

Вивчено кінетику окиснення нітрит до нітрат йонів калій фератом(VI) в широкому діапазоні рН, від нейтрального до лужного середовища. Проведено дві серії кінетичних експериментів, заснованих на різних технологіях одержання калій ферату(VI). В першій серії експериментів кристалічний калій ферат(VI) отримували хімічним синтезом. В діапазоні рН 6.5–11 твердий  $K_2FeO_4$  додавали до розчинів нітрит йонів при відомій концентрації та рН. Експерименти проводили під контролем рН та йонної сили. Кінетичні дослідження коливалися від мілісекунд до декількох хвилин. В другій серії експериментів розчину  $K_2FeO_4$  було отримано електрохімічним синтезом. Лужні розчини калій ферату(VI) в 8.0 М КОН готували електрохімічним розчиненням сталевих пластин ( $S=10 \text{ см}^2$ ), що містили: С – 0.16 %; Мп – 0.43 %; Si – 0.04 %; S – 0.03 %; Р – 0.04 %; решта Fe. Експерименти проводили з використанням свіжих розчинів калій ферату(VI) та розчинів, що витримувалися після синтезу декілька днів, під контролем концентрації нітрит йонів. Кінетичні дослідження коливалися від декількох хвилин до годин. Встановлено, що максимальна швидкість реакції окиснення досягається при використанні розчину  $K_2FeO_4$ , витриманого після синтезу 8 днів. Дві серії дослідів показали, що швидкість окиснення нітрит йонів залежить від концентрації протонованого ферату,  $HFeO_4^-$ . Досліджено залежність спостережуваних констант швидкості від рН, концентрацій нітриту та йонної сили. Розраховані істинні константи швидкості, порядки реакції за нітрит та ферат йонами, загальний порядок реакції. Знайдена константа швидкості реакції окиснення води фератом(VI). Дослідження, наведені в даній статті, важливі, тому що кінетику окиснення шкідливих неорганічних та органічних речовин фератами(VI) лужних металів широко застосовують для встановлення оптимальних параметрів технологічних процесів очищення поверхневих вод, промислових стічних вод та повітря

**Ключові слова:** калій ферат(VI), нітрит йони, кінетика окиснення, синтез фератів(VI), лужні розчини

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# STUDY OF THE OXIDATION KINETICS OF NITRITE IONS BY POTASSIUM FERRATE(VI)

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## 1. Introduction

In recent years, the interest in ferrate(VI) salts (especially  $K_2FeO_4$  and  $Na_2FeO_4$ ) as promising substances has increased. Their use in water and air purification has been proposed due to the strong oxidizing properties of Fe(VI). A large number of publications are devoted to the study of the kinetics and mechanism of interaction of  $FeO_4^{2-}$  with harm-

ful organic and inorganic substances in an acidic, neutral and weakly alkaline condition. The kinetics and products of the oxidation of caffeine by acid-activated ferrate(VI) are described in [1]. The oxidation processes of pentachlorophenol [2] and phenol [3] by ferrate(VI) in neutral and weakly alkaline condition are offered. The kinetics and mechanism of ferrates(Fe(VI), Fe(V), and Fe(IV)) oxidation of iodide with the formation of triiodide at pH 5–10.3 [4] are present-

ed. In the review [5], the engineering aspects of ferrate(VI) in water and wastewater treatment for removing inorganic and organic contaminants in an acidic, neutral and weakly alkaline condition are reported. The review [6] presents a critical assessment of the kinetics and mechanisms of the oxidation of organic compounds by ferrate(VI) and ferrate(V) at different pH. The kinetics and mechanism of oxidation of tryptophan by ferrate(VI) at pH 7–9 are offered in [7]. However, it is known [8] that the stability of ferrates at such pH values is extremely low, due to the rapid oxidation of water to form molecular oxygen. This process occurs in parallel with the reaction of oxidation of dissolved solutes. Therefore, we should take into account the process of parallel reaction of their spontaneous decomposition, the rate of which may considerably exceed the rate of the main oxidation process. It is known [9] that stability of ferrate solutions significantly increases with increasing pH. However, during this process the oxidation potential of the pair Fe(VI)/Fe(III) decreases. Oxidizing properties of ion  $\text{FeO}_4^{2-}$  are studied in the strongly alkaline condition in reaction with water, alcohols, phenols [10, 11] and Cr(III) solutions [12, 13]. At the same time, the interest in the study of the oxidation process of ferrate(VI) alkali metals of nitrogen-containing substances in surface waters, industrial wastewaters and air has increased. In this paper, the oxidation kinetics of nitrite ions, which are present in water, by potassium ferrate(VI) in a wide range of pH, from neutral to alkaline medium, has been studied.

