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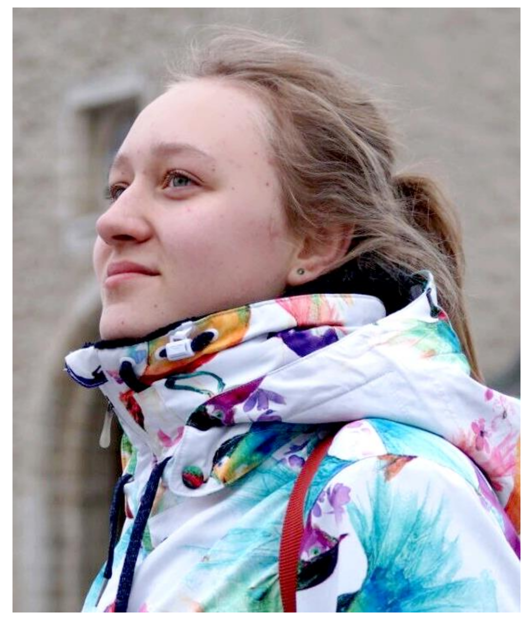
Успехи в науках о природе

Achievements in Natural Sciences /
Fortschritte in den Naturwissenschaften

Dolzhenko S.V.*,
Kadysheva A.M.**

S.V. Dolzhenko



A.M. Kadysheva

Study of the Influence of Sulfuric Acid Concentration Changes on the Course of Belousov–Zhabotinsky Reaction

Stepan V. Dolzhenko, Lyceum student in grade 10, Lyceum no. 1535 (Sechenov Lyceum), Moscow
ORCID ID https://orcid.org/0000-0002-8946-8018
E-mail: stepan-v-dolzhenko@j-spacetime.com; stepan5dol@gmail.com

Alexandra M. Kadysheva, Lyceum student in grade 10, Lyceum no. 1535 (Sechenov Lyceum), Moscow
ORCID ID https://orcid.org/0000-0002-8656-4338
E-mail: alexandra-m-kadysheva@j-spacetime.com; 1451sasha@gmail.com

Further research of the Belousov-Zhabotinsky reaction analogues gives impetus to developing such modern scientific directions as synergetics, theory of dynamic systems and deterministic chaos. We considered one of the numerous oscillatory reactions, in which the Ce3+ / Ce4+ ions and citric acid are used. The main goal of our research was to study the behavior of the autocatalytic oscillatory reaction system in dependence of the change in sulfuric acid concentration and the temperature of the reaction mixture. We confirmed that stability of the oscillatory system depends on the acidity of the reaction mixture. The increasing of sulfuric acid amount is the result of acceleration of Ce3+ ions oxidation, and as a consequence rate acceleration of the oscillatory reaction. The activation effect on the studied reaction is exerted by a temperature increasing, but observed effect can be partially replaced by a mechanical action. For living organisms, such sensitivity of the system to external changes means its inability to use one. However, this does not mean that Belousov-Zhabotinsky reaction analogues will behave accordingly. The data obtained can serve as a basis for comparing of the studied reaction and other types of oscillatory reactions.

Keywords: autocatalytic oscillatory reaction; Belousov-Zhabotinsky reaction; acidity of reaction medium; cerium ions catalyzed reactions; cellular clock.

It is known that the «cellular clocks» helps our cells to control the most important time-conjugated processes, e.g. meiosis and to coordinate different parts of metabolism. This process is qualitatively described in *[Winfree 1984]*. The name of this phenomenon comes from circadian rhythmicity as its main property. Scientists *[Purves 2004]* are interested in the unicellular organisms that live in circadian rhythms, e.g. Gonyaulax polyedra, which saves its rhythmic lifestyle without any changes even after replacing it's culture under the constant light. Such studies help us to find out that undergoing processes are controlled mostly by intercellular 'clock' that is likely to be non-equilibrium thermodynamic (autocatalytic oscillatory) reaction. The most common reaction of such a type is the Belousov-Zhabotinsky reaction. The Belousov-Zhabotinsky reaction is a class of chemical reactions occurring in an oscillatory mode, in which certain reaction parameters (color, concentration of components, temperature, etc.) change periodically, forming a complex spatial-temporal structure of the reaction medium *[Zhabotinsky 1964; Motoike, Adamatzky 2005; Sirimungkala et al. 1999]*.

