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Accuracy Level of the 7-Stage Belousov-Zhabotinskii's Reaction Model

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ABSTRACT

The 7-stage model of the Belousov-Zhabotinskii reaction proposed by R. J. Field, R.M. Noyes, E. Koros including organic reactants is considered in this paper. The mathematical model shows complex oscillating kinetics and close to the real reaction.

Keywords: *oscillating reaction, BZ-reaction, oscillation, the Oregonator model, mathematical modeling*.

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INTRODUCTION

Belousov-Zhabotinskii reaction is well known for its long sequences and forms of fluctuations. The Reaction demonstrates stable oscillations in a closed system, bistability, double oscillations, and complex periodic modes [1]. In 1959, B.P. Belousov discovered sustained repetitive oscillations of the ions of cerium (IV) and cerium (III) concentration in sulfuric acid during the oxidation reaction of citric acid by bromate catalyzed with ions of cerium (III). In 1954, similar oscillations were received by A.M. Zhabotinskii in the same system, but with malonic acid as the reducing agent. Subsequently Zhabotinskii showed that oscillating reaction can be carried out if citric acid is substituted with malonic acid or any other acid with an active methylene group, and the redox couple Ce (IV) / Ce (III) is substituted with a pair Mn (II) / Mn (III) or ferroin / ferrini [2].

EXPERIMENTAL

In 1972, American scientists Field, Noyes, and Koros developed the first mechanism of Belousov-Zhabotinskii's reaction to explain the nature of oscillations. This mechanism is called "Oregonator" [3].
One of the mechanisms of the reactions proposed by Field, Koros, Noyes, comprising also an organic step is [4]:

$$Br^- + HOBr + H^+ \rightarrow Br_2 + H_2O$$
$$Br^- + HBrO_2 + H^+ \rightarrow 2HOBr$$
$$BrO_3^- + Br^- + 2H^+ \rightarrow HBrO_2 + HOBr$$
$$2HBrO_2 \rightarrow BrO_3^- + HOBr + H^+$$
$$BrO_3^- + HBrO_2 + H^+ \rightarrow 2BrO_2 + H_2O$$
$$BrO_2 + Ce(III) + H^+ \rightarrow HBrO_2 + Ce(IV)$$
$$2Ce(IV) + CH_2(COOH)_2 + BrCH(COOH)_2 \rightarrow fBr^- + product$$

The system of differential equations corresponding to the above mechanism is:

$$R1 = k_7[CH_2(COOH)_2][Ce(IV)]$$
$$R2 = k_2[HBrO_2][Br^-][H^+]$$
$$R3 = k_3[BrO_3][Br^-][H^+]$$
$$R4 = k_1[Br^-][HOBr][H^+]$$
$$R5 = k_4[HBrO_2][HBrO_2]$$
$$R6 = k_5[BrO_3][HBrO_2][H^+]$$
$$R7 = k_6[BrO_2][Ce(III)][H^+]$$

$$\frac{d[Br^-]}{dt} = 0.5\,fR1 - R2 - R3 - R4$$
$$\frac{d[HOBr]}{dt} = R5 + R3 + 2R2 - R4$$
$$\frac{d[H^+]}{dt} = R6 - R2 + R5 - 2R3 - R7 - R4$$
$$\frac{d[HBrO_2]}{dt} = -R6 - R2 - R5 + R3 + R7$$
$$\frac{d[BrO_3]}{dt} = -R6 + R5 - R3$$
$$\frac{d[Ce(III)]}{dt} = R1 - R7$$
$$\frac{d[Ce(IV)]}{dt} = -R1 + R7$$
$$\frac{d[CH_2(COOH)_2]}{dt} = -R1$$
$$\frac{d[BrO_2]}{dt} = 2R6 - R7$$

Kinetic constants k_i $(i = 1..7)$ accept the following values [5]:

$$k_1 = 8 \cdot 10^9 (mole^{-2}s^{-1}),$$
$$k_2 = 10^6 (mole^{-2}s^{-1}),$$
$$k_3 = 2(mole^{-3}s^{-1}),$$
$$k_4 = 2 \cdot 10^3 (mole^{-3}s^{-1}),$$
$$k_5 = 10(mole^{-2}s^{-1}),$$
$$k_6 = 6 \cdot 10^5 (mole^{-2}s^{-1}),$$
$$k_7 = 1(mole^{-1}s^{-1}).$$

RESULTS AND DISCUSSION

The results of the integration of the system with the initial conditions (mole):

$[Br^-]_0 = 6.25 \cdot 10^{-4}$, $[HOBr]_0 = 1 \cdot 10^{-6}$,
$[H^+]_0 = 2$, $[HBrO_2]_0 = 1 \cdot 10^{-6}$,
$[BrO_3^-]_0 = 6.25 \cdot 10^{-2}$, $[Ce(III)]_0 = 10^{-6}$,
$[Ce(IV)]_0 = 2 \cdot 10^{-3}$,
$[CH_2(COOH)_2]_0 = 0.275$,
$[BrO_2]_0 = 1 \cdot 10^{-6}$, $F = 2$ is shown on figures (1) – (9).