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## 2. Literature review and problem statement

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The kinetics and products of the oxidation of nitrogen-containing inorganic and organic substances with using ferrates(VI) technology from acidic to the weakly alkaline condition are described in the review [14]. The oxidation processes of Ni(II)-cyano and Co(III)-cyano complexes at pH 9–11 [15], cyanide, thiocyanate, and copper(I) cyanide at pH 11–12 [16, 17] by ferrates(VI) are offered. The kinetics and mechanism of the ferrate(VI) oxidation of hydroxylamines in weakly alkaline condition are presented in [18]. The results of these studies are used for the surface water and industrial wastewater purification by ferrates(VI). Of all the papers reviewed on nitrogen-containing compounds, only the absorption of nitrogen(II) oxide by solutions of ferrate(VI) has been studied in strongly alkaline media. This process can be used to purify the air reported in [19].

As is known, nitrite is an intermediate in the destructive oxidation of a large number of small nitrogen-containing substances. For instance, azide, hydroxylamine, hydrazine, methyl amine and probably many other water-soluble substances all form HNO which is readily oxidized to nitrite ion in the destructive oxidation of these other undesirable compounds [20]. The reaction of ferrate with nitrite is often the slowest step in the oxidation of ferrate with such substances.

Therefore, this paper studies the kinetics of potassium ferrate(VI) oxidation of nitrite ion  $\text{NO}_2^-$ , for which at pH>11 there is no information in the literature. Previously it was reported on the influence of protonated forms of ferrate on the oxidation rate of cyanide, thiocyanate, and copper(I) cyanide [16]. In the study presented here, it was important to expand the pH range from neutral to highly alkaline and evaluate the effect on the kinetics of the oxidation process of the nitrite ions of various protonated forms of ferrate. At the same time, it was interesting to follow the oxidation

kinetics of nitrite ions by  $\text{K}_2\text{FeO}_4$ , obtained on the different technologies.

Oxidation processes of nitrite ion by peroxide [21], hypochlorite [22], and peroxomonophosphoric acid [23] have been reported elsewhere. These papers point to the nucleophilic activity of the nitrite nitrogen as the central feature of the oxidation mechanism.

Ferrate(VI) ion is a strong oxidizing agent, with an electrode potential of 2.2 V in acid solution [24, 25] and a deep purple color ( $\lambda_{\text{max}}=505$  nm,  $\epsilon_{505}=1170$  M<sup>-1</sup>cm<sup>-1</sup>). Ferrate(VI) oxidizes water rapidly in acid but slowly in alkaline solution. This process is always in parallel with the oxidation of aqueous solutes which may be present.

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## 3. The aim and objectives of the study

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The aim of this study is to investigate the oxidation kinetics of nitrite ions to nitrate by potassium ferrate(VI) obtained on the different technologies.

To achieve this aim, it was necessary to accomplish the following objectives:

- to prepare crystalline potassium ferrate(VI) by the chemical synthesis and solutions of potassium ferrate(VI) by the electrochemical synthesis;
- to conduct two series of kinetic experiments of oxidation of nitrite ions by ferrate(VI) based on the different methods of synthesis of potassium ferrate(VI);
- to investigate the dependence of the observed and true rate constants on pH, the observed rate constants on nitrite concentration and ionic strength;
- to calculate the particular orders of reaction for  $\text{NO}_2^-$  and  $\text{FeO}_4^{2-}$  ions, the overall order of reaction and the true rate constants.

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## 4. Materials and research methods for the oxidation kinetics of nitrite ions by potassium ferrate(VI) obtained on the different technologies

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### 4.1. Materials, substances and devices used for the synthesis of potassium ferrates(VI) by chemical and electrochemical methods

Two series of kinetic experiments based on the different methods of synthesis of potassium ferrate(VI) were conducted. Potassium hydroxide (analytical grade) and doubly distilled water were used for the preparation of base alkaline solutions. In the first series of experiments, solid potassium ferrate(VI) was prepared by the chemical method of Thompson [26]. This method has been reviewed in the modern investigation [27]. The purity of  $\text{K}_2\text{FeO}_4$  was determined by chromite titration [28, 29] and spectrophotometry by Specord 210 of Analytik Jena (Germany) as well as ion chromatography by Biorad IC–Anion–PW column (USA) to identify and quantitate impurity ions, chloride and nitrate. In the second series of experiments, solutions of ferrate(VI) in 8.0 M KOH were prepared by the electrochemical method [32, 33]. These solutions are resulting from  $t=20$  °C by electrochemical dissolution of steel plates ( $S=10$  cm<sup>2</sup>) containing: C – 0.16 %; Mn – 0.43 %; Si – 0.04 %; S – 0.03 %; P – 0.04 %; the rest is Fe. This composition is determined by ARL 3460 Optical Emission Spectrometer (Switzerland). The polarization of the electrodes was carried from direct current source B5-47 (Russia) to control the amount of elec-

tricity at constant current integrator IPT-1 (Belarus). The process was carried out in reactors of polymethylmethacrylate and polytetrafluoroethylene. The temperature of the working solutions was monitored and maintained using ultra thermostat U-2 (Germany) with an accuracy of  $\pm 0.1$  °C.

