.[50]

Reaction	Reaction rate <sup>a</sup>	No.
$\text{IO}_3^- + \text{I}^- + 2\text{H}^+ \rightleftharpoons \text{HIO} + \text{HIO}_2$	$r_1 = k_1 [\text{I}^-]$ $r_{-1} = k_{-1} \frac{[\text{HIO}][\text{HIO}_2]}{[\text{HIO}_2]}$	(R1) (R-1)
$\text{HIO}_2 + \text{I}^- + \text{H}^+ \longrightarrow \text{I}_2\text{O} + \text{H}_2\text{O}$	$r_2 = k_2 [\text{HIO}_2] [\text{I}^-]$	(R2)
$\text{I}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{HIO}$	$r_3 = k_3 [\text{I}_2\text{O}]$ $r_{-3} = k_{-3} [\text{HIO}]^2$	(R3) (R-3)
$\text{HIO} + \text{I}^- + \text{H}^+ \rightleftharpoons \text{I}_2 + \text{H}_2\text{O}$	$r_4 = k_4 [\text{HIO}] [\text{I}^-]$ $r_{-4} = k_{-4} [\text{I}_2]$	(R4) (R-4)
$\text{HIO} + \text{H}_2\text{O}_2 \longrightarrow \text{I}^- + \text{H}^+ + \text{O}_2 + \text{H}_2\text{O}$	$r_5 = k_5 [\text{HIO}] [\text{H}_2\text{O}_2]$	(R5)
$\text{I}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{HIO} + \text{HIO}_2$	$r_6 = k_6 [\text{I}_2\text{O}] [\text{H}_2\text{O}_2]$	(R6)
$\text{HIO}_2 + \text{H}_2\text{O}_2 \longrightarrow \text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}$	$r_7 = k_7 [\text{HIO}_2] [\text{H}_2\text{O}_2]$	(R7)
$\text{IO}_3^- + \text{H}^+ + \text{H}_2\text{O}_2 \longrightarrow \text{HIO}_2 + \text{O}_2 + \text{H}_2\text{O}$	$r_8 = k_8 [\text{H}_2\text{O}_2]$	(R8)
$(\text{H}_2\text{O}_2)_{\text{in}} \longrightarrow \text{H}_2\text{O}_2$	$r_9 = j_0 [\text{H}_2\text{O}_2]_{\text{in}}$	(R9)
$\text{H}_2\text{O}_2 \longrightarrow (\text{H}_2\text{O}_2)_{\text{out}}$	$r_{10} = j_0 [\text{H}_2\text{O}_2]$	(R10)
$\text{I}^- \longrightarrow (\text{I}^-)_{\text{out}}$	$r_{11} = j_0 [\text{I}^-]$	(R11)
$\text{HIO} \longrightarrow (\text{HIO})_{\text{out}}$	$r_{12} = j_0 [\text{HIO}]$	(R12)
$\text{HIO}_2 \longrightarrow (\text{HIO}_2)_{\text{out}}$	$r_{13} = j_0 [\text{HIO}_2]$	(R13)
$\text{I}_2\text{O} \longrightarrow (\text{I}_2\text{O})_{\text{out}}$	$r_{14} = j_0 [\text{I}_2\text{O}]$	(R14)
$\text{I}_2 \longrightarrow (\text{I}_2)_{\text{out}}$	$r_{15} = j_0 [\text{I}_2]$	(R15)