The 'cellular clock' is a phenomenon, which gives a great field for researching in modern science. Although basic discoveries have already been done, it is necessary to conduct more researches in such area of science to make a «great leap forward» in this direction. Despite the fact that great attention was paid to oscillating reactions, the statistical basis for them is extremely small and needs to be enlarged in the nearest future.

Belousov-Zhabotinsky reaction has become one of the most famous chemical reactions in modern science, nowadays a lot of scientists do researches connected with it. Analogues of Belousov-Zhabotinsky reaction were found in different chemical systems, for example organic self-propagating high-temperature synthesis. Discovery of this reaction has given a push to developing such parts of science as synergetics, theories of dynamic systems and deterministic chaos.

In this article we consider only one of the numerous oscillatory reactions in which the Ce^{3+} / Ce^{4+} ions and citric acid are used. The aim of this research is to study the behavior of the autocatalytic oscillatory reaction system in dependence of the change in the sulfuric acid concentration and the temperature of the reaction mixture.

History of Belousov-Zhabotinsky reactions

The priority in the discovery of the reaction belongs to Boris Belousov *[Belousov 1959]*. He carried out investigations of Krebs cycle in attempt to find its non-organic analog. As a result, after one of the experiments held in 1951, B. Belousov found an interesting reaction: the oxidation of citric acid with potassium bromate in an acidic medium in the presence of a Ce^{+3} ion as catalyst, he was discovered self-oscillations *[Belousov 1959]*. Further development of the research of this reaction occurred, when Professor Simon Shnol offered his researcher, future Lenin Award laureate Anatoly Zhabotinsky, to investigate the reaction mechanism. The Zhabotinsky's group carried out detailed studies of the reaction, including its different variants, and also compiled the first mathematical model. The main results were outlined in Zhabotinsky's monograph *Concentration Oscillations [Zhabotinsky 1974]*.

Fig. 1. Boris P. Belousov (1893—1970), chemist and biophysicist, who discovered the Belousov-Zhabotinsky reaction in the early 1950s. Photo ca. 1956—1958

Fig. 2. Anatol M. Zhabotinsky (1938—2008), biophysicist, who created a theory of the chemical clock known as Belousov-Zhabotinsky reaction in the 1960s. Photo of 1983

Fig. 3. Simon E. Shnol (born 1930), biophysicist, historian of Soviet science. Photo of 1980

The discovery of the reaction actually gave impetus to the development of such sections of modern science as synergetics, the theory of dynamical systems and deterministic chaos. The solutions of this scientific work will give ground for many future studies in various fields of science, such as biology (organic analogues of the reaction used by many living organisms), physics (physical understanding of the interaction of molecules), and chemistry (further study of oscillatory systems) *[Goodwin 1979; From the history of the discovery … 2001]*.

The Simplest Scheme of the Reaction Mechanism

The first model of observed processes was proposed by A. Zhabotinsky. The cycle of reaction considered by him consists of two stages. The first stage (I) is the oxidation of trivalent cerium with bromate anion:

$$Ce^{3+}\ (BrO_3^-) \rightarrow Ce^{4+} \qquad \textbf{(I)}$$

The second stage (II) is the reduction of tetravalent cerium with malonic acid:

$$Ce^{4+} + CHBr(COOH)_2 \rightarrow Ce^{3+} + Br^- + \text{other products} \qquad \textbf{(II)}$$

The bromate reduction products formed in stage (I) are being edited to malonic acid. The resulting brominated derivatives of malonic acid are destroyed with the release of bromide-anion, which is a strong inhibitor of the reaction.

