Int. J. Chem. Sci.: 14(3), 2016, 1613-1620
ISSN 0972-768X
www.sadgurupublications.com

NUMERICAL INVESTIGATION OF THE 7-STAGE BELOUSOV-ZHABOTINSKII'S REACTION MODEL

SVETLANA MUSTAFINA[a], RUSTAM IKRAMOV[a] and OLEG LARIN[b]

[a]Bashkir State University, Deparment of Physics and Mathematics, Russian Federation, Republic of Bashkortostan, Sterlitamak City, Lenin Avenue, 37; Postal Index – 453103
[b]South-West State University, Electric Power Deparment, Russian Federation, Kursk, St. October 94; Postal Index – 305040

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.

Key words: Oscillating reaction, BZ-reaction, Oscillation, Oregonator model, Mathematical modeling.

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 has shown that oscillating reaction can be carried out if citric acid is substituted for malonic acid or any other acid with an active methylene group, the redox couple Ce(IV)/Ce(III) is substituted for a pair Mn(II)/Mn(III) or ferroin/ferrini[2].

---

[*]Author for correspondence; E-mail: Mustafina_SA@mail.ru, rustam_ikramov@mail.ru, promif@mail.ru; Ph.: + 7917-4044558, + 7906-3708808, + 7917-35419 54

EXPERIMENTAL

In 1972, american scientists R. Field, R. Noyes, E. 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]:

$$Br^- + HOBr + H^+ \longrightarrow Br_2 + H_2O$$

$$Br^- + HBrO_2 + H^+ \longrightarrow 2\ HOBr$$

$$BrO_3^- + Br^- + 2\ H^+ \longrightarrow HBrO_2 + HOBr$$

$$2\ HBrO_2 \longrightarrow BrO_3^- + HOBr + H^+$$

$$BrO_3^- + HBrO_2 + H^+ \longrightarrow 2\ BrO_2 + H_2O$$

$$BrO_2 + Ce(III) + H+ \longrightarrow HBrO_2 + Ce(IV)$$

$$2\ Ce(IV) + CH_2\ (COOH)_2 + BrCH\ (COOH)_2 \longrightarrow fBr^- + Products$$

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

$$\frac{d[Br^-]}{dt} = 0.5\ fR1 - R2 - R3 - R4$$

$$\frac{d[HOBr]}{dt} = R5 + R3 - 2\ R2 - R4$$

$$\frac{d[H^+]}{dt} = R6 - R2 + R5 - 2\ R3 - R7 - R4$$

$$\frac{d[HBrO_2]}{dt} = -\ R6 + R2 - R5 + R3 + R7$$

$$\frac{d[BrO_3]}{dt} = -\ R6 + R5 - R3$$

$$\frac{d[Ce(III)]}{dt} = -R1 - R7$$

$$\frac{d[Ce(IV)]}{dt} = -R1 + R7$$

$$\frac{d[CH_2(COOH)_2]}{dt} = -R1$$

$$\frac{d[BrO_2]}{dt} = 2R6 - R7$$

$R1 = k_7 [CH_2 (COOH)_2][Ce(IV)]$

$R2 = k_2 [HbrO_2][Br^-][H^+]$

$R3 = k_3 [BrO_3][Br^-][H^+]$

$R4 = k_1 [Br^-][HOBr][H^+]$

$R5 = k_4[HBrO_2][HBrO_2]$

$R6 = k_5 [BrO_3][HBrO_2][H^+]$

$R7 = k_6 [BrO_2][Ce(III)][H^+]$

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

$k_1 = 8.10^9$ ($mole^{-2}$ s^{-1})

$k_2 = 10^6$ ($mole^{-2}$ s^{-1})

$k_3 = 2$ ($mole^{-3}$ s^{-1})

$k_4 = 2.10^3$ ($mole^{-3}$ s^{-1})

$k_5 = 10^9$ ($mole^{-2}$ s^{-1})