<sup>a</sup> Reaction rate constants at 60°C:  $k_1 = 1.383 \times 10^2 \text{ min}^{-1}$ ;  $k_{-1} = 7.91 \times 10^7 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_2 = 4.79 \times 10^{10} \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_3 = 5.00 \times 10^3 \text{ min}^{-1}$ ;  $k_{-3} = 3.15 \times 10^8 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_4 = 3.00 \times 10^{11} \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_{-4} = 46.97 \text{ min}^{-1}$ ;  $k_5 = 1.487 \times 10^4 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_6 = 5.00 \times 10^5 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_7 = 2.00 \times 10^3 \text{ mol}^{-1} \times \text{dm}^3 \times \text{min}^{-1}$ ;  $k_8 = 2.2303 \times 10^{-4} \text{ min}^{-1}$ . In CSTR we distinguish inflow species  $(X_i)_{\text{in}}$  and outflow species  $(X_i)_{\text{out}}$ . The concentrations of iodate and hydrogen ions, taken as constant in simulations ( $[\text{IO}_3^-] = 0.0474 \text{ mol} \times \text{dm}^{-3}$  and  $[\text{H}^+] = 0.0958 \text{ mol} \times \text{dm}^{-3}$ ) are included in corresponding rate constants. The inflow concentration of hydrogen peroxide was  $[\text{H}_2\text{O}_2]_{\text{in}} = 0.155 \text{ mol} \times \text{dm}^{-3}$ . Flow rate as control parameter is designated as  $j_0$ .

Hydrogen peroxide is now considered as dynamical variable, but since it has largest concentration and is changed at smallest extent, it is now included in the list of slow species. Thus, now there are two slow and four fast variables. The

stationary values of fast variables are now positioned on the two-dimensional surface in six-dimensional phase space. It is known as *manifold*. It is nearly the same as the folded surface formed by merging nullclines of the smaller model M(1-8) for batch reactor. However, manifold surface is constructed from the larger extended model and this surface now consists of points representing steady states of the fast subsystem, which is functionally dependent on instantaneous values of both slow variables. In the domain where relaxation oscillations are present, this surface is folded, having at least two stable and one unstable branch. Such a manifold calculated with the studied model can be seen in Fig. 7. Fast variables in that case often alternate between two stable branches resulting in relaxation oscillatory evolution of considered dynamical system.



**Figure 7.** Surface of slow manifold and trajectory of the BL reaction obtained for the Model(1-15) in the CSTR.

In singular perturbation theory all variables are usually classified just as slow or fast ones, such that we are dealing, there, with the models having usually just two fast and one slow, or just one fast and two slow ones. These models exhibit different dynamical characteristics. Moreover, dynamical system with two slow and one fast variable can often be rescaled to system with one slow and two fast variables. [67],[68] Considered model is selforganized in such manner that its dynamical states can alternate during the course of reaction, between the ones characteristic for two slow and one fast variable to the others characteristic for one slow and two fast variables. [67]

In chemical, physicochemical and biochemical nonlinear dynamical systems the multiple-time-scale models consist commonly of three time-scale types of variables. There are, usually, several slow ones (external species, generally, reactants and products), several fast ones (internal species, intermediates) and often a middle one (the slow-fast one) having either internal or external characteristics in different regions of phase space. Necessary condition for such alternations is that some species belong to middle scale in both, concentration and time scale.

Hence, the situation in BL system is analogous to dynamical systems with two slow and several fast species. However, fast species in the BL system are all synchronized so that they oscillate either in the same phase (HIO, HIO<sub>2</sub> and I<sub>2</sub>O), or in the anti-phase (I) with each other. Thus, they can be considered as mutually coupled variables, so that only one of them is really independent. In many ways, such a system could be considered as the system with two slow and only one fast species.

In multiple-time-scale systems with more than one slow variable, mixed-mode oscillations (MMOs) may appear within the region with simple sustained oscillations. They generally consist of two types of oscillations with distinct amplitudes: LAOs and SAOs. The LAOs are *global phenomena*, generated by the geometry of the critical manifold having an unstable branch between two stable ones. They are well known as relaxation type dynamics governed by slow sliding of the system over the stable branches of critical manifold, periodically interrupted by much faster jumps from one to another stable branch of this hyper-surface in phase space (as already described at previous level). These fast jumps usually occur at special points (*fold points forming the fold line*) of the critical manifold where the stable branch is connected with unstable one.