The scheme of the self-oscillatory reaction can be qualitatively described in the following way: let there be Ce^{4+} ions in the system, they catalyze the formation of Br^- (stage II). If the concentration of Br^- is sufficiently large, reaction (**I**) is completely blocked. When the concentration of Ce^{4+} ions decreases as a result of reaction (**II**) to the threshold value, the concentration of Br^- decreases, thereby unblocking the reaction (**I**). Thus, the rate of the reaction (**I**) increases and Ce^{4+}concentration increases too. When the upper threshold value Ce^{4+} is reached, the Br^- concentration also reaches high values, and this again leads to the blocking of the reaction (**I**). And so on (**Fig. 4**).

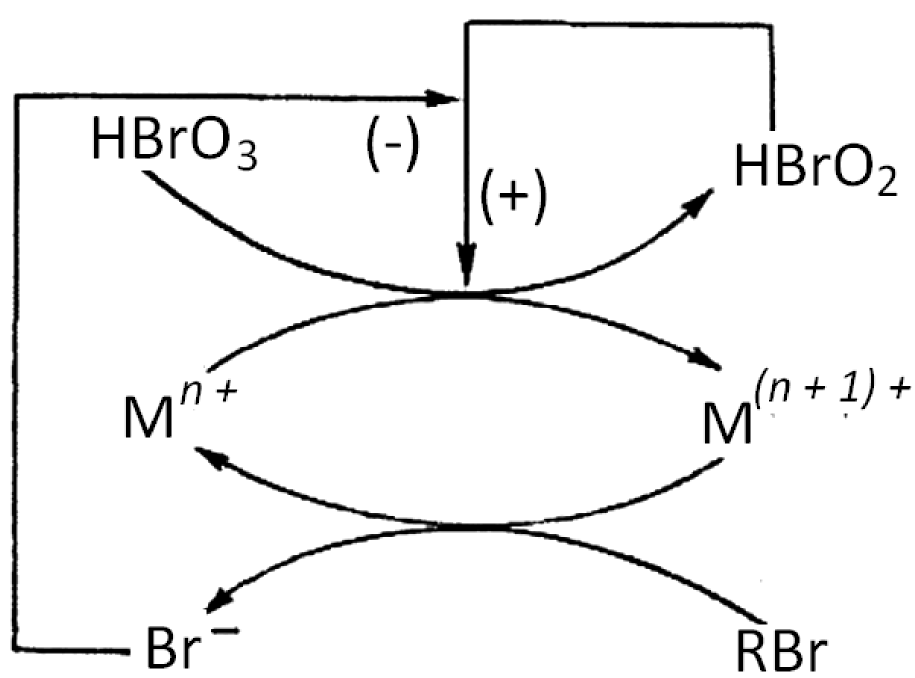


Fig 4. Simplest Scheme of autocatalytic oxidation reaction (RBr is bromo derivative of a reducing agent).