The integration step is $h = 10^{-3}$. Due to the large spread of values of the rate constants, the system of differential equations has a high coefficient of stiffness. So the integration is carried out by L-stable Rosenbrock's method with complex coefficients. Because of this, integration will not be effective with a small step with explicit and A-stable methods.

Figures show that there are oscillations of concentrations of reagents, and the system monotonically tends to equilibrium over time. The oscillations of concentrations of reagents Br^-, $HBrO_2$ are characterized by damped oscillations over time with gradual increasing of the oscillation period and decreasing of the amplitude. Concentrations of H^+, malonate, BrO_3^- monotonically tends to their stationary state.

Valence of the catalyst $Ce(III)$ is periodically varies from 3 to 4, and vice versa. These changes are well seen in Fig. (6) – (7), the frequency and periods are similar, and oscillations are opposite.

Period was numerical investigated and equals 63 sec and slowly increase. Stationary state occurs after about 3 hours after the start of the reaction, and the oscillations stop.

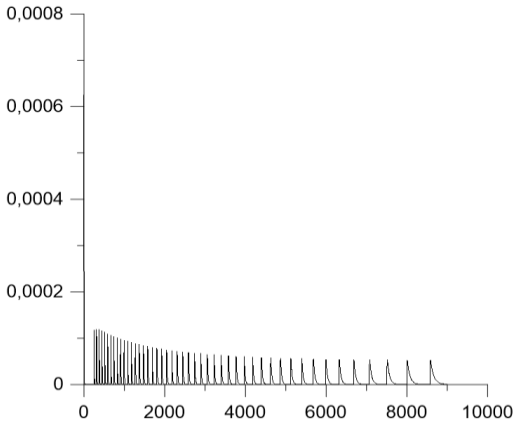

Fig. 1. Oscillations of values of Br^- concentration over time.

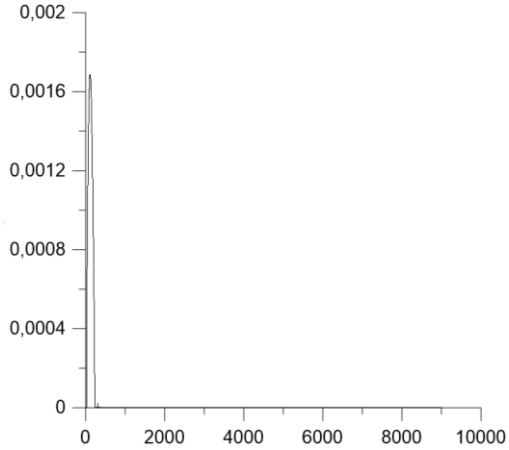

Fig. 2. Oscillations of values of BrO_2 concentration over time.

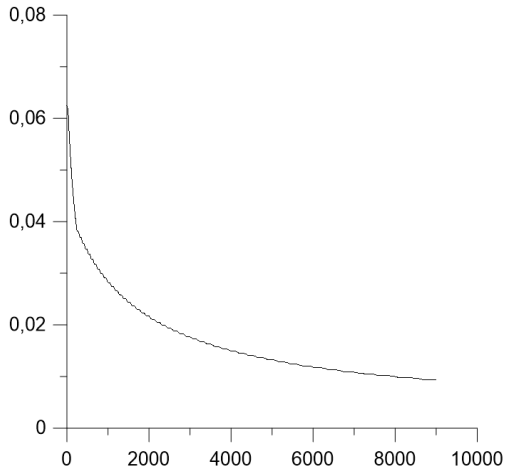

Fig. 3. Oscillations of values of BrO_3^- concentration over time.

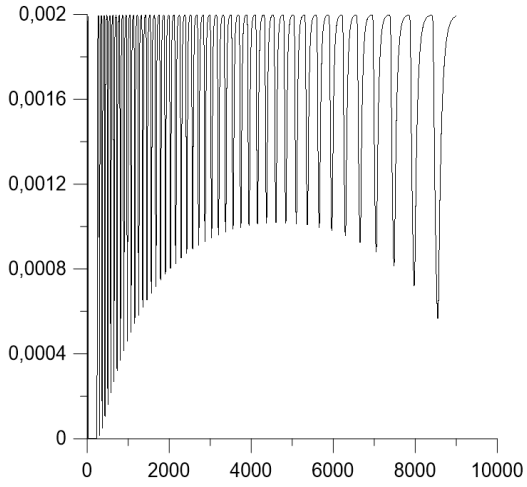

Fig. 4. Oscillations of values of $Ce(III)$ concentration over time.