However, in mixed-mode, LAOs are mixed with SAOs of different nature. They occur at the fold points as a *local phenomena* generated by some *folded singularities*. In the mixed-mode region we can also expect the occurrence of complex dynamic phenomena known as *canards* and *tourbillion*. [67],[69]-[72] For complex phenomena in dynamical systems on multiple time scales, the fold is an object of special importance, just as steady state is for linear systems and limit cycle for simple oscillations. Fold points are determined according to ref. [67], from the condition:

$$\text{Det}(J(X_i)) = 0, \quad (5)$$

where  $X_i$  denotes the fast species HIO, HIO<sub>2</sub>, I<sub>2</sub>O and I and J is the Jacobian of corresponding fast subsystem. This request must be fulfilled on the border between stable and unstable branch of the critical manifold, Fig. 8. Concentrations of slow species are treated here (in evaluation of the Jacobian for fast subsystem) as they are constant. This assumption seems to be

appropriate since they are changing on much slower time scale than the fast ones.

The singularity point on the fold line was calculated according to ref. [67], from the condition:

$$\frac{df_1}{dt} \cdot \frac{\partial g}{\partial x_1} + \frac{df_2}{dt} \cdot \frac{\partial g}{\partial x_2} = 0, \quad (6)$$

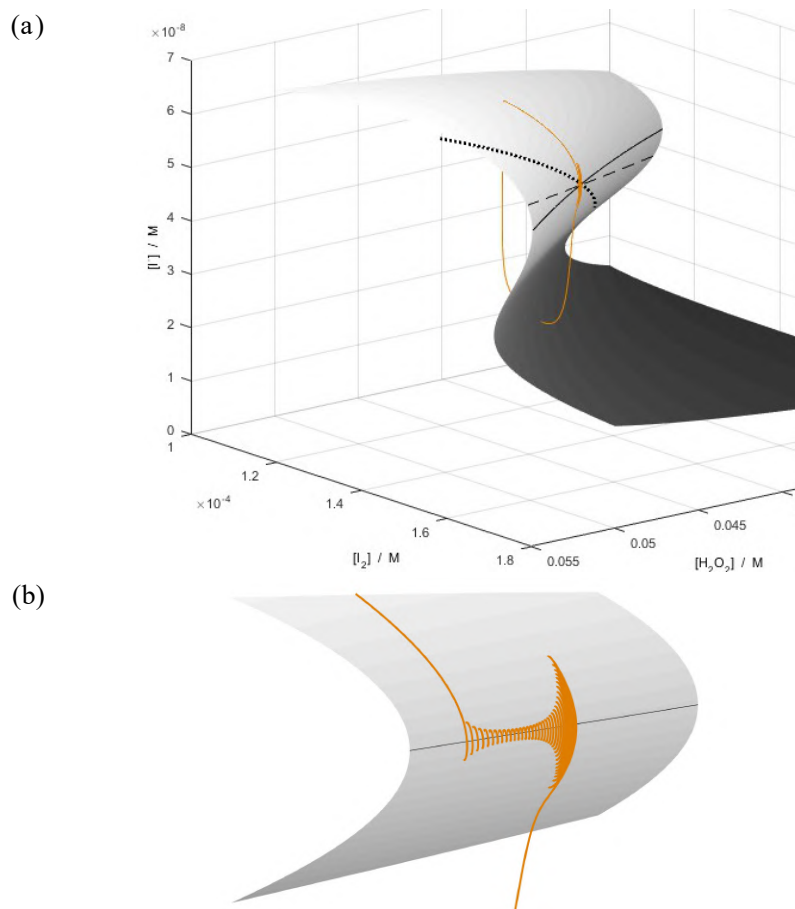
where  $x_1$  and  $x_2$  are concentrations of slow species,  $f_1$  and  $f_2$  are their corresponding rates and  $g$  is a rate of the fast variable. In our case this gives for e.g. [HIO]:

$$\frac{d}{dt} \left( \frac{d[\text{H}_2\text{O}_2]}{dt} \right) \cdot \frac{\partial}{\partial [\text{H}_2\text{O}_2]} \left( \frac{d[\text{HIO}]}{dt} \right) + \frac{d}{dt} \left( \frac{d[\text{I}_2]}{dt} \right) \cdot \frac{\partial}{\partial [\text{I}_2]} \left( \frac{d[\text{HIO}]}{dt} \right) = 0. \quad (7)$$

