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OSCILLATORY CHEMICAL REACTIONS

КОЛЕБАТЕЛЬНЫЕ ХИМИЧЕСКИЕ РЕАКЦИИ

In this paper we consider the special case of WRA, oscillatory chemical reactions. Oscillation reaction is a whole class of oxidation reactions of organic compounds with catalyst having redox properties. This process is cyclic, i.e. it consists of repetition. [1]

Oscillatory reactions were discovered and scientifically proved in 1951 by the Soviet scientist Boris Petrovich Belousov. B.P. Belousov studied the oxidation of citric acid in its reaction with sodium bromate in sulfuric acid solution. To enhance the response, he added in a salt solution of cerium. Cerium - metal with varying valence (3 + or 4 +), so it can be a catalyst for the oxidation-reduction reactions. B.P. Belousov noticed an interesting phenomenon: the color of the solution changed from time to time - it became yellow, then colorless. He added ferrous iron phenanthroline (ferroin) to a solution of the complex, so the color of the solution was periodically changed from purple-red to blue and back again. [2]

He discovered the reaction which has become famous. It was known all over the world and called "reaction of Belousov-Zhabotinsky". A.M. Zhabotinsky did much for understanding this amazing phenomenon. Since then a large number of similar reactions were discovered.

Let us consider the perspectives of possible applications of oscillatory chemical processes. A distinctive feature of such reactions is their high sensitivity to small external disturbances. The sensitivity of the chemical reaction to minor changes in the conditions of the experiment was noted in the Belousov-Zhabotinsky reaction. [1,2] Thus, it was shown that the transition between different modes can be implemented by changing the concentration of trace impurities contained in the mixture. Researches in this area can have great prospects for the development of

fundamentally new methods of analyzing trace substances.

Study of the mechanism of oscillating reactions.

The detailed mechanism of Belousov`s reaction is still not completely known. To explain the nature of the oscillations it`s only enough to imagine what way citric acid forms bromine citric acid and then reacts with KBrO3 to turn into KBr. Anion Br- inhibits further oxidation of bromine citric acid. Then the catalyzed form of permanganate ion is accumulated and oxidizes bromine citric acid. As a result the accumulation of Br- stops and oxidation of bromine citric acid continues.

First, bromate ion interacts with the bromide ion in the presence of H + with the formation of bromide and hypobromous acids:

$BrO_3^{--} + Br^{--} + 2H^+ = HBrO_2 + HOBr$ (A1)

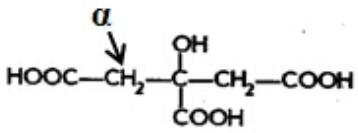
Next, bromide acid reacts with bromide ion, forming hypobromous acid:

$HBrO_2 + Br^{--} + H^+ = 2HOBr$ (A2)

Hypobromous acid, in turn, reacts with bromide ion to form free bromine:

$HOBr + Br^{--} + H^+ = Br_2 + H_2O$ (A3)

Because of the proximity of the carboxyl groups in citric acid have mobile α-protons. In this way it is easyly brominated by free bromine.



$Br_2 + (HOOCCH_2)_2C(OH)COOH = (HOOCCHBr)_2C(OH)COOH + Br^{--} + H^+$ (A4)

The first step in the reaction as a result of autocatalytic reaction produces hydrobromic acid (fast, like an explosion process).

The second step - permanganate interacts with the organic component and is slowly transformed into manganate and simultaneously bromide ion starts forming. This stage is characterized by change of color into brown.

The third step - bromide ion is an effective inhibitor of the autocatalytic reaction (Step 1). As a consequence, bromide acid stops its formation and quickly decomposes.

The fourth step - the decomposition of permanganate started on the 2nd phase is completed, the bromide ion is removed from the system. As a result, the system returns to a state in which it was in 1st phase and the color of the solution become pale yellow. This process is repeated periodically. [3]

Experimental part:

The reaction of citric acid with potassium bromate:

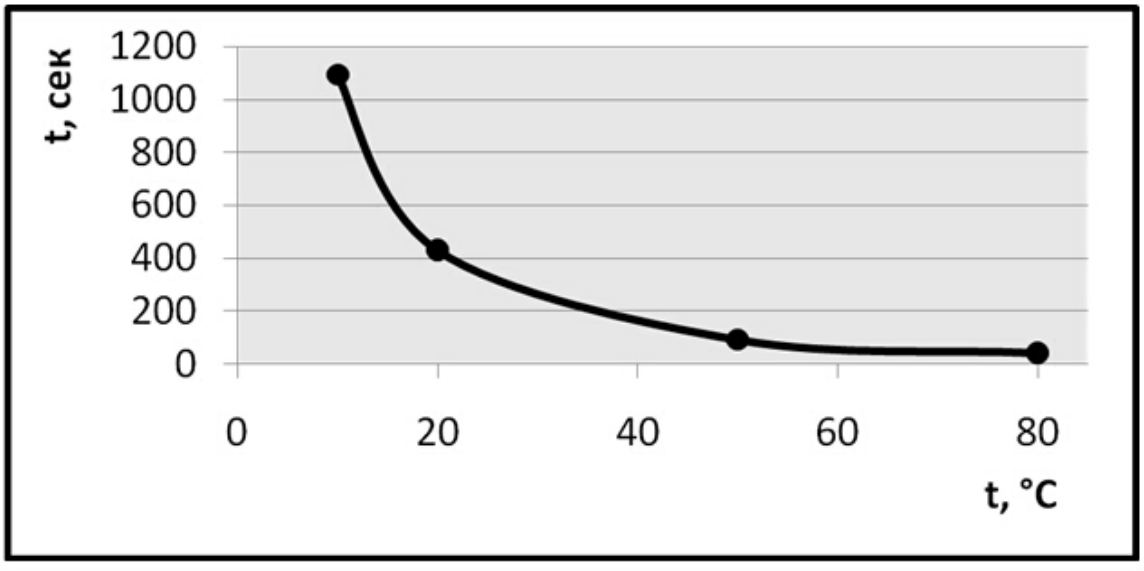
Course of reaction. Experimental data have established the appropriate environmental conditions and the concentration of the reagents for the most appropriate for the study reactions. Thus, the additional acidification reduced the total duration of the reaction. An increase in temperature gave more transmission in color, but it significantly reduced the total time, but lowering the temperature leads to slowing or stopping the process. Dependence on the concentration of reagents (1) and temperature (2) is provided in tables.