$k_6 = 6.10^5$ ($mole^{-2}$ 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):

$[Br^{-}]_0 = 6.25.10^{-4}$, $[HOBr]_0 = 1.10^{-6}$, $[H^{+}]_0 = 2$, $[HBrO_2]_0 = 1.10^{-6}$, $[BrO_3^{-}]_0 = 6.25.10^{-2}$, $[Ce(III)]_0 = 10^{-6}$, $[Ce(IV)]_0 = 2.10^{-3}$, $[CH_2(COOH)_2]_0 = 0.275$, $[BrO_2]_0 = 1.10^{-6}$, $F = 2$ is shown on Fig. 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 (1) 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.[6,7]

Figures are shown that there are oscillations of concentrations of reagents, the system monotonically tends to equilibrium over time. The oscillations of concentrations of reagents Br^{-}, $HBrO_2$ 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-oscillations are opposite.

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

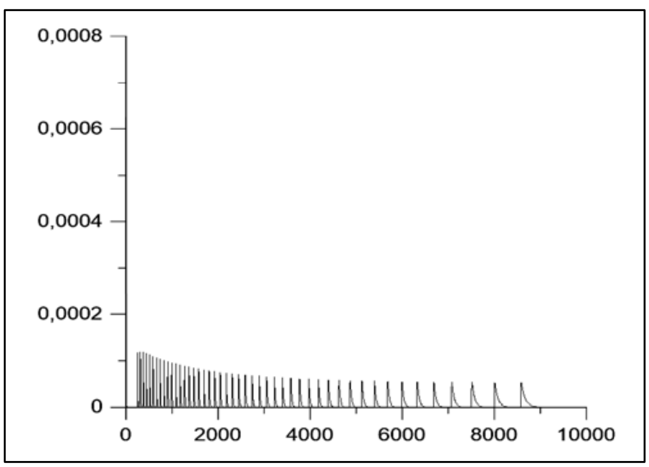

Fig. 1: Oscillations of values Br^{-} concentration over time

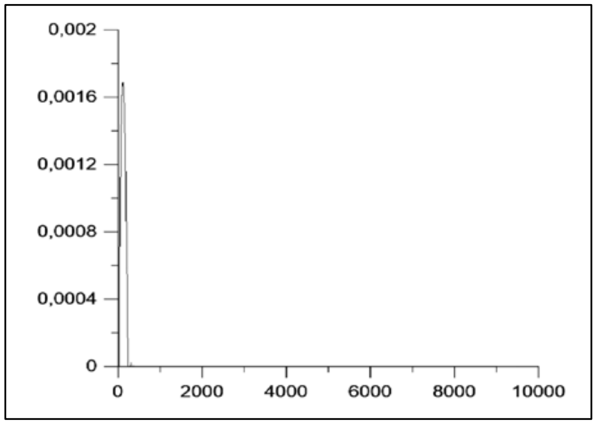

Fig. 2: Oscillations of values BrO_2 concentration over time

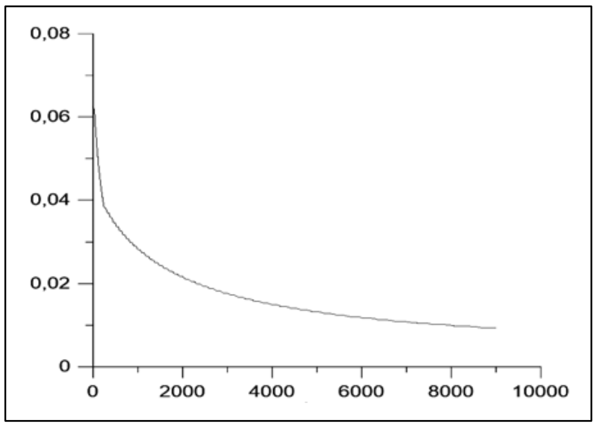

Fig. 3: Oscillations of values BrO_3^- concentration over time