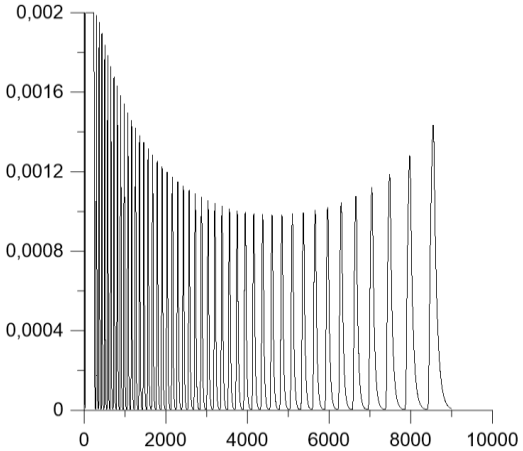

Fig. 5. Oscillations of values of $Ce(IV)$ concentration over time.

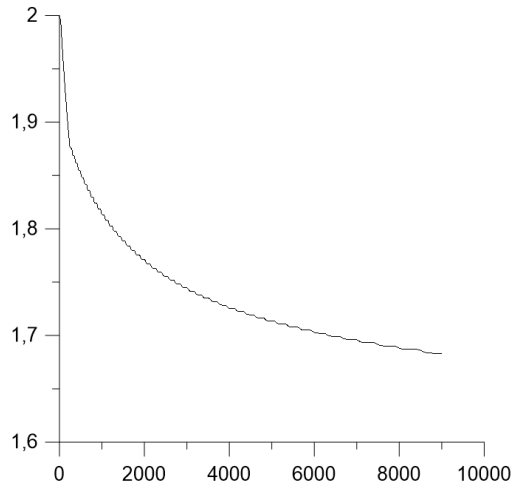

Fig. 6. Oscillations of values of H^+ concentration over time.

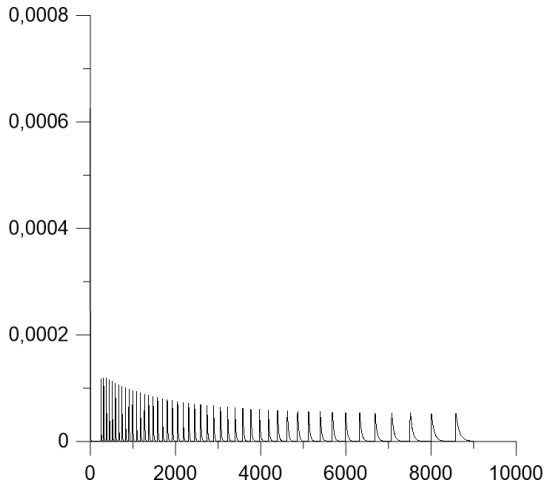

Fig. 7. Oscillations of values of $HBrO_2$ concentration over time.

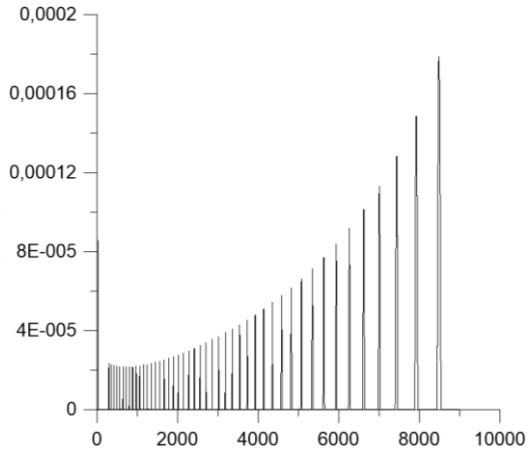

Fig. 8. Oscillations of values of $HOBr$ concentration over time.

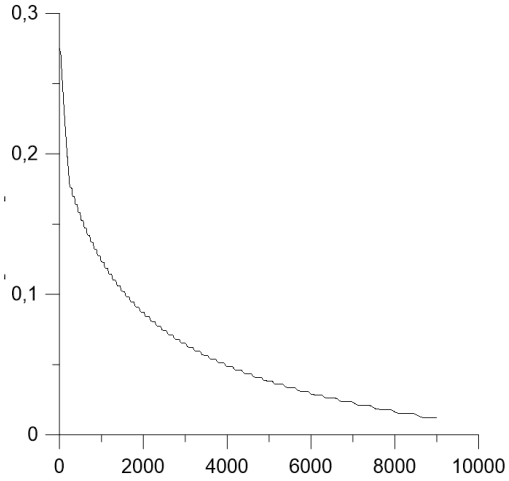

Fig. 9. Oscillations of values of $CH_2(COOH)_2$ concentration over time.

CONCLUSION

In this paper, we considered a model of the Belousov-Zhabotinskii reaction, which showed a similar behavior with reaction. The model shows decrease of the concentration of the initial reactants and accumulation of reaction products and intermediates oscillations. Also the model adequately describes the transition to the steady state with the consumption of the starting reagents.

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