

Nickel hydroxides are widely used as electrochemically active substances in alkaline batteries and hybrid supercapacitors; they can be used for electrocatalysis, in electrochemical sensors, and as pigments. Knowledge of the formation mechanism of nickel hydroxides is necessary for developing and optimizing targeted synthesis methods. The thermal effects of processes in the formation of nickel hydroxide from nitrate were studied by the calorimetry method. The mechanism of precipitate formation was investigated by the method of simultaneous potentiometric (with a glass universal electrode) and conductometric titration. The nickel content in the samples obtained at the determined NaOH/Ni<sup>2+</sup> ratios was investigated by the chemical method of trilonometry after preliminary dissolution.

Calorimetric investigations showed that the reaction of nickel nitrate with NaOH was exothermic with  $\Delta H_{\text{reaction}} = -28328.5 \text{ J/mol}$ . The exothermic nature of the NaOH dilution process was revealed with  $\Delta H_{\text{dilution}} = -2454 \text{ J/mol}$ .

According to the results of potentiometric titration, the formation of a basic salt of the NiOHNO<sub>3</sub> type was not detected. Analysis of the results of conductometric titration revealed a two-stage chemical mechanism for the formation of nickel hydroxide from nitrate. At the first stage, which had a high rate, due to the liquid-phase reaction of the nickel cation with the hydroxyl anion, a primary precipitate of the composition Ni(OH)<sub>1.87</sub>(NO<sub>3</sub>)<sub>0.13</sub> was formed. In the second stage, as a result of a slow topochemical reaction of the primary precipitate with hydroxyl anions, nitrate ions were displaced from the precipitate to form nickel hydroxide. These data are confirmed by the analysis of precipitate obtained at NaOH/Ni<sup>2+</sup> ratios of 1.87 and 2.2: the Ni content was 52.95 % and 55.63 %, corresponding to the formulas Ni(OH)<sub>1.87</sub>(NO<sub>3</sub>)<sub>0.13</sub>·0.68H<sub>2</sub>O and Ni(OH)<sub>2</sub>·0.71H<sub>2</sub>O. This clearly indicated that the primary precipitate was nitrate-doped α-Ni(OH)<sub>2</sub> and the final precipitate corresponded to the α-modification of nickel hydroxide

**Keywords:** nickel hydroxide, nickel nitrate, two-stage formation mechanism, α-modification, nitrate-doped nickel hydroxide, primary precipitate, potentiometry, conductometry

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# INVESTIGATION OF THE MECHANISM OF NICKEL HYDROXIDE FORMATION FROM NICKEL NITRATE

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## 1. Introduction

Nickel hydroxides and materials based on them (layered double hydroxides (LDH), nano- and micro composites, etc.) are widely used in various fields. Nickel hydroxides are known to have rather high electrochemical activity [1]. Therefore, these substances are used in various electrochemical devices. Nickel monohydroxides and LDHs based on them can be

used in nickel electrodes of alkaline nickel-cadmium, nickel-iron, and nickel-metal hydride batteries [2, 3]. Oxides for lithium batteries are obtained from them [4].

Various types of nickel hydroxides are used as the active substance of the Faraday electrode of hybrid supercapacitors. Ni(OH)<sub>2</sub> is used both individually [5] (in the form of nanoparticles [6] or ultrafine particles [7]) and as composite materials with nanocarbon structures (graphene oxide [8],

carbon nanotubes [9]). For thin-layer supercapacitors, a Ni(OH)<sub>2</sub> film is formed during the manufacture of electrodes on a conductive basis [10, 11].

Various forms of nickel hydroxide are used in electrocatalysis, for example, for the electrochemical oxidation of methanol [12, 13] or oxygen evolution [14], as well as in sensors [15, 16].

Nickel hydroxide has a light green color. Therefore, using various dye anions for intercalation in nickel hydroxide-based LDHs, it is possible to obtain pigments with different colors [17, 18]. At the same time, in thin layers, Ni(OH)<sub>2</sub> is practically transparent, while NiOOH is colored brown-black. As a result, nickel hydroxide is used as an electrochromic substance [19, 20].