#### 4. 2. Materials and methods for the oxidation kinetics of nitrite by solid potassium ferrate(VI) prepared on the chemical synthesis

Kinetic studies were performed under pH and ionic strength controlled conditions in the first series of experiments. A phosphate buffer with potassium counterion controlled pH and potassium sulfate was used to control the ionic strength in some experiments. Fe(VI) concentrations were typically approximately  $10^{-5}$ – $10^{-4}$  M whereas nitrite concentrations were 10–300 times greater. One set of reactions was run in water from which oxygen had been removed by bubbling with nitrogen. No difference was noted in this set from those reactions run in air-saturated water.

Reaction rates were measured by monitoring the disappearance spectrophotometrically of the Fe(VI) ion. Reactions run in the alkaline solution (pH 9–11) were run on a Specord 210 spectrophotometer at 505 nm at 20 °C in 10 cm quartz cells. Reactions run in more acid solutions (pH 6.5–8.5) were run in triplicate on a Durham-Gibson stopped flow spectrophotometer interfaced to a Northstar-Horizon (Z-80 microprocessor) computer. All reactions were monitored for approximately 2.5 half-lives. Kinetic data were treated using programs [30, 31].

Identification and quantitation of reaction products were done using an Orion 93–07 nitrate electrode with a double junction model 90–02 reference electrode and an Orion model 701 pH-meter. Nitrate determinations were based on calibration curves developed with interfering phosphate buffers but with sulfamic acid additions to remove unreacted nitrite. Nitrate standards and experimental samples were prepared and handled in an identical manner to ensure identical background conditions. Dissolved oxygen was monitored using a Yellow Springs model 5331 probe and meter. The oxygen probe was calibrated using a deoxygenated buffer and air saturated buffer.

All experimental solutions contained 20 mL of 0.63 M phosphate buffer and 10 mL of 0.10 M  $\text{KNO}_2$ . These solutions were deoxygenated by bubbling with nitrogen before addition of milligram amounts of solid  $\text{K}_2\text{FeO}_4$ . Nitrite and nitrate ion concentrations after the reaction were also measured using a single column, non-suppressed ion chromatography using a Biorad IC-Anion-PW column and pH 5.1 potassium hydrogen phthalate mobile phase with a Wescan conductivity detector.

#### 4. 3. Materials and methods for the oxidation kinetics of nitrite by solutions of potassium ferrate(VI) prepared on the electrochemical synthesis

In the second series, the kinetic experiments were performed with fresh solutions of potassium ferrate(VI) and solutions, aged after synthesis for no more than 18 days. In this case, the concentration of potassium nitrite was two orders of magnitude higher (0.5–2.0 M). Stock solution  $\text{KNO}_2$  (2.0 M) was diluted with KOH to obtain similar concentrations of working solutions: 0.5 M, 1.0 M, 1.5 M and 2.0 M  $\text{KNO}_2$ . The samples of alkaline solutions of potassium ferrate(VI) were taken by polyethylene syringes.

Equivalent volumes (5 mL) of ferrate(VI) and potassium nitrite were mixed in plastic weighing bottles, sealed up and mixed thoroughly for 10–15 minutes. The experiments were conducted at different concentrations of reagents,  $\text{K}_2\text{FeO}_4$  ( $10^{-5}$ – $10^{-4}$  M) and  $\text{KNO}_2$  (0.5–2.0 M).

The kinetics process of potassium nitrite oxidation by potassium ferrate(VI) in alkaline media according to the reaction with the formation of iron(III) oxohydroxide  $\text{FeO}(\text{OH})$ :



was studied by measuring the change in time of ferrate(VI) concentration using spectrophotometry on Specord 210 of Analytik Jena (Germany) at 505 nm where ferrate has a molar absorptivity of  $1170 \text{ M}^{-1}\text{cm}^{-1}$ . Each experiment was carried out for 300 minutes, with measurement of ferrate(VI) concentration every 15 minutes.

### 5. The results of the oxidation kinetics of nitrite ions by potassium ferrate(VI) obtained on the different technologies

#### 5. 1. The oxidation kinetics of nitrite by solid potassium ferrate(VI) prepared on the chemical synthesis

In the first series of experiments, the rate law for ferrate – nitrite reaction was shown to be as in equations (2) and (3):

$$\begin{aligned} \text{Rate} &= -d[\text{Fe(VI)}]/dt = \\ &= (k_1 + k_s[\text{NO}_2^-])[\text{Fe(VI)}] + k_2[\text{Fe(VI)}]^2, \end{aligned} \quad (2)$$

$$\text{Rate} = k_{1(\text{obs})}[\text{Fe(VI)}] + k_2[\text{Fe(VI)}]^2. \quad (3)$$

In all cases, nitrite concentration was maintained at concentrations sufficiently greater than ferrate(VI) that its concentration was taken to be constant throughout the reaction. Plots of  $k_{1(\text{obs})}$  versus  $[\text{NO}_2^-]$  were linear at pH 8.5 (Fig. 1) and pH 10 (Fig. 2), yielding a slope of  $k_s$ , the rate constant for the oxidation of nitrite by Fe(VI) and an intercept of  $k_2$ , the rate constant for the oxidation of water by Fe(VI). Values of  $k_s$  as true rate constants are shown in Table 1.