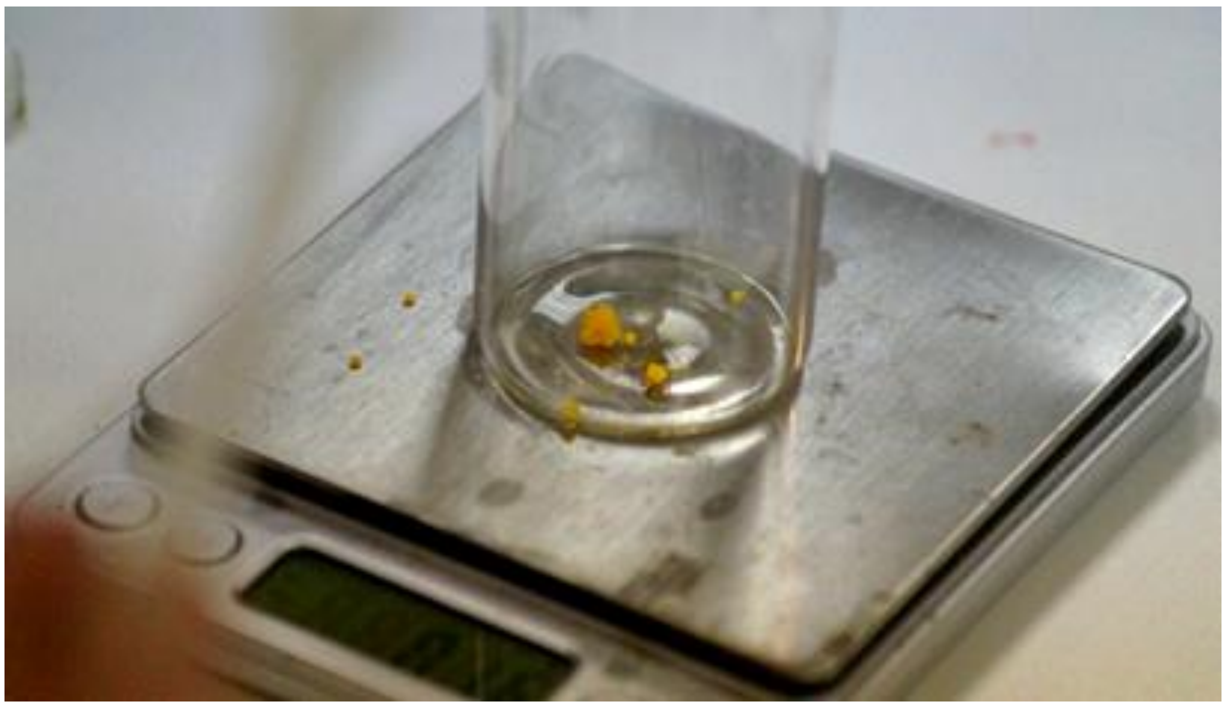
The overall equation is:

$$3CH_2(COOH)_2 + 4BrO_3^- \rightarrow 4Br^- + 9CO_2 + 6H_2O$$

Removal of the carbon dioxide from the system allows us to understand that this exchange reaction will not last forever, so alive cell must maintain the level of all parts of it to maintain such kinds of systems.

Experimental Findings

The original reaction made by B. Belousov was a departure point for us in this experiment. We found a primary recipe in *[Zhang et al. 1993]* and used it as a standard, changing only molar concentration value of sulfuric acid and temperature of a reaction mixture. As an organic reducing agent we used citric acid ($C_6H_8O_7$). Five experiments were carried out including the original one (**Figs. 5—7**).


A


B

Fig. 5. Sampling preparation: weighting of cerium (III) sulfate **(A)** and potassium bromate **(B)**.
Photo © S. Dolzhenko, A. Kadysheva

Original Reaction Recipe

2.00 g of $C_6H_8O_7$

0.16 g of $Ce_2(SO_4)_3$

0.20 g of $KBrO_3$

2.0 ml of H_2SO_4 (1:3 by volume)

Distilled water is up to 10.0 ml; heating on an alcohol burner.

Observations: the beginning of the reaction is about 30 s. The oscillation duration is more than 30 min. The period of one oscillation is equal to 2 s.

Recipe of Set no. 1

2.00 g of $C_6H_8O_7$

0.16 g of $Ce_2(SO_4)_3$

0.20 g of $KBrO_3$

10.0 ml of H_2SO_4 (1:3 by volume)

1. Without heating.

Observations: the beginning of the reaction is 15 min. Without mechanical influence the oscillations are practically invisible. The oscillation duration is less than 5 minutes. The period of one oscillation is equal to 30 seconds.

2. Heating on an alcohol burner.

Observations: the beginning of the reaction is 30 s. The oscillation duration is no more than 20 min. The period of one oscillation is equal to 1—1.5 s.