Nickel hydroxides for various applications can be obtained by various methods. It should be noted that the development of methods for the targeted synthesis of nickel hydroxides with the required characteristics is very promising.

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## 2. Literature review and problem statement

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One of the main characteristics of Ni(OH)<sub>2</sub> is the parameters of the crystal lattice [21], in particular, inhomogeneity [22], microstructure [23], and crystallinity [24, 25]. These parameters are determined by the method and conditions of synthesis [26].

First of all, the synthesis method determines the type of Ni(OH)<sub>2</sub> [27]. Nickel hydroxide exists in the form of two modifications [28]:  $\beta$ -form (Ni(OH)<sub>2</sub>, brucite structure) and  $\alpha$ -form (3Ni(OH)<sub>2</sub>·2H<sub>2</sub>O, hydrotalcite-like structure). The existence of a form intermediate between  $\alpha$ -Ni(OH)<sub>2</sub> and  $\beta$ -Ni(OH)<sub>2</sub> was described in [29]. Nickel hydroxides with a mixed ( $\alpha$ + $\beta$ ) crystal structure were obtained in [30, 31].

$\beta$ -Ni(OH)<sub>2</sub> has higher electrochemical and thermal stability. Therefore, the  $\beta$ -form is widely used as an active agent in alkaline batteries [32] and hybrid supercapacitors [33]. The production of  $\beta$ -Ni(OH)<sub>2</sub> can be carried out by chemical deposition at low supersaturation, and electrolysis in a slit diaphragm electrolyzer [34]. High-temperature two-stage synthesis [35], decomposition method [32], and  $\alpha$ -Ni(OH)<sub>2</sub> etching method [36] are also applied.

$\alpha$ -Ni(OH)<sub>2</sub> has a higher electrochemical activity than  $\beta$ -Ni(OH)<sub>2</sub>. However, the pure  $\alpha$ -form has low stability, especially in concentrated alkalis at high temperatures. Under these conditions, the metastable  $\alpha$ -modification turns into a low-active type of  $\beta$ -modification, named by the authors  $\beta_{bc}$  (bc – badly crystalline) [37]. Additives are introduced to stabilize the  $\alpha$ -form [38, 39], in which case layered double hydroxides (LDHs) are formed [40, 41]. LDHs have a “host” hydroxide crystal lattice, in which part of the “host” cations (Ni<sup>2+</sup>) are replaced by “guest” cations, for example, Al<sup>3+</sup> [42] or V<sup>4+</sup> [43]. To compensate for the resulting excess charge, various anions are intercalated into the interlayer space of the crystal lattice [44]. These anions can be either anions of precursor salts (nitrates [45]) or anions formed during synthesis (cyanates [46]), or specially introduced anions (carbonates [46, 47]).  $\alpha$ -Ni(OH)<sub>2</sub> (both mono  $\alpha$ -Ni(OH)<sub>2</sub> and LDH) can be obtained by chemical synthesis [48, 49], homogeneous precipitation [49], in a slit diaphragm electrolyzer [50].

It should be noted that the type of the nickel hydroxide crystal lattice and its characteristics will be primarily

determined by the mechanism of Ni(OH)<sub>2</sub> formation. Three hierarchical types of formation mechanisms can be distinguished: chemical, crystallographic (topochemical), and volumetric. The chemical mechanism describes the chemistry of the reaction and determines the composition of the sample, the crystallographic mechanism describes the formation of the crystal structure and the type of crystal lattice, as well as crystallinity. The volumetric mechanism describes the formation and properties (size and morphology) of precipitate particles, both at the time of preparation and as a final product.

