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KINETICS AND STOICHIOMETRIC MECHANISM OF THE REACTION OF NICKEL CHLORIDE WITH SODIUM DITHIONITE

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Abstract. The paper investigates the kinetics of the reaction of nickel chloride with sodium dithionite in an aqueous solution, proceeding with the formation of metallic nickel via the reduction of nickel cations. As a result, parallel to the main process stage, reactions of sodium dithionite decomposition occur, yielding sulfite, thiosulfate, and sulfide as final products. Based on the analysis of experimental data and literature, a stoichiometric mechanism of the process has been proposed. Using mathematical modelling, the inverse kinetic problem of determining the rate constants of individual process stages has been solved. According to the comparison of experimental and calculated kinetic dependencies, the proposed mathematical model correlates with the experimental data.

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Introduction

Conducting processes of chemical reduction of metal salts from solutions to obtain metallic coatings on various materials, metal powders, and nanofilms requires detailed knowledge of the mechanism and kinetics of the chemical transformations involved. One of the traditionally used reducing agents is sodium dithionite, $\text{Na}_2\text{S}_2\text{O}_4$ (technical name: sodium hydrosulfite). It is inexpensive bulk chemical product providing a high reduction rate even at room temperature [1]. The highly negative redox potential of sodium dithionite allows it to reduce a wide range of metal cations and their complex salts [2-4], as well as various organic compounds [5-8]. Its instability, especially in aqueous solutions, is a disadvantage.

Previously, we studied the patterns of the reaction between sodium dithionite and nickel cations under conditions of metallising Nitron fiber (pH 4.00, temperature 303 K) [9]. As a result, nickel sulfide as one of the by-products of metallic nickel was formed. Moreover, an excess of sodium dithionite was not resulted in complete reduction of nickel cations. It is associated with the parallel process of reductant decomposition. Based on kinetic data, a



reaction scheme was proposed. It includes pathways involving dithionite anions $\dot{S}O_2^-$ and sulfur dioxide radical $S_2O_4^{2-}$ as reducing agents. Raising of the temperature increases the contribution of the pathway. Using the quasi-steady-state approximation method, a rate equation for the reaction on nickel cation concentration was derived.

However, the stoichiometric mechanism proposed in that work and the kinetic description within the quasi-steady-state approximation model are insufficient for a complete quantitative account of all stages of this reaction. For example, side reactions related to the decomposition of sodium dithionite were not considered, despite available literature data on the chemistry of this process under various external conditions (temperature, acidity) [1, 10]. The presented kinetic description within the quasi-steady-state approximation allows calculation of the decrease in nickel concentration over time. However, it cannot be applied for the calculation of concentrations of other reaction participants: dithionite, metallic nickel, nickel sulfide, and dithionite decomposition products.

The purpose of the study is to provide a complete kinetic description of the reaction of nickel chloride with sodium dithionite in an aqueous solution.

Main body

For the study we used nickel chloride $NiCl_2 \cdot 6H_2O$ of chemical purity grade (ChP) GOST 4038-79 (Russia) and sodium dithionite $Na_2S_2O_4$ grade Ch (pure) produced by ALBITE SRL (Italy) with a main substance content of 89%.

The reaction of nickel chloride with sodium dithionite was conducted in a universal Robinson-Britton buffer solution at pH = 4.0 [11] with the addition of KCl (0.2 mol/L) to maintain constant ionic strength. According to the previous experiments, atmospheric oxygen does not affect on the extent and rate of the reduction process. Therefore, the studies were conducted in air. To obtain kinetic curves, the "time-slice" method was used. A series of working solutions with the same initial concentrations was prepared in 10 mL test tubes by mixing equal volumes of oxidiser and reducer solutions. At specific time intervals, the reaction was stopped by adding 1 mL of a 36% formaldehyde solution; the concentrations of reagents and products in the reaction system were determined. The titration results were referred to the moment of formaldehyde introduction. The sodium hydroxymethanesulfinate formed during the interaction of CH_2O and $Na_2S_2O_4$ practically does not decompose under the experimental conditions. The concentration of nickel ions was determined by complexometric titration [12]; the concentration of dithionite was determined iodometrically by [13]. The precipitate, containing metallic nickel and nickel sulfide, was separated from the solution by centrifugation and dried. The nickel sulfide content was determined iodometrically after dissolving the precipitate in 2N hydrochloric acid [12]. The amount of metallic nickel formed was found from the material balance.

