



## Bifurcation phase diagrams for Field, Koros and Noyes model of the Belousov-Zhabotinsky reaction in CSTR

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### ABSTRACT

The present study is an effort to simulate the Belousov-zhabotinskii system containing mixed organic substrate system in a CSTR. The model used is a simplified version of Field and Boyd mechanism. This model was considered under CSTR conditions and the evolution of the mixed organic substrate under the constraints of various input concentrations has also been investigated. The results have been indicated as bifurcation phase diagrams. © 2012 Trade Science Inc. - INDIA

### KEYWORDS

BZ reaction;  
Periodic oscillations;  
Simulations;  
Bifurcation diagrams.

### INTRODUCTION

The Belousov-Zhabotinskii<sup>[1,2]</sup> (BZ) reaction is the earliest well-understood example of a chemical system that results in oscillations. It was discovered in 1951 by the Soviet biophysicist Boris Belousov. At the time, chemists were skeptical of the possibility of chemical oscillators because of a misconception about the second law of thermodynamics. As a result, Belousov was unable to get his work published. A decade later, another Soviet scientist named Anatol Zhabotinskii reproduced Belousov's experiment and successfully persuaded more chemists to accept the idea of chemical oscillators. In 1972, three researchers at the University of Oregon, Field, Koros, and Noyes, published a complete mechanism describing the BZ reaction, known as the FKN<sup>[3]</sup> mechanism. However, their equations were too complex for numerical analysis by the computers of the time.

### THEORY

As stated before, early skeptics of the BZ reaction held that chemical oscillators would violate the 2nd law of thermodynamics. They believed the second law meant that all chemical concentrations in a reaction must move directly towards equilibrium. Many compared the BZ reaction to a damped pendulum, which passes through its equilibrium position during each oscillation and eventually comes to rest. A chemical system that did this would indeed violate the second law of thermodynamics. Passing through the equilibrium point and then moving away from it would require an increase in Gibbs free energy, which must always decrease. However, the BZ reaction (like all other chemical oscillators) does not reach its equilibrium point until after the oscillations are finished—oscillatory behavior is a process involving only intermediates. The BZ reaction is actually a system of several chemical reactions with dozens of elementary steps, but the overall process is the oxidation

of malonic acid by bromate producing carbon dioxide. As the system slowly progresses towards equilibrium, the concentrations of several intermediate species oscillate while the concentrations of products move monotonically towards equilibrium.

The following is a quick summary of the development of oscillatory behavior: Normally bromide reduces the bromate. This reaction is fast, quickly using up the available bromide. Once bromide drops below a critical level, bromous acid takes over the reduction of bromate in a reaction that autocatalytically produces more bromous acid. This leads to exponential growth in  $[\text{HBrO}_2]$ . This is eventually checked by a reaction that converts  $\text{HBrO}_2$  to  $\text{HOBr}$  and bromate. Meanwhile, the decomposition of Malonic acid results in the reduction of bromine to bromide, nearly restoring the initial concentration and allowing the whole process to begin again. Much of our understanding of the BZ reaction stems from the FKN mechanism.

TABLE 1 describes the FKN mechanism consisting of 15 variables and 17 reaction steps of which 6 and 16 are reversible. The relevant rate constants are given in TABLE 2.

### Simulation methodology

There are several reports in the literature simulating the behavior of the experimentally observed oscillating chemical system in batch as well as in a CSTR either with catalyzed or an uncatalyzed systems<sup>[4,5,6]</sup>. Presently various numerical integrators (software) are available to solve such a system. "Simulate" is one such software available with us<sup>[7]</sup>, which incorporates the powerful Rosenbrock's integrator for Stiff differential system of equations<sup>[8]</sup>. The simulate sets up its own differential equations and the result is provided as integrated values, when appropriate mechanism, initial and inflow concentrations of various species and the flow rate are provided. It performs the calculation of the temporal behavior of the system. The results can be presented as numerical values of logarithmic concentration versus time in a specified file and it is possible to ask for a printed figure of the logarithmic concentration vs time curve. These plots can be also obtained by the software called 'Origin 6.0' also. For all simulation studies reported here the error tolerance of integrator is  $10^{-7}$ , the initial step-size is  $10^{-8}$  and maximum step size is 2.0.