The crystallochemical mechanism of hydroxide formation is well-studied. During the formation of nickel hydroxide, the rate of nucleation (formation of crystal nuclei) is several orders of magnitude higher than the rate of crystal growth. As a result, nickel hydroxide particles are formed by a complex two-stage topochemical mechanism [51]:

– 1<sup>st</sup> stage (high-speed) – the formation of nuclei, their agglomeration, and formation of a primary amorphous particle;

– 2<sup>nd</sup> stage (slow) – crystallization (aging) of the primary amorphous particle. The crystallization process can take up to several hours and is determined by the composition of the mother liquor, duration, and temperature.

The investigation of the volumetric mechanism of Ni(OH)<sub>2</sub> formation showed that the formation of agglomeration of nuclei does not lead to the formation of continuous particles, but to the formation of branched filaments, between which the mother liquor remained. As a result, freshly deposited Ni(OH)<sub>2</sub> has a matrix structure similar to organic-organic [52] and inorganic-inorganic [53] composites. The matrix former is nickel hydroxide, and the filler is the mother liquor.

At the same time, the chemical mechanism of the formation of hydroxides, including nickel hydroxide, has not been studied enough.

It should immediately be noted that nickel hydroxide has two hydroxo groups and the formation of nickel hydroxide is possible by a two-stage mechanism through the formation of a basic salt. However, no evidence was found in the literature to support this mechanism. At the same time, it was shown in [54–57] that nickel hydroxide obtained by chemical precipitation did not fully correspond to the formula Ni(OH)<sub>2</sub> and contained salt anions of the precursor, which indicated their participation in the formation of nickel hydroxide. When investigating the formation of a precipitate from a solution of zinc sulfate by adding alkali by the titration method [51], it was found that at a molar ratio of OH<sup>-</sup>/Zn<sup>2+</sup>=1.6, a primary precipitate of basic sulfate was formed, which, upon further introduction of alkali, transformed into hydroxide. For nickel hydroxide, no data on the formation mechanism could be found in the literature, especially when obtained from nitrate salt. This does not allow both fully and purposefully choosing a synthesis method, and optimizing the technological parameters of production with the formation of nickel hydroxide with the required characteristics. Another unresolved issue is the preferential formation of  $\alpha$ -Ni(OH)<sub>2</sub> in the synthesis from nickel nitrate, while  $\beta$ -Ni(OH)<sub>2</sub> is formed in the synthesis from the sulfate. Clarification of this issue will make it possible to substantiate the choice of nitrate salts for the preparation of LDH having an  $\alpha$ -type lattice. To this end, it is mandatory to have information on the mechanism of nickel hydroxide formation.

### 3. The aim and objectives of the study

The study aims to determine the mechanism of nickel hydroxide formation during precipitation from nickel nitrate. This will justify the choice of precursor salts and conditions for the synthesis of nickel hydroxide and Ni LDH.

To achieve the aim, the following objectives were set:

- to investigate the thermal effects of the processes occurring during the formation of nickel hydroxide;
- to investigate the formation process and precipitate composition of nickel hydroxide.

### 4. Materials and methods

#### 4. 1. Object and hypothesis of the study

The object of the study was the process of nickel hydroxide formation. The hypothesis during the study is that the formation of nickel hydroxide proceeds by a complex chemical mechanism and the composition of the precipitate differs from the Ni(OH)<sub>2</sub> formula. During the study, a simplification was introduced to ignore the effect of concentration.

#### 4. 2. Materials used

During the study, Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and NaOH of high analytical grade qualifications were used without preliminary purification.

#### 4. 3. Methods for investigating the process of nickel hydroxide formation

The thermal effects of the processes occurring during the formation of nickel hydroxide were studied by direct calorimetry. To determine the thermal effect of the Ni(OH)<sub>2</sub> formation reaction, 300 ml of nickel nitrate solution (C<sub>Ni(2+)</sub>=0.1456 M) was placed in a calorimeter, and 8 ml of 11.25 M NaOH solution was placed in a special crushable ampoule. To determine the heat of dilution of an alkali solution, 300 ml of distilled water was placed in the calorimeter, and 8 ml of 11.25 M NaOH solution was placed in the ampoule. The calculation of the thermal effect was carried out by the formula:

$$\Delta H = -K \frac{\Delta T}{V \cdot C}, \quad (1)$$

where *K* is the instrument constant determined from the dissolution of KCl.