All experiments were performed at a constant temperature of 303 ± 0.1 K, as at lower temperatures the rate of reduction of nickel ions to metal is low; at higher temperatures large amounts of nickel sulfide are formed. An initial excess of the reducing agent compared to the amount of nickel chloride is necessary for the reaction to proceed at a noticeable rate. The



solution pH choice is as follows: at higher pH nickel chloride hydrolyses to form hydroxide; at lower pH the decomposition rate of sodium dithionite is high.

Figure 1 shows the dependencies of the concentrations of sodium dithionite, nickel cations, and nickel sulfide on the reaction time.

According to the experimental data, the decrease in dithionite concentration significantly exceeds the amount of reacted nickel chloride. Therefore, the consumption of the reducing agent is unproductive. It is necessary to be considered both for this and other reactions with sodium dithionite.

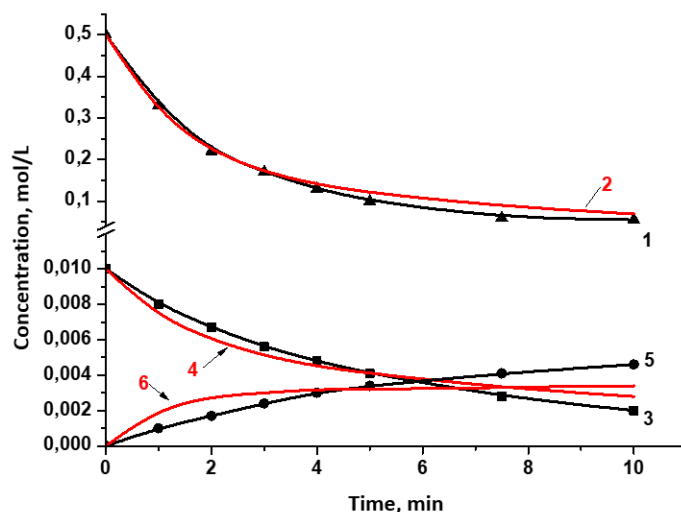


Fig. 1. Changes in the concentrations of dithionite (1,2), nickel cations (3,4), and nickel sulfide (5,6). Black kinetic curves with points show experimental data; red continuous fine line curves show calculations.

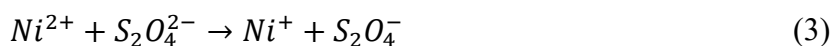
According to the introduction, the reducing particles of dithionite anions $S_2O_4^{2-}$ and sulfur dioxide anion radicals in sodium dithionite solutions are formed through the reversible disproportionation reaction:



However, the numerical values of the equilibrium constant for reaction (1) reported in the literature range from $0.51 \cdot 10^{-9}$ mol/L [14] to $3.80 \cdot 10^{-9}$ mol/L [15]. As claimed by these values, the concentration of anion radicals in the dithionite solution is neglected. Therefore, nickel cations are reduced to metal primarily by dithionite ions via the reaction:



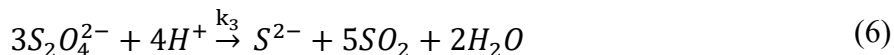
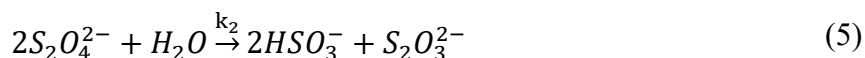
Moreover, stage (2) is not elementary and refers to the stoichiometric mechanism of the reaction. In particular, as indicated in study [9], the formation of nickel occurs through sequential reactions:



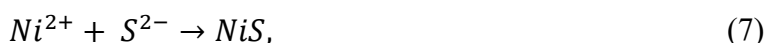
However, since lower valence ions exhibit high reactivity, reaction (4) proceeds rapidly than reaction (3); formally, the interaction between nickel ions and dithionite can be described by equation (2).