TABLE 1

(1)	$\text{BrO}_3^- + \text{Br}^- + 2\text{H}^+ \rightarrow$	$\text{HBrO}_2 + \text{HOBr}$
(2)	$\text{HBrO}_2 + \text{Br}^- + \text{H}^+ \rightarrow$	$2 \text{HOBr}$
(3)	$\text{BrO}_3^- + \text{HBrO}_2 + \text{H}^+ \rightarrow$	$2 \text{BrO}_2^* + \text{H}_2\text{O}$
(4)	$\text{Ce}^{+3} + \text{BrO}_2^* + \text{H}^+ \rightarrow$	$\text{Ce}^{+4} + \text{HBrO}_2$
(5)	$2 \text{HBrO}_2 \rightarrow$	$\text{BrO}_3^- + \text{H}^+ + \text{HOBr}$
(6)	$\text{HOBr} + \text{Br}^- + \text{H}^+ \rightleftharpoons$	$\text{Br}_2 + \text{H}_2\text{O}$
(7)	$\text{Ce}^{+4} + \text{MA} \rightarrow$	$\text{Ce}^{+3} + \text{HCO}_2^*$
(8)	$\text{Ce}^{+4} + \text{HCO}_2^* \rightarrow$	$\text{Ce}^{+3} + \text{OP}$
(9)	$\text{BrO}_3^- + \text{MA} + \text{H}^+ \rightarrow$	$\text{HBrO}_2 + 2 \text{CO}_2 + \text{H}_2\text{O}$
(10)	$\text{HBrO}_2 + \text{MA} \rightarrow$	$2 \text{CO}_2 + \text{HOBr} + \text{H}_2\text{O}$
(11)	$\text{BrO}_3^- + \text{H}^+ + \text{HC O}_2 \rightarrow$	$2\text{BrO}_2^* + \text{CO}_2 + \text{H}_2\text{O}$
(12)	$\text{HOBr} + \text{MA} \rightarrow$	$\text{Br}^* + \text{HCO}_2 + \text{CO}_2 + \text{H}_2\text{O}$
(13)	$\text{Br}^* + \text{Br}^* \rightarrow$	$\text{Br}_2$
(14)	$\text{HC O}_2 + \text{HOBr} \rightarrow$	$\text{Br}^* + \text{CO}_2 + \text{H}_2\text{O}$
(15)	$\text{Br}^* + \text{MA} \rightarrow$	$\text{Br}^- + \text{HC O}_2 + \text{H}^+$
(16)	$\text{Acetone} + \text{H}^+ \rightleftharpoons$	$\text{Enol} + \text{H}^+$
(17)	$\text{Br}_2 + \text{Enol} + \text{H}^+ \rightarrow$	$\text{Br}^- + \text{OP}$

TABLE 2 : Rate constants used

$k_1 = 1.6 \text{ M}^{-3} \text{ S}^{-1}$	$k_2 = 2.0 \times 10^7 \text{ M}^{-2} \text{ S}^{-1}$
$k_3 = 3.0 \times 10^{-3} \text{ M}^{-2} \text{ S}^{-1}$	$k_4 = 8.5 \times 10^4 \text{ M}^{-2} \text{ S}^{-1}$
$k_5 = 3.0 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$	$k_6 = 8.0 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$
$k_7 = 27.5 \text{ M}^{-1} \text{ S}^{-1}$	$k_8 = 1.0 \times 10^6 \text{ M}^{-1} \text{ S}^{-1}$
$k_9 = 220 \times 10^{-4} \text{ M}^{-2} \text{ S}^{-1}$	$k_{10} = 1.0 \text{ M}^{-1} \text{ S}^{-1}$
$k_{11} = 2.70 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$	$k_{12} = 75.0 \text{ M}^{-1} \text{ S}^{-1}$
$k_{13} = 1.0 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$	$k_{14} = 3.0 \times 10^9 \text{ M}^{-1} \text{ S}^{-1}$
$k_{15} = 2.0 \times 10^3 \text{ M}^{-1} \text{ S}^{-1}$	$k_{16} = 8.3 \times 10^{-5} \text{ M}^{-1} \text{ S}^{-1}$
$k_{17} = 1.03 \times 10^7 \text{ M}^{-2} \text{ S}^{-1}$	

### Bifurcation phase diagrams

For bifurcation studies, simulations were performed by taking the initial concentrations of all the chemical species as  $1 \times 10^{-10} \text{ M}$  as reported earlier. A bifurcation phase diagram is useful in describing the dynamical behavior of chemical systems. Two parameter phase plots were constructed by increasing and decreasing one of the parameters under considerations. The results are presented as two parameter diagrams, namely  $[\text{BrO}_3^-]_0 - [\text{Oxalic acid}]_0$  and  $[\text{BrO}_3^-]_0 - [\text{acetone}]_0$ . Here the behavior of the system is observed with fixed inflow concentrations corresponding to the points on the parameter space without in way varying them during the flow mode. In contrast to a true bifurcation analysis, one starts with a flow mode corresponding to the initial point and then variety any of the parameters in increas-

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ing and decreasing order in either way of the two parameter space. Thus in these studies behavior of the system is observed with fixed inflow concentrations for about 20,000 seconds and the date obtained in indicated in the diagram as oscillatory, non-oscillatory etc.