The formation process was studied by the method of simultaneous potentiometric and conductometric titration. For this, a Ni(NO<sub>3</sub>)<sub>2</sub> (C<sub>Ni(2+)</sub>=0.3011 M) solution was titrated with a

0.8015 M NaOH solution with constant stirring. A single portion of the titrant was 1 ml, and the waiting time between the introduction of the titrant and recording the pH values and solution resistance was 3 min. pH was measured using a pH-150MI meter (Ukraine) with a universal electrode. Conductometry was carried out by measuring the resistance of the solution using a high-frequency bridge (10 kHz). The arms of the bridge circuit were balanced according to the readings of a two-coordinate oscilloscope. The resistance of the solution was measured in a cell with two rigidly fixed smooth Pt electrodes with an area of 2 cm<sup>2</sup>. When measuring the resistance of the solution, the magnetic stirrer was turned off.

Determination of Ni content in the precipitate at points with different molar ratios of NaOH:Ni<sup>2+</sup> (according to the introduced components) was carried out by trilonometric titration in an ammonia medium in the presence of murexide. The precipitate was preliminarily dissolved in sulfuric acid with a slight excess.

### 5. Results of investigating the formation of nickel hydroxide

#### 5. 1. Results of determining the thermal effects of processes

Fig. 1, *a, b* shows thermochronograms of calorimetric measurements of the reaction of nickel nitrate with alkali, and Fig. 1, *c* shows the alkali dilution process.

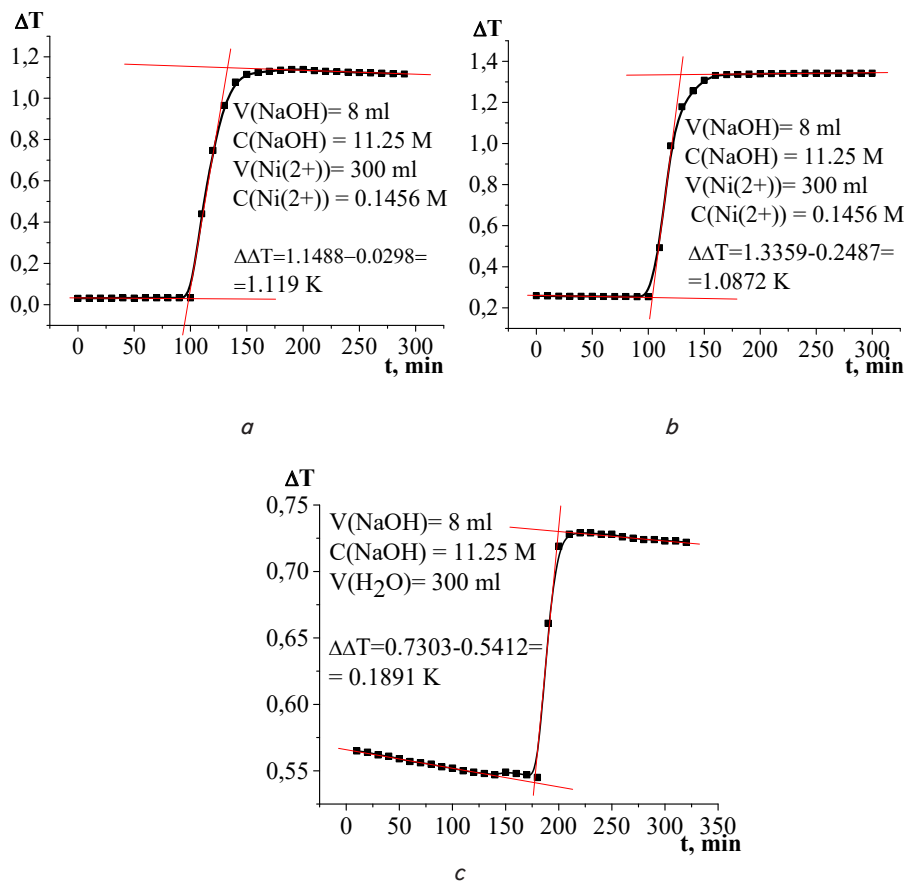


Fig. 1. Results of the calorimetric investigation of the processes occurring in the formation of nickel hydroxide from nickel nitrate: *a, b* – reactions of solutions of nickel nitrate and alkali; *c* – dilution of an alkali solution