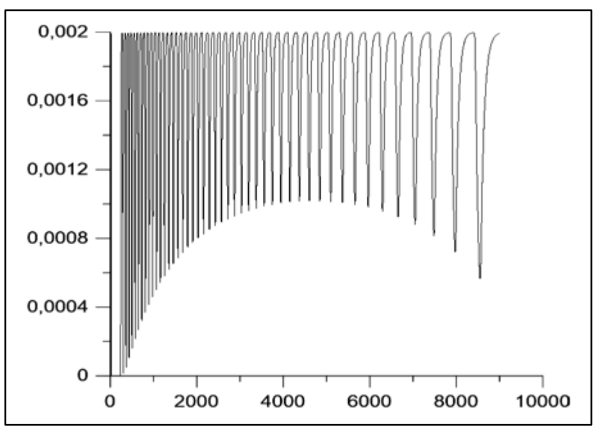

Fig. 4: Oscillations of values Ce(III) concentration over time

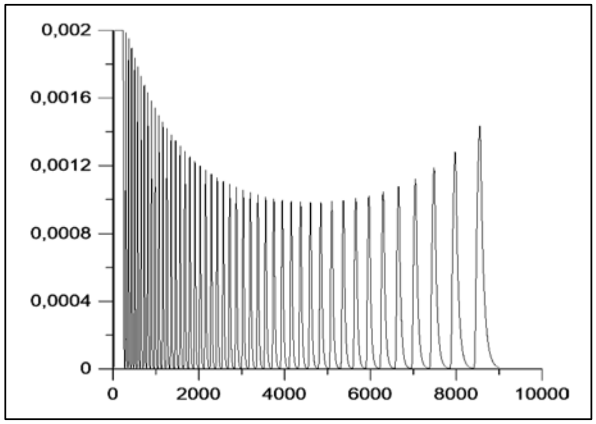

Fig. 5: Oscillations of values Ce(IV) concentration over time

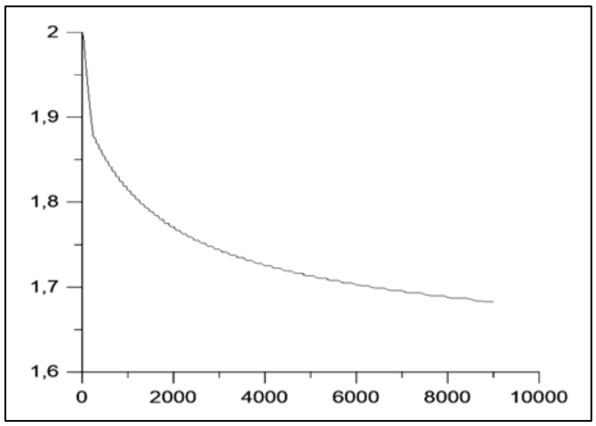

Fig. 6: Oscillations of values H^+ concentration over time

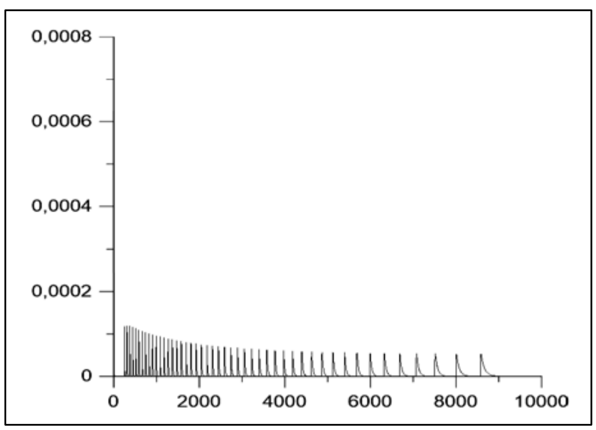

Fig. 7: Oscillations of values $HBrO_2$ concentration over time

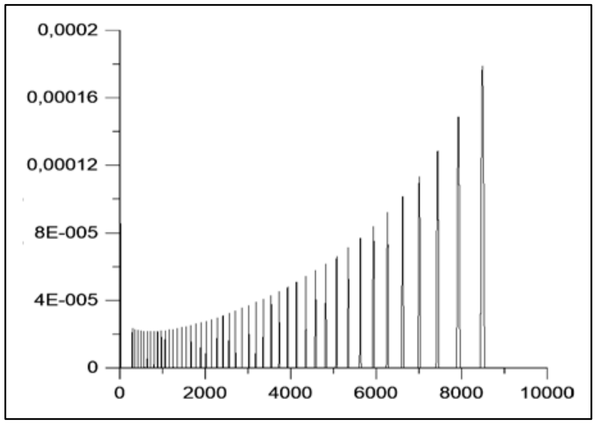

Fig. 8: Oscillations of values HOBr concentration over time

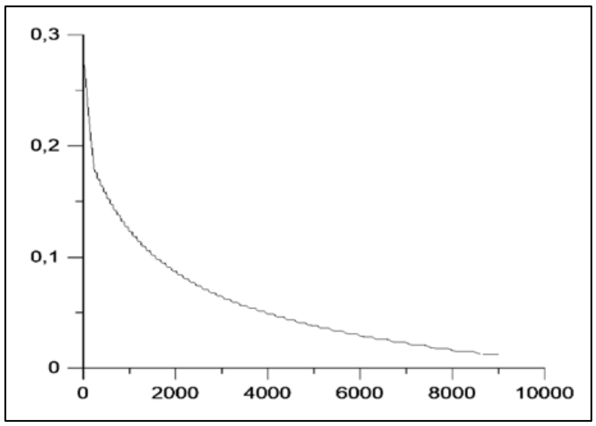

Fig. 9: Oscillations of values $CH_2(COOH)_2$ concentration over time

CONCLUSION

In this paper, we consider a model of the Belousov-Zhabotinskii reaction, which shows 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.

REFERENCES

1. R. D. Ikramov and S. A. Mustafina, Numerical Study of the Belousov-Jabotinsky's Reaction Models on the Basis of the Two-Phase Rozenbrock's Method with Complex Coefficients, Int. J. Appl. Engg. Res., **9(22)**, 12797-12801 (2014).