Furthermore, two *nullclines* were evaluated from corresponding rate equations for sets of all four fast species combined with each of two slow ones, Fig. 8. Hence, we have one nullcline that describe the steady state condition of species  $\text{I}_2$ , HIO,  $\text{HIO}_2$ ,  $\text{I}_2\text{O}$  and  $\Gamma$  (the iodine nullcline) and the other one for the combination  $\text{H}_2\text{O}_2$ , HIO,  $\text{HIO}_2$ ,  $\text{I}_2\text{O}$  and  $\Gamma$  (the hydrogen peroxide nullcline). Each one of two subsystems gives as a solution a line, located in the critical manifold of the fast species. Steady state of the full system is placed in the point where two nullclines intersect, and it will be shortly referred below as the *equilibrium*, keeping in mind that our system is of non-equilibrium type. More precisely, in our papers this is known as disproportionation steady-state.[50]

Finally, *Andronov-Hopf point* was identified numerically on the iodine nullcline using simple test ensuring that the real part of two complex eigenvalues (corresponding to corresponding five dimensional Jacobian) is passing through zero.

The SAO occurs when trajectory comes close to the fold line and starts spiral damped circling around nullcline which contains steady states of slow-fast subsystem including iodine with other fast species. The system becomes closest to the nullcline and amplitude of SAOs are the smallest when this spiral circling gets him nearest to the Andronov-Hopf point. From this point on, spiralling makes system go away from the Andronov-Hopf point and SAO amplitudes are raising leading finally to new global jump representing LAO excursion.



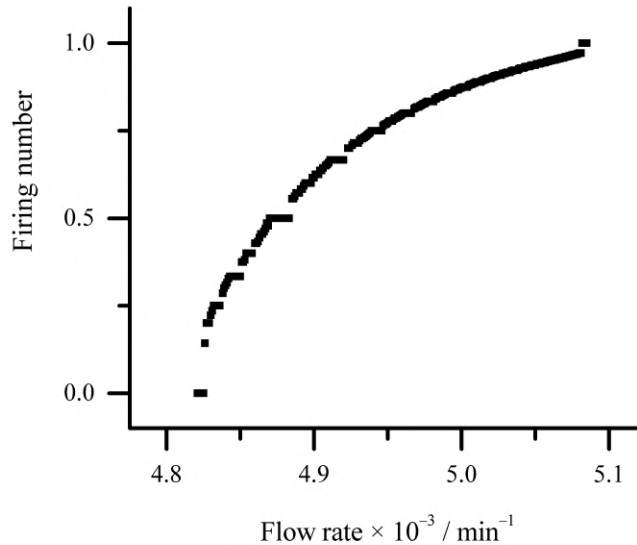
**Figure 8.** Slow manifold and trajectory of the MMOs for the Model(1-15). (a) The fold line (presented by solid line) and two nullclines (iodine nullcline presented by dashed line and peroxide nullcline by dotted line) are given. (b) Enlarged part showing structure of SAOs around the fold line.

Hence, observed complex mixed mode oscillations are decomposed in three segments by the properties of the analyzed model. First, in the LAOs itself, clear fast dynamic in jumps from one to another manifold branch are alternating with clear slow dynamics over the manifold surface. Then, in SAOs, the third component with mixed slow-fast dynamics leads to spiralling near the fold line. Therefore, the decisive role for the MMO appearance must be ascribed to the iodine species, due to their dynamical role changing from the slow one in LAOs to the fast one in SAOs.