Based on the measurement results, the enthalpy of dilution of the NaOH solution was calculated:  $\Delta H_{\text{dilution}} = -2,454 \text{ J/mol}$ . The calculated enthalpy of the reaction of nickel nitrate with NaOH was  $\Delta H_{\text{reaction} + \text{dilution}} = -29496.5 \text{ J/mol}$ . Taking into account the enthalpy of dilution, the true enthalpy of the reaction of nickel nitrate with alkali was  $\Delta H_{\text{reaction}} = \Delta_{\text{reaction+dilution}} - \Delta H_{\text{dilution}} = -29496.5 - (-2454) = -28328.5 \text{ J/mol}$ .

## 5.2. Results of investigating the formation process and composition of nickel hydroxide

Fig. 2 shows the curves of complex potentiometric (pH-metric) and conductometric titration.

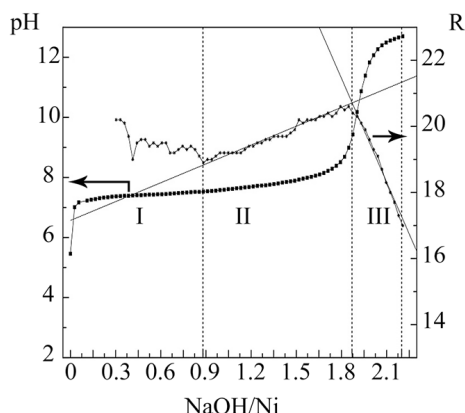


Fig. 2. Curves of complex potentiometric and conductometric titration of  $\text{Ni}(\text{NO}_3)_2$  solution with NaOH alkali solution

On the potentiometric curve  $\text{pH} = f(\text{NaOH}/\text{Ni}^{2+})$ , there is one plateau (in the range of  $\text{NaOH}/\text{Ni}^{2+}$  ratios of 0.1–1.8) and one titration jump. On the conductometric curve  $R = f(\text{NaOH}/\text{Ni}^{2+})$ , three different sections can be distinguished: section I –  $\text{NaOH}/\text{Ni}^{2+} = 0.3\text{--}0.88$ , section II –  $\text{NaOH}/\text{Ni}^{2+} = 0.88\text{--}1.87$ , and section III –  $\text{NaOH}/\text{Ni}^{2+} = 1.87\text{--}2.2$ . In section I, the resistance of the titrated solution decreased slightly, in section II, the resistance of the titrated solution increased, and in section III, the curve underwent a break, and the resistance decreased sharply.

The content of nickel was determined trilonometrically in the precipitate obtained at two molar ratios: at  $\text{NaOH}/\text{Ni}^{2+} = 1.87\text{--}52.95 \%$  Ni; at  $\text{NaOH}/\text{Ni}^{2+} = 2.2\text{--}55.63 \%$  Ni.

## 6. Discussion of the results of investigating the hydroxide formation

It was determined by calorimetric measurements that both the reaction between nickel nitrate and alkali and the dilution process were exothermic (Fig. 1). This must be taken into account when analyzing the potentiometric and coulometric titration curves.

The course of the potentiometric (pH-metric) curve was uniquely determined by the number of free  $\text{OH}^-$  ions. The initial pH of the nickel nitrate solution was 5.35 due to the hydrolysis of the nickel cation. The addition of the first portion of the NaOH titrant shifted the pH to the area of formation of insoluble nickel hydroxocompounds. On the potentiometric curve, there is one wide plateau in the range of  $\text{NaOH}/\text{Ni}$  ratios from 0.07 to 1.8. On the titration curve, there is only one titration jump. There is no jump on the titration curve at the  $\text{NaOH}/\text{Ni} = 1$  ratio. This indicates that

the potentiometric curve did not reveal the formation of a basic salt of the  $\text{NiOHNO}_3$  type.