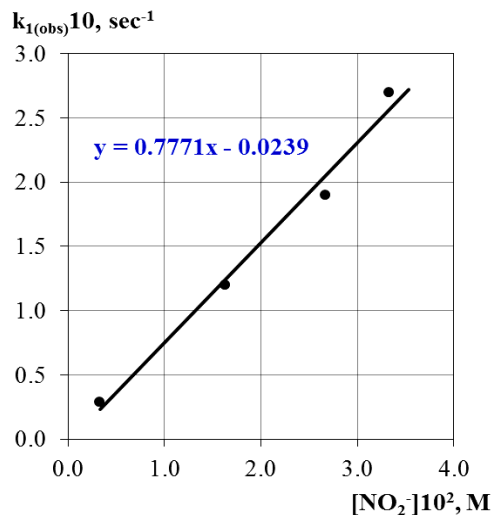


Fig. 1. The dependence of the observed rate constants on the concentration of nitrite ions interaction solutions ferrate(VI) with  $\text{KNO}_2$  for experiments at pH 8.5

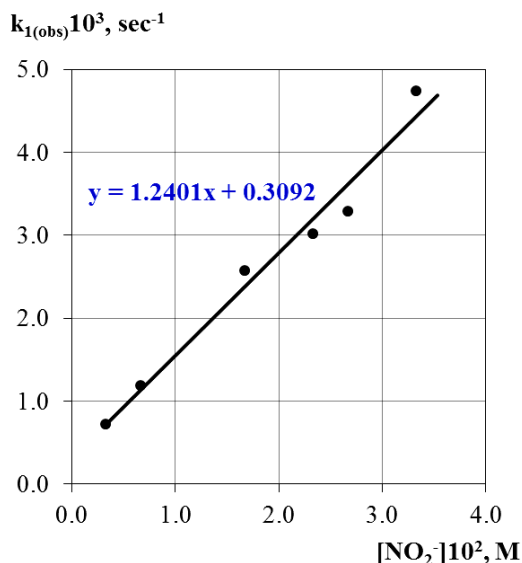


Fig. 2. The dependence of the observed rate constants on the concentration of nitrite ions interaction solutions ferrate(VI) with KNO<sub>2</sub> for experiments at pH 10

Table 1

The true rate constants for nitrite oxidation by ferrate(VI)

pH	k <sub>s</sub> , M <sup>-1</sup> s <sup>-1</sup>
10.80	1.29·10 <sup>-2</sup>
10.00	1.24·10 <sup>-1</sup>
9.78	1.26·10 <sup>-1</sup>
9.58	1.28·10 <sup>-1</sup>
9.38	2.63·10 <sup>-1</sup>
9.26	3.33·10 <sup>-1</sup>
9.23*	3.55·10 <sup>-1</sup>
9.00	1.20
8.50*	7.80
8.00	14.2
8.00*	92.3
7.00	1.84·10 <sup>3</sup>
7.00*	2.26·10 <sup>3</sup>
6.50	9.85·10 <sup>3</sup>
6.50*	9.92·10 <sup>3</sup>

Note: \* – ionic strength 0.64 (Na<sub>2</sub>SO<sub>4</sub>). Otherwise, ionic strength ~1.6 for experiments at pH>9 and 0.2–0.6 at pH<9

As we can see from Table 1, the true rate constants (k<sub>s</sub>) for nitrite oxidation by ferrate(VI) decrease with increasing pH, which correspond with the data [6].

### 5. 2. Analysis of the reaction products of nitrite oxidation by potassium ferrate(VI) obtained on the chemical synthesis

The products, nitrate ion and molecular oxygen, were determined as a function of original solution composition. A set of six reactions at pH 9.3 with initial nitrite concentration of 3.3 mM and initial ferrate(VI) concentrations from 0.12–0.27 mM resulted in an average amount of nitrate produced being 59.7±1.2 %, the theoretical amount based on ferrate based on equation (4) and the average amount of oxygen corresponding to 46.9±3.8 %, the amount of ferrate based on equation (5). Moles of nitrite which disappears and moles of nitrate formed in the reaction were shown by ion chromatography to be equal and to increase and approach a

limiting value of ca. 1.5 mole nitrate formed per mole of ferrate reacted as the initial nitrite concentration is increased at pH 6.5. Simultaneously the amount of oxygen formed decreased and approached zero under these conditions.

It was shown by ion chromatography that potassium ferrate(VI) contained a small nitrate impurity from the ferric nitrate used in the ferrate synthesis which was not corrected for in the selective ion electrode measurements (Table 2).