Complex oscillations in the BL system, including LAO and SAO type MMO, could be periodic or aperiodic - chaotic. It depends only on specific ratio between control parameters. Continuous increase of the flow rate, with fixed all other parameters, leads to discontinuous increase (Figure 9) of so called firing number  $F$ , indicating fraction of SAOs in MMOs:

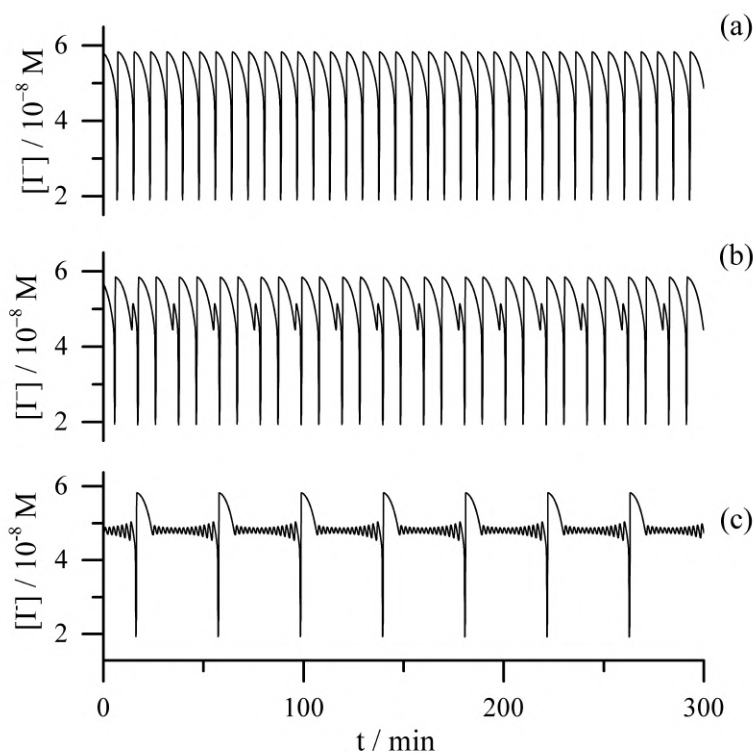
$$F = \frac{S}{S + L} \quad (8)$$

where  $S$  and  $L$  are numbers of SAOs and LAOs in one period, or more generally, total numbers of SAOs and LAOs in long enough sequence of any kind of oscillations, either periodic or aperiodic ones.

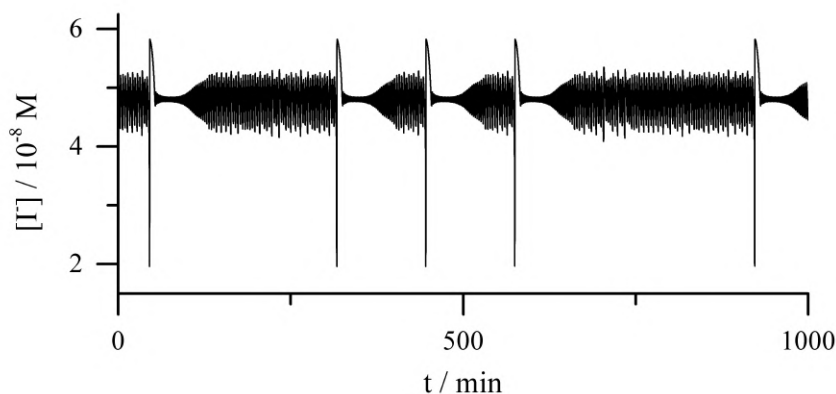


**Figure 9.** Devil's staircase. Firing number as a function of flow rate for the Model(1-15).

Chaotic windows occur between each pair of periodic dynamic states, Fig. 10. In chaotic dynamic states, irregular alterations of LAO and SAO cycles occur with properties typical for neighboring periodic windows. Hence, the fraction of SAOs and LAOs in MMOs is the only important factor determining if the system will be periodic or chaotic. Furthermore, we explained that this fraction is determined by the fraction of the slow-fast character of the iodine species depending on the flow rate value. Hence, our model successfully explained deterministic dynamic state shifts with controlled changes of the flow rate, Figure 11.