In conductometric titration, the resistance of a solution depends on the ions present in the solution, their concentration, and electrical conductivity. The resistance of the solution is also affected by changes in temperature and the presence of a dispersed phase in the solution. It should be noted that the equivalent electrical conductivity of ions with infinite dilution was:  $\text{OH}^- - 198.3 \text{ S}\cdot\text{cm}^2/\text{mol}$ ,  $\text{Na}^+ - 50.1 \text{ S}\cdot\text{cm}^2/\text{mol}$ ,  $\frac{1}{2}\text{Ni}^{2+} - 54.0 \text{ S}\cdot\text{cm}^2/\text{mol}$ . When sodium alkali was added to a solution of nickel nitrate, the  $\text{Ni}^{2+}$  cation reacted with  $\text{OH}^-$  to form a precipitate. The  $\text{Ni}^{2+}$  cation was removed from the solution, and the  $\text{Na}^+$  cation entered the solution. In this case, based on the equivalent electrical conductivity of the cations, the conductivity of the solution slightly decreased, and the resistance increased respectively.

In section I (Fig. 2), a decrease in resistance was observed with an increase in the NaOH/Ni ratio. This contradicts the conclusions made on the basis of equivalent electrical conductivities of cations. It was hypothesized that resistance reduction was possible in two ways. The first way was associated with the formation of small colloidal particles, which, due to the charge, could be additional current carriers. The formation of a sparingly soluble nickel compound with small particles in section I was visually confirmed: no precipitation was observed in the solution. However, charged colloidal particles had significantly lower mobility than ions, and this way could not make a significant contribution to the increase in electrical conductivity. The influence of the second way seemed to be more significant. In calorimetric investigations, it was found that the reaction of nickel nitrate with alkali was exothermic. As a result, the temperature of the solution rose, while the ion mobility and electrical conductivity increased significantly, and the resistance decreased. Some fluctuations in resistance most likely indicate system instability.

In section II ( $\text{NaOH}/\text{Ni}$  ratio = 0.88–1.87), an increase in solution resistance with an increase in the ratio was observed. At the same time, the formation of a precipitate is visually observed in the solution due to the coagulation of particles. As mentioned above, the replacement of  $\text{Ni}^{2+}$  cations by  $\text{Na}^+$  in the reaction during titration should slightly increase the resistance of the solution. In section II, small charged colloidal particles (which increased electrical conductivity) coagulated into larger uncharged particles, which reduced electrical conductivity. It should be pointed out that another effect had a greater influence. The resistance of the solution was inversely proportional to the electrical conductivity and directly proportional to the length of the current path (2):

$$R = \frac{1}{\kappa} \cdot \frac{l}{S}, \quad (2)$$

where  $\kappa$  is the electrical conductivity;  $S$  is the cross-section of current flow;  $l$  is the length of the current path.

In a true solution, the length of the current path was equal to the geometric distance between the electrodes. However, in a suspension that formed in section II and contained a large number of rather large non-conducting particles, the length of the current path increased significantly, since the electric field lines went around the insulators. In this case, the resistance of the solution increased.