Table 2

Product analysis by ion chromatography at solution volume 10 mL and pH 6.5

[FeO <sub>4</sub> <sup>2-</sup> ] <sub>0</sub> mM	[NO <sub>2</sub> <sup>-</sup> ] <sub>0</sub> mM	[NO <sub>2</sub> <sup>-</sup> ] <sub>e</sub> mM	[NO <sub>3</sub> <sup>-</sup> ] <sub>e</sub> mM	Σ mM	$\frac{[NO_3^-]}{[Fe(VI)]}$
3.9	10.0	6.9	2.46	9.4	0.63
7.9	10.0	5.5	3.42	8.9	0.43
11.8	10.0	4.0	4.58	8.6	0.39
15.8	10.0	2.2	5.84	8.0	0.37
4.0	10.0	7.3	1.7	9.0	0.43
4.0	20.0	15.1	3.1	18.2	0.78
4.0	50.0	41.5	4.9	46.4	1.23
4.0	100.0	95.8	6.7	102.5	1.68

The total oxidizing power of ferrate(VI) going to Fe(III) is accounted for by the amounts of nitrate found in these analyses, based on reactions (1) and (4):



Solutions studied by ion chromatography contained 20 mL of 0.63 M phosphate buffer and 10 mL of 0.10 M KNO<sub>2</sub>. After deoxygenating by bubbling with nitrogen, milligram quantities of solid K<sub>2</sub>FeO<sub>4</sub> were added to 10 mL aliquots of these solutions. A series of reactions at pH 9.3 with [Fe(VI)]<sub>0</sub>=0.2 mM yielded enough oxygen to account for 46.9±3.8 % of the Fe(VI) and enough nitrate to account for 59.7±1.2 % of the Fe(VI).

Values of k<sub>1(obs)</sub> were plotted vs [NO<sub>2</sub><sup>-</sup>] to obtain values of k<sub>s</sub> at several values of pH. These true rate constants are shown in Table 1. Typical graphs are shown as Fig. 1, 2. Fig. 3 shows the pH dependence of logk<sub>s</sub>.

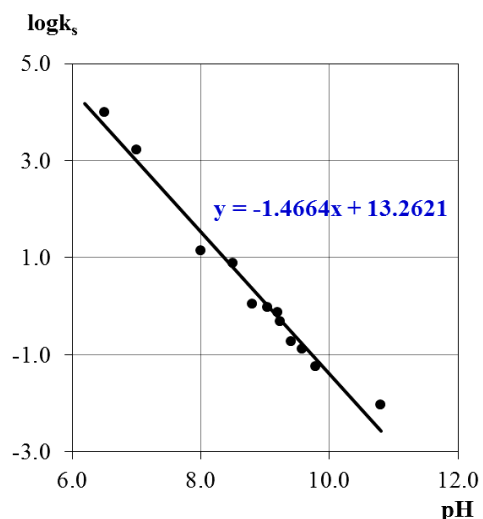


Fig. 3. The pH dependence of logk<sub>s</sub> for experiments at ionic strength 0.64 (Na<sub>2</sub>SO<sub>4</sub>)

Fig. 3 shows that the true rate constants for nitrite oxidation by ferrate(VI) decrease with increasing pH.

### 5. 3. The oxidation kinetics of nitrite by solutions of potassium ferrate(VI) prepared on the electrochemical synthesis

In the second series of experiments, it has been observed that the rate of interaction of potassium ferrate(VI) with potassium nitrite depends on the time elapsed from the start of preparation of ferrate(VI) solutions. The experiments were performed with a fresh solution of potassium ferrate(VI) and solutions, aged for 1–18 days after the synthesis. This dependence is complex: at first it increases and reaches the maximum value for the solutions of ferrate(VI), aged after synthesis for 8 days, then it decreases again. Consequently, further kinetic experiments were performed at starting time preparation of solutions of ferrate(VI) in 8 days after the synthesis. At the same time, inevitably we should take into account the process of parallel reaction of spontaneous decomposition of ferrate(VI) (Fig. 4).

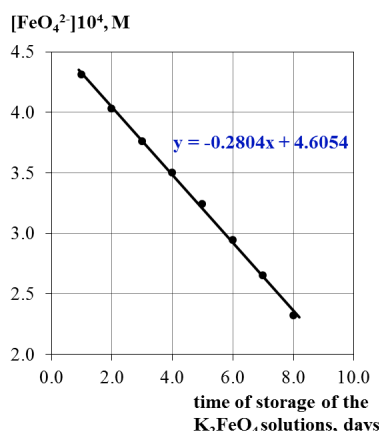


Fig. 4. The dependence of the concentration of ferrate(VI) solutions on the number of days of storage of the K<sub>2</sub>FeO<sub>4</sub> solutions at pH 14.9 and t=20 °C

The kinetic curves of interaction solutions K<sub>2</sub>FeO<sub>4</sub> with 2.0 M KNO<sub>2</sub> in 8.0 M KOH at starting time of ferrate(VI) solutions preparation after the synthesis for 1–8 days are shown in Fig. 5.