Recipe of Set no. 2

2.00 g of $C_6H_8O_7$

0.16 g of $Ce_2(SO_4)_3$

0.20 g of $KBrO_3$

1.0 ml of H_2SO_4 (1:3)

Distilled water is up to 10.0 ml.

1. Without heating.
Observations: the reaction does not proceed.

2. Heating on an alcohol burner.
Observations: the reaction does not proceed.

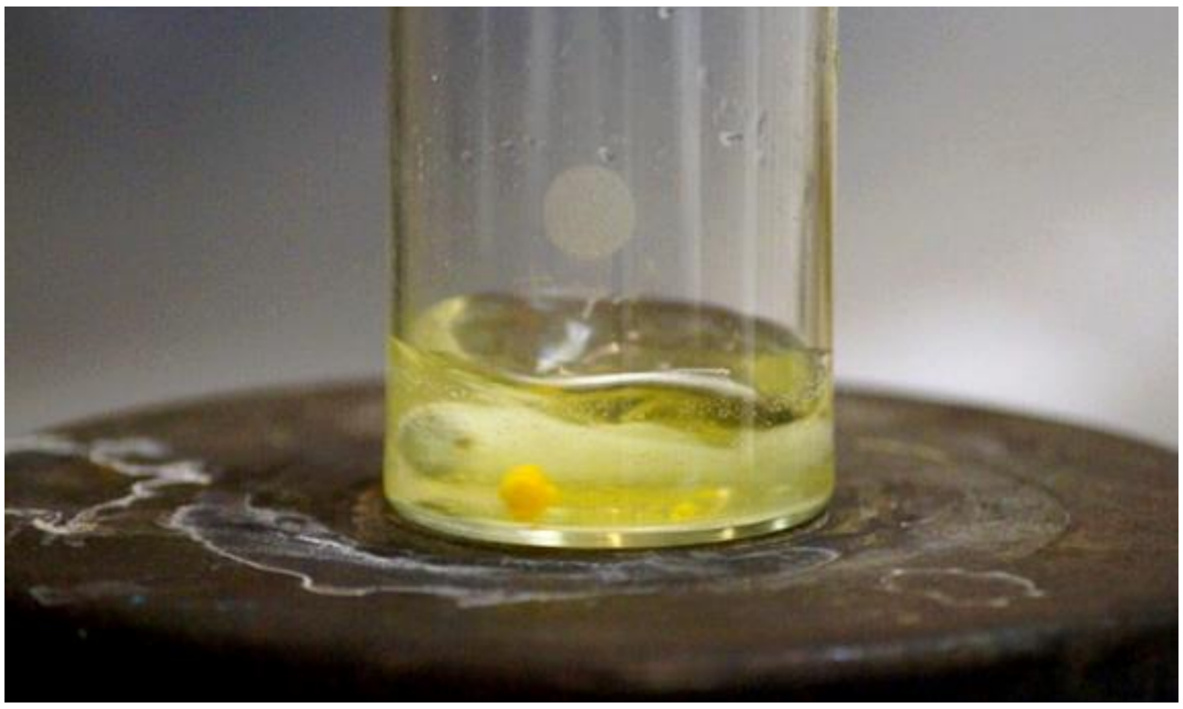


Fig. 6. Dissolution of reagents in sulfuric acid using of magnetic stirrer.
Photo © S. Dolzhenko, A. Kadysheva

Fig. 7. The course of the Belousov-Zhabotinsky reaction.
Photo © S. Dolzhenko, A. Kadysheva

The mechanism of the studied reaction can described using the following chemical reactions in the simplest manner:

(I) $Ce^{3+} + BrO_3^- + 6H^+ \rightarrow Ce^{4+} + Br^- + 3H_2O$
(**colorless → yellow**)

(II) $(HOOCCH_2)_2C(OH)COOH + 2Ce^{4+} \rightarrow (HOOCCH_2)_2C(O) + 2Ce^{3+} + CO_2 + 2H^+$
(**yellow → colorless**)