At the junction of sections II and III, there was a sharp break in the resistance curve at a molar ratio of  $\text{NaOH}/\text{Ni}^{2+} = 1.87$ , with a sharp decrease in the resistance

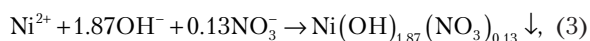
of the solution in section III. Since the equivalent electrical conductivity of  $\text{OH}^-$  was almost 4 times higher than that of  $\text{Na}^+$ , a sharp decrease in resistance could only be explained by the appearance of free  $\text{OH}^-$  anions in the solution. And this was possible if, at a molar ratio of  $\text{NaOH}/\text{Ni}^{2+}=1.87$  in the titrated solution, the formation of the primary form of the precipitate was completed and there were no free  $\text{Ni}^{2+}$  cations in the solution. However, for the formation of a precipitate with the formula  $\text{Ni}(\text{OH})_2$ , the molar ratio  $\text{NaOH}/\text{Ni}^{2+}=2$  was necessary. It should be concluded that the primary form of the precipitate contained both  $\text{OH}^-$  anions and  $\text{NO}_3^-$  anions and could be described by the formula  $\text{Ni}(\text{OH})_{1.87}(\text{NO}_3)_{0.13}$ . Such a formula could correspond to both the basic salt and the nitrate-doped nickel hydroxide. At the same time, it is known [51] that basic nickel salts have a double-layered lattice corresponding to the crystal lattice of  $\alpha\text{-Ni}(\text{OH})_2$ . Due to the low content of the nitrate anion, it is most correct to consider the primary form of the precipitate as nitrate-doped  $\alpha\text{-Ni}(\text{OH})_2$ . For clarification, the content of Ni in the precipitate obtained at  $\text{NaOH}/\text{Ni}^{2+}$  ratios of 1.87 and 2.2 was determined. The precipitate obtained with  $\text{NaOH}/\text{Ni}^{2+}=1.87$  contained 52.95 % Ni. In this case, the Ni content in the substance with the formula  $\text{Ni}(\text{OH})_{1.87}(\text{NO}_3)_{0.13}$  should be 59.56 %. This contradiction was resolved taking into account that the  $\alpha$ -modification of hydroxides and basic salts contained water molecules in the interlayer space and was actually a crystalline hydrate. With this in mind, according to the results of the analysis for nickel, the formula of the primary precipitate was  $\text{Ni}(\text{OH})_{1.87}(\text{NO}_3)_{0.13}\cdot 0.68\text{H}_2\text{O}$ . The content of Ni in the precipitate obtained with  $\text{NaOH}/\text{Ni}^{2+}=2.2$  turned out to be higher and amounted to 55.63 %. Taking into account the water of crystallization, the formula of the final precipitate was  $\text{Ni}(\text{OH})_2\cdot 0.71\text{H}_2\text{O}$ , which correlated well with the formula of the  $\alpha$ -modification of nickel hydroxide ( $\text{Ni}(\text{OH})_2\cdot 0.66\text{H}_2\text{O}$ ). It can be stated that in section II, the nickel content in the precipitate increased with the formation of  $\alpha\text{-Ni}(\text{OH})_2$  at the end.

At a molar ratio of  $\text{NaOH}/\text{Ni}^{2+}=1.87$ , there was an abrupt transition from the liquid-phase reaction of  $\text{Ni}^{2+}$  and  $\text{OH}^-$  ions, which had a high rate [51] to a much slower topochemical reaction of the primary precipitate with the  $\text{OH}^-$  anion with the replacement of nitrate ions by hydroxyl anions with the transition of the precipitate into  $\alpha$ -nickel hydroxide. Most likely, the reaction rate of the primary precipitate with alkali was so low that the reaction time of the alkali contained in 1 ml of titrant (0.8 M NaOH solution) with the primary precipitate exceeded 3 minutes, after which the resistance measurement took place. As a result, at the time of measurement, the titrated solution contained a certain amount of free  $\text{OH}^-$  ions.