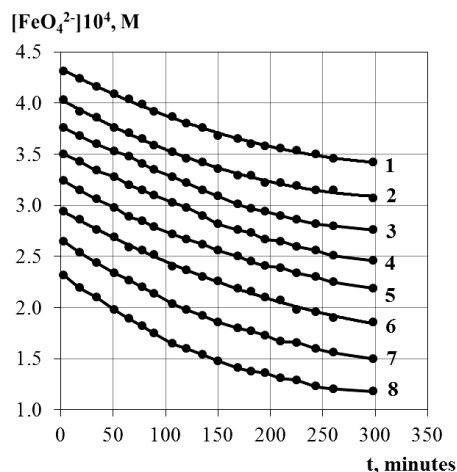


Fig. 5. The kinetics of interaction solutions of ferrate(VI) in 8.0 M KOH with 2.0 M KNO<sub>2</sub> at t=20 °C and starting time of K<sub>2</sub>FeO<sub>4</sub> solutions preparation after the synthesis: 1 – fresh solution; 2–8 – solutions, aged respectively for 2–8 days

With reference to the experimental data, kinetic curves of the interaction solutions of potassium ferrate(VI) in 8.0 M KOH with various concentrations of KNO<sub>2</sub> are presented in Fig. 6.

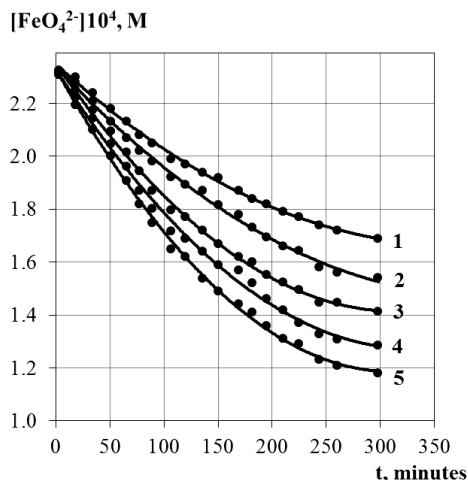


Fig. 6. The kinetics of interaction solutions of ferrate(VI) in 8.0 M KOH with KNO<sub>2</sub> at starting time of making solutions after the synthesis for 8 days, [Fe(VI)]<sub>0</sub>=2.32·10<sup>-4</sup> M, t=20 °C: 1 – base solution K<sub>2</sub>FeO<sub>4</sub> without KNO<sub>2</sub>; 2–5 – solutions K<sub>2</sub>FeO<sub>4</sub>+0.5; 1.0; 1.5; 2.0 M KNO<sub>2</sub>

Fig. 6 shows that the reaction rate increases classically with increasing of potassium nitrite concentration from 0.5 to 2.0 M KNO<sub>2</sub>.

After estimation of the slope of the curves in Fig. 6, we have got the initial rate. Plotting the initial rate versus nitrite molarity gives a line with a slope of 1.36·10<sup>-7</sup> min<sup>-1</sup> (Fig. 7) and 2.27·10<sup>-9</sup> s<sup>-1</sup>. This is the observed rate constant for nitrite ions. Particular reaction order by nitrite ions is equal to one.

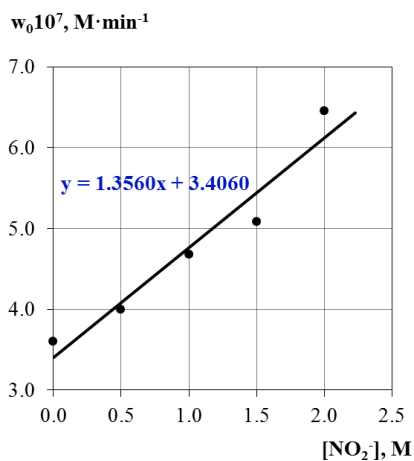


Fig. 7. The dependence of the initial rate reaction of ferrate(VI) in 8.0 M KOH with KNO<sub>2</sub> at time the storage of K<sub>2</sub>FeO<sub>4</sub> after the synthesis for 8 days on nitrite molarity

The differential equation for the chemical reaction rate is:

$$w = \frac{-d[\text{FeO}_4^{2-}]}{dt} = k[\text{FeO}_4^{2-}]^m[\text{NO}_2^-]^n, \tag{5}$$

where [FeO<sub>4</sub><sup>2-</sup>] and [NO<sub>2</sub><sup>-</sup>] – molar concentrations of potassium ferrate(VI) and potassium nitrite respectively; m and

$n$  – orders of reaction for ferrate and nitrite ions;  $k$  – rate constant of reaction (1).

After processing experimental data, the values of the observed rate constants for nitrite ions have been calculated (Table 3).