(III) $Br^- + BrO_3^- + 2H^+ \rightarrow HBrO + HBrO_2$

(IV) $Br^- + HBrO + H^+ \rightarrow Br_2 + H_2O$
(**colorless → yellow**)

(V) $3H^+ + 3Br^- + HBrO_2 \rightarrow 2Br_2 + 2H_2O$
(**colorless → yellow**)

(VI) $(HOOCCH_2)_2C(O) + 5Br_2 \rightarrow C(O)(CHBr_2)(CBr_3) + 5Br^- + 2CO_2 + 5H^+$
(**yellow → colorless**)

Conclusions

Stability of the oscillatory system depends on the acidity of the reaction mixture. The increasing of the sulfuric acid amount is the result of the acceleration of Ce^{3+} ions oxidation, and as a consequence the rate acceleration of the oscillatory reaction. However, simultaneously the amount of the oxidized insoluble bromo derivatives is increased too, which leads to an accelerated decrease in the bromate ions concentration value. Therefore, the oscillations of the system are rapidly decayed.

If the amount of sulfuric acid is reducing, the acidity of the medium is not enough to oxidize a sufficient amount of Ce^{3+} ions. This is the reason of the decreasing of the bromate ions concentration level, which are the main autocatalysts of the studied reaction. The activation effect on the studied reaction is exerted by a temperature increasing, but observed effect can be partially replaced by a mechanical action.

For living organisms such sensitivity of the system to external changes means its inability to use one. However, this does not mean that Belousov-Zhabotinsky reaction analogues will behave accordingly. The data obtained can serve as a basis for comparing of the reaction studied and other oscillatory reactions.

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ИЗУЧЕНИЕ ВЛИЯНИЯ ИЗМЕНЕНИЯ КОНЦЕНТРАЦИИ СЕРНОЙ КИСЛОТЫ НА ХОД РЕАКЦИИ БЕЛОУСОВА–ЖАБОТИНСКОГО

Долженко Степан Владимирович, ученик 10 класса лицея № 1535 им. И.М. Сеченова (Сеченовский Лицей), Москва
ORCID ID https://orcid.org/0000-0002-8946-8018
E-mail: stepan-v-dolzhenko@j-spacetime.com; stepan5dol@gmail.com

Кадышева Александра Михайловна, ученица 10 класса лицея № 1535 им. И.М. Сеченова (Сеченовский Лицей), Москва
ORCID ID https://orcid.org/0000-0002-8656-4338
E-mail: alexandra-m-kadysheva@j-spacetime.com; 1451sasha@gmail.com

Исследование аналогов реакций Белоусова-Жаботинского дает импульс развитию таких направлений современной науки, как синергетика, теория динамических систем и детерминированного хаоса. В данной работе нами изучена одна из многочисленных колебательных реакций, для проведения которой используют ионы Ce3+ / Ce4+ и лимонную кислоту. Основной целью исследования было изучение поведения автокаталитической колебательной реакционной системы в зависимости от изменения концентрации серной кислоты и температуры реакционной смеси. В ходе эксперимента мы подтвердили, что устойчивость колебательной системы зависит от кислотности реакционной смеси. Увеличение количества серной кислоты является результатом ускорения окисления ионов Ce3+ и, как следствие, ускорения скорости колебательной реакции. Активирующий эффект на изученную реакцию оказывает повышение температуры, однако наблюдаемый эффект может быть частично заменен механическим воздействием на реакционную систему. Для живых организмов такая чувствительность системы к внешним изменениям означает неспособность ее использования. Однако это не означает, что аналоги реакции Белоусова-Жаботинского будут вести себя соответствующим образом. Полученные данные могут служить основой для сравнения исследуемой реакции и других видов колебательных реакций.

Ключевые слова: автокаталитическая колебательная реакция; реакция Белоусова-Жаботинского; кислотность реакционной среды; церий–катализируемые реакции; клеточные часы.

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