As a result of the analysis of the conductometric curve, the chemical mechanism of  $\text{Ni}(\text{OH})_2$  formation from nitrate can be described as a two-stage one:

1) homogeneous reaction with the formation of a primary precipitate with the formula of nitrate-doped  $\alpha$ -nickel hydroxide;

2) topochemical reaction of nitrate-doped nickel hydroxide with an additional amount of alkali to form  $\alpha\text{-Ni}(\text{OH})_2$ . The chemical reactions of both stages can be written as:



The high rate of the liquid-phase reaction (4) described in [51] was confirmed by the almost instantaneous (within 5–7 s) determination of the resistance value of the solution after the introduction of a portion of the titrant in sections I and II. An analysis of equation (2) showed that in the course of the reaction, not only the replacement of the nickel cation by the sodium cation occurred in the solution, but also the removal of nitrate anions from the solution. As a result, it should be concluded that an additional factor in increasing the resistance of the solution in section II was a decrease in the number of charge carriers due to the transition of  $\text{NO}_3^-$  from the solution to the precipitate.

It should also be noted that the results of the study allowed us to practically substantiate the known fact of the preferential formation of  $\alpha\text{-Ni}(\text{OH})_2$  from nickel nitrate.

The main limiting factor of this study is the confirmation of the composition of the primary precipitate only by the results of conductometric titration and chemical analysis for nickel of precipitate samples obtained only at two  $\text{NaOH}/\text{Ni}^{2+}$  ratios. To eliminate this limitation, it is necessary to obtain samples for several  $\text{NaOH}/\text{Ni}^{2+}$  ratios with the further determination of their composition. It is also necessary to confirm the  $\alpha$ -modification of the crystal lattice by X-ray phase analysis. A limitation of the study is that the mechanism for the formation of nickel hydroxide from nickel nitrate alone has been determined, while this nickel salt is more expensive than other salts (sulfates and chlorides). As a result, the data obtained can be used in the synthesis of nickel hydroxides and nickel LDHs, especially in homogeneous precipitation. The revealed mechanism for the formation of the  $\alpha$ -modification of nickel hydroxide will justify the choice of nitrate precursors for the synthesis of  $\alpha\text{-Ni}(\text{OH})_2$ , and especially LDH, which have a similar crystal lattice. In addition, the revealed formation of the nitrate-doped primary form of nickel hydroxide puts forward the requirements for the need to hold the precipitate with the mother liquor for the topochemical reaction to occur with the formation of complete hydroxide.

## 7. Conclusions

1. A calorimetric investigation of the thermal effects of processes occurring during the interaction of nickel nitrate with alkali has been carried out. It is shown that the reaction of nickel nitrate with NaOH is exothermic with  $\Delta H_{\text{reaction}} = -28328.5 \text{ J/mol}$ . The exothermic nature of the NaOH dilution process with  $\Delta H_{\text{dilution}} = -2454 \text{ J/mol}$  was revealed.

2. The mechanism of formation of nickel hydroxide from nickel nitrate solution was investigated by the method of simultaneous potentiometric and conductometric titration. According to the results of potentiometric titration, the formation of a basic salt of the  $\text{NiOHNO}_3$  type was not revealed. The results of conductometric titration revealed a two-stage chemical mechanism for the formation of nickel hydroxide from nitrate. At the first stage, which has a high rate, the liquid-phase reaction of the nickel cation with the hydroxyl anion results in the formation of a primary precipitate of the composition  $\text{Ni}(\text{OH})_{1.87}(\text{NO}_3)_{0.13}$ . In the second stage, as a result of a slow topochemical reaction of the primary precipitate with hydroxyl anions, nitrate ions are displaced from the precipitate to form nickel hydroxide. These data were confirmed by analysis

of precipitates obtained at NaOH/Ni<sup>2+</sup> ratios of 1.87 and 2.2. The Ni content in this precipitate was shown to be 52.95 % and 55.63 %, corresponding to the formulas Ni(OH)<sub>1.87</sub>(NO<sub>3</sub>)<sub>0.13</sub>·0.68H<sub>2</sub>O and Ni(OH)<sub>2</sub>·0.71H<sub>2</sub>O. These data clearly indicate that the primary precipitate is nitrate-doped α-Ni(OH)<sub>2</sub> and the final precipitate corresponds to the α-modification of nickel hydroxide.

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#### Conflict of interest

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The authors declare no conflicts of interest in relation to this paper, as well as the published results of the

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#### Data availability

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The manuscript has no associated data.

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