Table 3

Dependence of the observed rate constants for  $\text{NO}_2^-$  ions on potassium nitrite concentration at  $t=20^\circ\text{C}$

$[\text{KNO}_2], \text{M}$	$k_{1(\text{obs})}$ for nitrite ions, $\text{min}^{-1}$
0.5	$4.0 \times 10^{-4}$
1.0	$8.0 \times 10^{-4}$
1.5	$1.0 \times 10^{-3}$
2.0	$1.4 \times 10^{-3}$

According to the graphic dependence  $k_{1(\text{obs})}=f([\text{NO}_2^-])$  (Fig. 8), the true rate constant of the reaction is calculated yielding a slope of  $k_s=6.42 \times 10^{-4} \text{ M}^{-1}\text{min}^{-1}$  which is  $1.07 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$ .

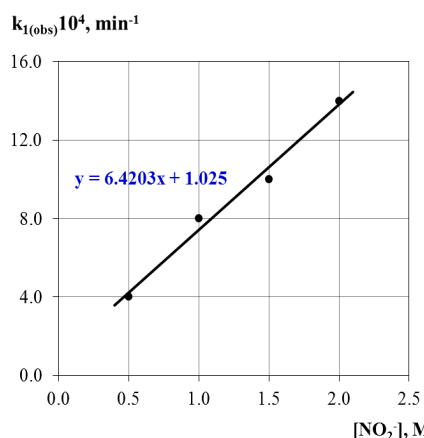


Fig. 8. The dependence of the observed rate constants on the concentration of nitrite ions interaction solutions ferrate(VI) in 8.0 M KOH with  $\text{KNO}_2$  at  $[\text{Fe(VI)}]_0=2.32 \cdot 10^{-4} \text{ M}$  and aging solutions after the synthesis for 8 days

The values of the observed rate constants for ferrate ions are given in Table 4.

Table 4

Dependence of the observed rate constants for  $\text{FeO}_4^{2-}$  ions on potassium nitrite concentration at  $t=20^\circ\text{C}$

$[\text{KNO}_2], \text{M}$	$k_{1(\text{obs})}$ for ferrate ions, $\text{min}^{-1}$
0.5	$6.32 \times 10^{-11}$
1.0	$8.16 \times 10^{-11}$
1.5	$1.22 \times 10^{-10}$
2.0	$2.29 \times 10^{-10}$

Tables 3, 4 show that the observed rate constants for nitrite and ferrate ions increase with increasing of  $[\text{NO}_2^-]$ .

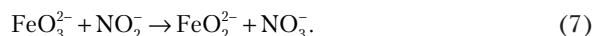
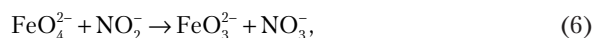
## 6. Discussion of the results of the oxidation kinetics of nitrite by potassium ferrate(VI) obtained on the different technologies

The results presented in this paper demonstrate that the oxidation kinetics of nitrite ions by ferrate(VI) does not

depend on the method of synthesis of potassium ferrate(VI). In the second series of experiments, Fig. 7 shows that the observed rate constant for  $\text{NO}_2^-$  ions is  $1.36 \times 10^{-7} \text{ min}^{-1}$  and  $2.27 \times 10^{-9} \text{ s}^{-1}$ . It is compared well with the value of the observed rate constant obtained from the solving data of the first series of experiments at pH 14.9. This value is  $2.60 \times 10^{-9} \text{ s}^{-1}$ .

It should be noted that the general order reaction of ferrate(VI) with nitrite ions interaction is defined as the sum of particular orders for nitrite and ferrate ions. By analogy with the data [16], particular orders reactions for each reactant are equal to one (Tables 3, 4). The general order reaction of ferrate(VI) with nitrite is equal to two and completed by two-electron transfer.

As it follows from the first series of experiments when 1,10-phenanthroline is added to the buffered nitrite solution before adding ferrate(VI), an orange color of Fe(II) phenanthroline is observed. This indicates that the reaction occurs with Fe(II) as an intermediate in an atom transfer reaction on equations (6) and (7):



The Fe(II) is then oxidized to Fe(III) by oxygen or any other oxidizing agent present. When phenanthroline is added after the ferrate(VI) reaction has occurred, no orange color is observed. Therefore, Fe(II) is an intermediate but not a final product. This is consistent with the observation of moles of nitrate formed being double the moles of  $\text{K}_2\text{FeO}_4$  used when nitrite is in large excess over ferrate.

So, equations (6) and (7) show that first Fe(VI) reacts with a molecule of nitrite to form Fe(IV) and nitrate, then Fe(IV) with another molecule of nitrite reacts further to generate Fe(II) and nitrate. At last, Fe(IV) reacts with Fe(II) to generate Fe(III). At the same time, the second-order oxidation rate constant of water by Fe(VI) contributes but little to the disappearance of Fe(VI).