2. S. A. Mustafina, E. N. Miftakhov and T. A. Mikhailova, Solving the Direct Problem of Butadienestyrene Copolymerization, Int. J. Chem. Sci., **12(2)**, 564-572 (2014).
3. O. Garel and D. Garel, Oscillating Chemical Reactions, Moscow: Mir (World, in Rus) (1986) p. 148.
4. R. J. Field, E. Koros and R. M. Noyes, Oscillations in Chemical Systems II, Through Analysis of Temporal Oscillations in the Bromate-Cerium-Malonic Acid System, J. Am. Soc., **94**, 8649-8664 (1972).
5. S. A. Mustafina, A. V. Balaev, R. S. Davletshin, S. I. Spivak and U. M. Dzhemilev, Modeling of Gas-Liquid α-Pinene Hydrogenation in Tubular Reactors, Doklady Chemistry, T. **406(2)**, C. 26-29 (2006).
6. S. A. Mustafina, E. N. Miftakhov and T. A. Mikhailova, Mathematical Simulation Study of Copolymer Composition and Compositional Heterogeneity During the Synthesis of Emulsion-Type Butadiene-Styrene Rubber, Int. J. Chem. Sci., **12(4)**, 1135-1144 (2014).
7. R. D. Ikramov and S. A. Mustafina, Numerical Study of the Oregonator Models on the Basis of the Two-Phase Rozenbrock's Method with Complex Coefficients, Engg. J., **20(1)**, 155-163 (2016).

Revised : 11.04.2016 *Accepted : 14.04.2016*