Figure 1 represents these results in  $[\text{BrO}_3^-]_0$  -  $[\text{oxalic acid}]_0$  plane. During these studies the values of other fixed constraints are  $[\text{H}^+]_0 = 2.0\text{M}$ ,  $[\text{Ce(IV)}]_0 = 0.004\text{M}$ ,  $[\text{acetone}]_0 = 0.8\text{M}$  and the flow rate ( $k_0$ ) =  $13 \times 10^{-4}/\text{s}$ . Both  $[\text{BrO}_3^-]_0$  &  $[\text{oxalic acid}]_0$  were varied from an initial value of  $0.001\text{M}$  to  $0.2\text{M}$  and back again. No oscillations were observed at both low and high  $[\text{oxalic acid}]_0$  as well as at both low and high  $[\text{BrO}_3^-]_0$ . Region A is characterized by oscillations & steady state. This region is bounded by  $[\text{oxalic acid}]_0$  between  $\approx 0.005$ - $0.04\text{M}$  and  $[\text{BrO}_3^-]_0$  between  $\approx 0.025$  -  $0.2\text{M}$ . Region B is characterized by oscillations after which the system behaves monotonic. This region is bounded by  $[\text{oxalic acid}]_0$  between  $\approx 0.04$  -  $0.19\text{M}$  and  $[\text{BrO}_3^-]_0$  between  $\approx 0.025$  -  $0.1\text{M}$ .

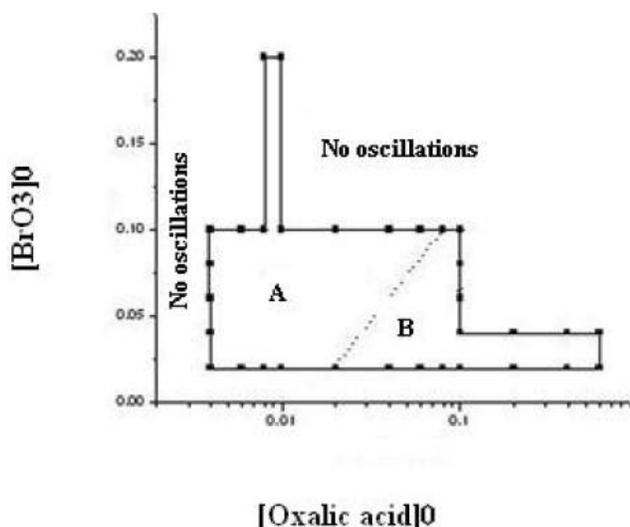


Figure 1 : Bifurcation phase diagram of  $[\text{BrO}_3]_0$ - $[\text{Oxalic acid}]_0$

Figure 2 represents the results in  $[\text{BrO}_3^-]_0$  -  $[\text{acetone}]_0$  plane. During these studies the values of other fixed constraints are  $[\text{H}^+]_0 = 2.0\text{M}$ ,  $[\text{Ce(IV)}]_0 = 0.004\text{M}$ ,  $[\text{oxalic acid}]_0 = 0.04\text{M}$  and flow rate ( $k_0$ ) is taken as  $13 \times 10^{-4}/\text{s}$ . The concentration of bromate is varied in the range of  $0.001\text{M}$  to  $0.06\text{M}$  and the concentration of acetone is varied in the range of  $0.001\text{M}$  to  $0.1\text{M}$ . No oscillations were observed at low and high  $[\text{acetone}]_0$  as well as at both low and high  $[\text{BrO}_3^-]_0$ .

Region A & B are characterized by transient oscillations after which the system behaves monotonic. Region A is bounded by  $[\text{Acetone}]_0$  between  $\approx 0.006$  -  $0.04\text{M}$  and  $[\text{BrO}_3^-]_0$  between  $\approx 0.002$ - $0.005\text{M}$ . Region B is bounded by  $[\text{Acetone}]_0$  between  $\approx 0.04$  -  $0.1\text{M}$  and  $[\text{BrO}_3^-]_0$  between  $\approx 0.002$ - $0.06\text{M}$ . Region C is also characterized by oscillations and steady state. This region is bounded by  $[\text{Acetone}]_0$  between  $\approx 0.006$ - $0.08\text{M}$  and  $[\text{BrO}_3^-]_0$  between  $\approx 0.002$ - $0.04\text{M}$ .

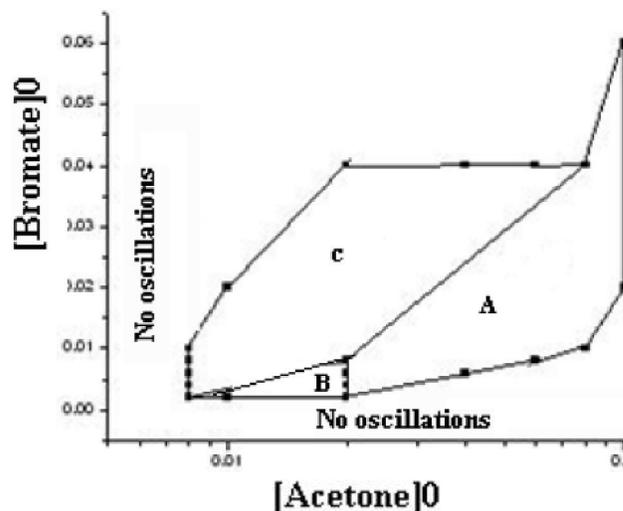


Figure 2 : Bifurcation phase diagram of  $[\text{BrO}_3]_0$ - $[\text{Acetone acid}]_0$

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