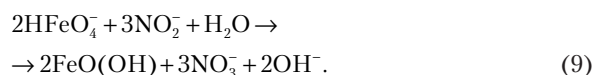
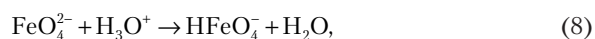
As it was mentioned in Table 1 and Fig. 3, the observed and true rate constants decrease with increasing of  $[\text{OH}^-]$ , the same as in the paper [16]. The values of  $k_2$ , the second-order oxidation rate constant of water by Fe(VI) were independent of nitrite concentration. The values of  $k_1$  and  $k_2$  are similar to the values obtained in the absence of nitrite or other oxidizable solutes and are reported in [34]. The values of the observed rate constants for nitrite and ferrate ions are increasing with the accretion of nitrite concentration (Fig. 1, 2, 8), which correspond with the data [35].

It is important to note that in strongly alkaline solutions in the second series of experiments, the rate of reaction of  $\text{NO}_2^-$  with  $\text{HFeO}_4^-$  is higher than with  $\text{FeO}_4^{2-}$ . The reaction of ferrate(VI) with nitrite is driven primarily by the reaction of the deprotonated  $\text{H}_2\text{FeO}_4$ . The pKa values of  $\text{H}_2\text{FeO}_4$  and  $\text{HFeO}_4^-$  are 3.2 and 7.8 respectively. The dianion,  $\text{FeO}_4^{2-}$  is very slow and only becomes important at very high pH. It can be restrictions imposed on the use of the results of the proposed research.

Consequently, the observed rate constants for ferrate oxidation reactions show a strong pH dependence, with the reactions being faster at low pH. We attribute this to the difference in the rate of oxidation by protonated forms of ferrate. The second-order rate constants decreased with increasing pH because the deprotonated species,  $\text{FeO}_4^{2-}$  is less reactive than the protonated Fe(VI) species,  $\text{HFeO}_4^-$  [16].

Therefore, above pH 9.8 less than 1.0 % of the ferrate(VI) is protonated (>99 % is the dianion). If the dianion,  $\text{FeO}_4^{2-}$  was an important reactant, one would expect the rate constant to stabilize at higher pH. This is not observed and rather the reaction continues to slow down even at 8.0 M KOH. The pKa of nitrous acid is 3.15 so nitrite ion is the dominant form over the entire pH range studied.

Obviously in the ferrate(VI) solutions with increasing pH, it decreases the concentration of  $\text{HFeO}_4^-$  and increases the content of  $\text{FeO}_4^{2-}$ . It is likely that before the direct interaction of nitrite and ferrate anion, there must be protonation of ferrate anion (accession proton from a proton donor, such as  $\text{H}_3\text{O}^+$ ):



We can assume that in a strongly alkaline medium, when the concentration of  $\text{H}_3\text{O}^+$  is negligible, the limiting step may be the reaction (8) and not the reaction (9), which defines as generally low rate the nitrite oxidation of ferrate(VI).

The features of the conducted investigations are the two series of experiments utilizing very different techniques for synthesis of  $\text{K}_2\text{FeO}_4$  give similar values of the observed rate constants. So, these results give the conclusion that the protonated form of ferrate,  $\text{HFeO}_4^-$  has a dominant role in the reaction of the ferrate(VI) interaction with nitrite ions.

The ratio of the observed rate constant for oxidation of dissolved solute to that of the oxidation of water puts a limit of the efficiency of water purification. This ratio depends on the solution pH. Previously, the range pH 6.5–11 was investigated in order to find the conditions for the oxidation of various nitrogen-containing solutions [20, 34]. As advantages of this study, the facts can be considered that the range of pH to 14.9 was extended and the oxidation of nitrite ions

by potassium ferrate(VI) obtained on the different technologies was studied.

The kinetics results of two series of experiments can be used to determine optimal conditions when oxidation of nitrite ions to nitrate by ferrate(VI) can be successful. These data can be useful for the purification of surface water and wastewater from contaminants of nitrite ions.

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## 7. Conclusions

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1. The crystalline potassium ferrate(VI) was obtained by the chemical synthesis and the alkaline solutions of potassium ferrate(VI) were prepared by the electrochemical synthesis.

2. Two series of kinetic experiments based on the chemical and electrochemical synthesis of  $\text{K}_2\text{FeO}_4$  were conducted. The peculiarities of the oxidation kinetics of nitrite ions by potassium ferrate(VI) obtained on the different technologies are considered.

3. It has been shown that the observed and true rate constants for nitrite oxidation by ferrate(VI) decrease with increasing pH, the observed rate constants increase with the accretion of nitrite concentration and increasing of ionic strength.

4. The kinetic parameters of the oxidation process have been calculated. The true rate constants of ferrate(VI) with nitrite interaction have been found, particular orders of reaction for  $\text{NO}_2^-$  and  $\text{FeO}_4^{2-}$  ions are equal to one and the overall order of reaction is equal to two.

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