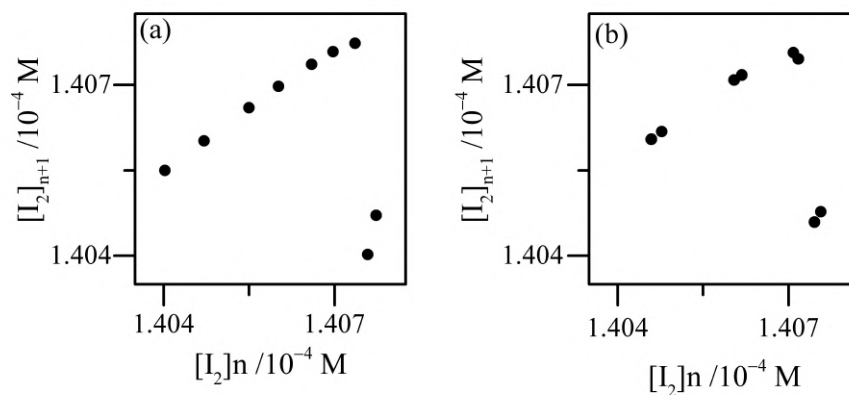


**Figure 10.** Numerical simulations of the oscillatory dynamics of the BL reaction realized in open reactor (segment from 0 to 300 min) presented by means of the iodide concentration (in  $\text{mol} \times \text{dm}^{-3}$ ). (a) Regular oscillations,  $k_f = 4.70 \times 10^{-3} \text{ min}^{-1}$ ; (b) and (c) mixed-mode oscillations,  $k_f = 4.842200 \times 10^{-3} \text{ min}^{-1}$  and  $k_f = 5.05 \times 10^{-3} \text{ min}^{-1}$ , respectively.



**Figure 11.** Numerical simulations oscillatory dynamics of the BL reaction realized in open reactor (segment from 0 to 1000 min) presented by means of the iodide concentration (in  $\text{mol} \times \text{dm}^{-3}$ ). Deterministic chaos with chaotically distributed number of the small-amplitude oscillations between the large-amplitude ones,  $k_f = 5.0815 \times 10^{-3} \text{ min}^{-1}$ .

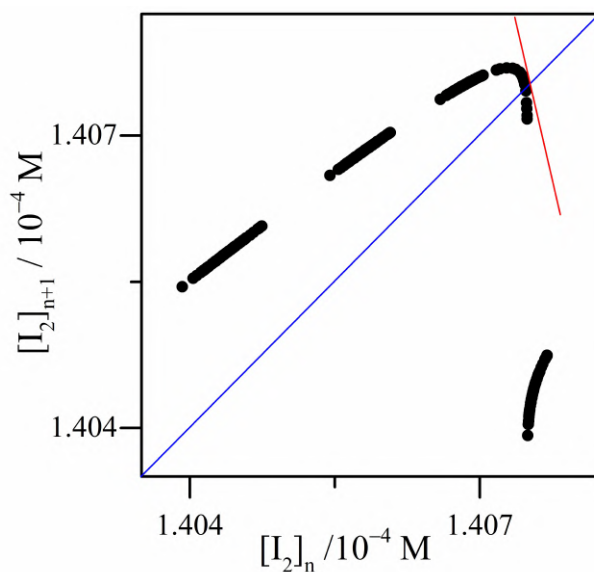
Generally, chaotic dynamics occurs when limit cycle loses stability with changes of the control parameter values. This kind of behavior is easier to understand through the changes in iteration maps. Two neighbouring periodic states of the BL reaction model are given in Figure 12, one of them corresponding to the dynamic of  $4^1 3^1$  type, and the other of  $(3^1)_2$  type.