Citric acid g	2	3	2	1	2	2
KBO_3 g	0,2	0,5	0,2	0,5	0,3	0,2
H_2SO_4 ml	0,7	0,7	1	0,5	0,7	0,7
$KMnO_4$ g	0,04	0,1	0,05	0,1	0,09	0,02
Number of graphic peaks	4	- 3	3	2	4	2
Total time sec	430	- 390	4 315	4 210	5625	490

t, °C	5	10	20	50	80
Общее время, сек	-	1094	430	924	42
Кол-во пиков	-	3	2	4	2

(Table 1)

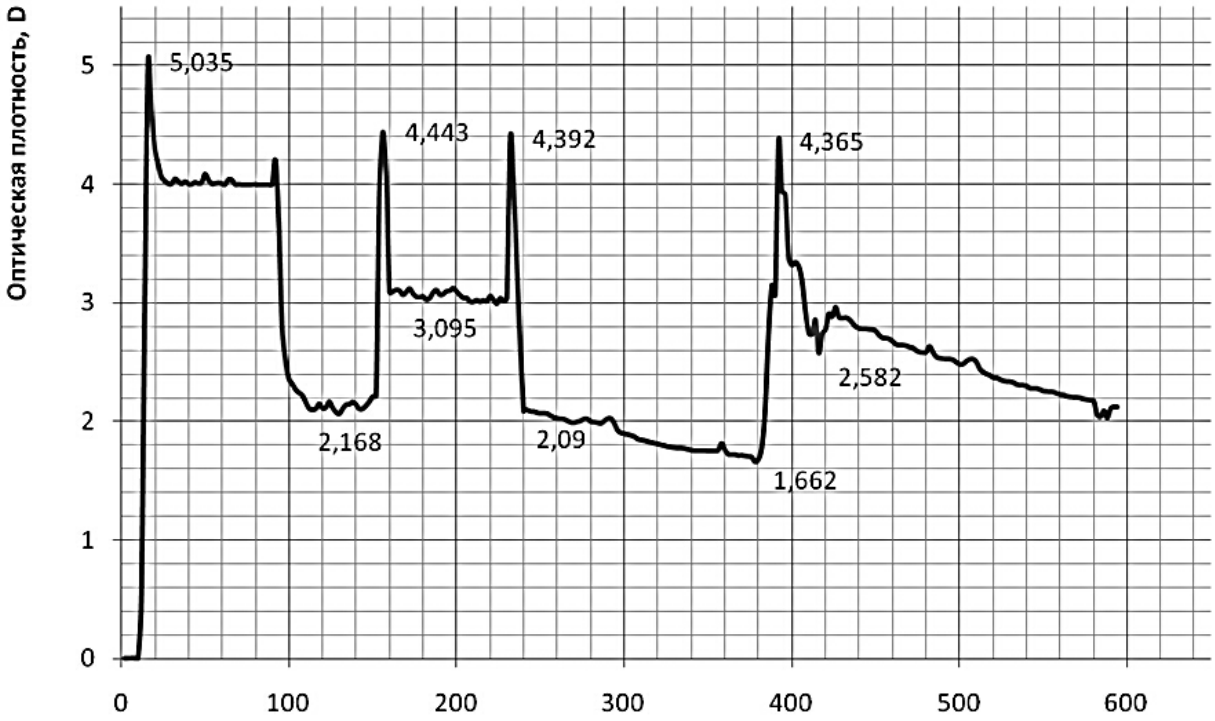
(Table 2)



Thus, 20° C and the following concentrations should be considered as the optimal conditions:

1. Citric acid - 2 g
2. 10 ml of H_2O
3. KBO_3 - 0.2 g

4. 0.7 ml H_2SO_4
5. 0.04 g $KMnO_4$



With the help of optical density sensor from the laboratory L-micro we can see what way optical density of the solution is changed in a definite period of time.

On the vertical scale, we can see the data of light transmission of the solution and on the horizontal one - time. Heterogeneity graph shows periodicity of changes in color of the solution. As a result, in the course of the reaction nine visible color changes were obtained and a lot of small variations of color. The average amplitude between major transitions is 86 seconds. The interval between the first two "jumps" was 106 seconds, and between the last two changes - 160 seconds. Last visible change in color occurred at 430 seconds, and then the solution is clarified and the sensor assessments decreased. In ten minutes after the reaction, the color stops changing and became milky-white.

Conclusion: The studies of oscillating reactions of colorimetric method, allows to monitor the reaction, its speed and impact of conditions (changes in temperature, concentration of reactants). Knowing the external environment, we can determine the of the impurity concentration, and concentration reagents themselves by data of optical density.

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