**Figure 12.** Poincaré iteration maps: (a) for  $4^1 3^1$  dynamics, and (b) for  $(3^1)_2$  dynamics of the Model(1-15).

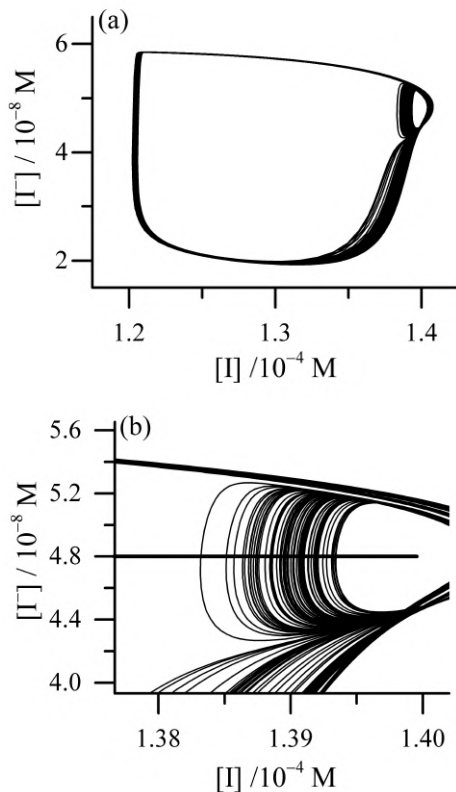


Between these two states, chaotic one was obtained and its iteration map is given in Figure 13. The position of the fixed point is identified in the crosspoint of the main diagonal (blue line) and imaginary line connecting the points on the iteration map. The fixed point corresponds to the point where the closed orbit (limit cycle) intersects the corresponding Poincare section. The slope of the tangent line (red line) in the fixed point is the criterion determining the stability of the limit cycle for the particular value of the control parameter. If the absolute value of the slope is higher than one the limit cycle is unstable and chaotic attractor is born.



**Figure 13.** Poincaré iteration map for chaotic dynamics of the Model(1-15) obtained with control parameter values between the ones used in Figure 11 (a) and (b).

Corresponding attractor of the iteration map given in Fig. 13 is given below, with enlarged part where Poincaré section was made, Fig. 14.



**Figure 14.** The chaotic attractor (a) of the Model(1-15) corresponding to the iteration map given in Fig. 13. (b) Enlarged part of the attractor with indicated position of the Poincare section.

Stability of the periodic orbit is global property of the dynamic system and its phase space. It may not be directly connected with steady state properties but rather with its manifold and trajectories over it. Hence, the transition to chaos is not generally the consequence of single dominating set of reaction steps, but rather of sequences of states laying on periodic orbit, where several sets of reactions subsequently dominate over others.

### 3. Summary

The stoichiometry of the Bray-Liebafsky reaction corresponds to the hydrogen peroxide decomposition to water and oxygen in an acidic environment, in the presence of iodate ions as a catalyst. During this

reaction an oscillatory change of the intermediate species concentration, along with a cascade change in the hydrogen peroxide concentration and oxygen removal can be obtained. By selecting the experimental conditions, the simple periodic or complex chaotic concentration changes can be generated. Concentration oscillations are a consequence of alternating dominance of different reaction pathways present in the reaction mechanism. The spontaneous selforganized alteration of dominating reaction pathways was used in this paper to explain occurrence of simple and complex oscillations in this system. Fundamental importance of processes on multiple time scales was identified and demonstrated.

**Keywords:** Linear and nonlinear reaction system, feedback, autocatalysis, autocatalator, Bray-Liebhafsky oscillatory reaction

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