The significant decrease in dithionite concentration (curve 1, Fig. 1) is primarily due to its decomposition; in an acidic medium it occurs via two parallel pathways [10, 16, 17]:



It is assumed that stage (5) is non-catalytic, while stage (6) is catalytic and accelerated by so-called "active sulfur" [10], formed during the decomposition of thiosulfate anions $S_2O_3^{2-}$. The source of nickel sulfide (curve 5, Fig. 1) is the reaction:



preceded by stage (6), and it is highly probable that stage (7) proceeds instantaneously. Thus, the rate of nickel sulfide accumulation is limited by the rate of reaction (6).

Therefore, to solve the inverse kinetic problem (determining the rate constants of individual stages of the studied reduction process of nickel chloride by sodium dithionite using experimentally obtained kinetic dependencies) the stoichiometric model consisted of stages (2), (5), and (6).

The mathematical model was represented by a system of differential equations:

$$-\frac{dC_{Ni^{2+}}}{d\tau} = k_1 C_{Ni^{2+}} \cdot C_{S_2O_4^{2-}} \quad (8)$$

$$-\frac{dC_{S_2O_4^{2-}}}{d\tau} = k_1 C_{Ni^{2+}} \cdot C_{S_2O_4^{2-}} + 2k_2 C_{S_2O_4^{2-}}^2 + 3k_3 C_{S_2O_4^{2-}}^3 \quad (9)$$

$$\frac{dC_{Ni}}{d\tau} = k_1 C_{Ni^{2+}} \cdot C_{S_2O_4^{2-}} \quad (10)$$

$$\frac{dC_{SO_2}}{d\tau} = k_1 C_{Ni^{2+}} \cdot C_{S_2O_4^{2-}} + k_2 C_{S_2O_4^{2-}}^2 + k_3 C_{S_2O_4^{2-}}^3 \quad (11)$$

$$\frac{dC_{S_2O_3^{2-}}}{d\tau} = k_2 C_{S_2O_4^{2-}}^2 \quad (12)$$

$$\frac{dC_{NiS}}{d\tau} = k_3 C_{S_2O_4^{2-}}^3 \quad (13)$$

The concentration of SO_2 in equation (11) included the total concentration of sulfite sulfur for the reactions (2), (6), and (5); in the latter, in the form of HSO_3^- anions.

Mathematical modelling of studied reaction kinetics was performed using the KINET software for numerical simulation of complex chemical reaction kinetics (Abramenkov A.V., Department of Physical Chemistry, Faculty of Chemistry, Lomonosov Moscow State University, Russia). To find the optimal values of the rate constants, experimental dependencies of the concentrations of dithionite, nickel ions, and nickel sulfide on time were used, along with the following initial reagent concentrations: $C_{S_2O_4^{2-}}^0 = 0.5$ mol/L; $C_{Ni^{2+}}^0 = 0.01$ mol/l. The initial concentrations of sulfide, sulfite, thiosulfate, and nickel metal were set to zero.



However, the search for rate constants with arbitrarily chosen initial approximations was unsuccessful. Therefore, the inverse kinetic problem was addressed in two stages. At the first stage, reaction (6) was excluded from the system; the concentration arrays for nickel ions and dithionite were adjusted accordingly. Equation (13) was removed from the system of rate equations; the last terms in equations (9) and (11) were omitted. Initial approximations for constants k_1 and k_2 were estimated from the initial segments of the adjusted kinetic curves for nickel ions and dithionite. The search for optimal values of the constants yielded the following results: $k_1 = 0.308 \text{ L}/(\text{mol}\cdot\text{min})$; $k_2 = 0.608 \text{ L}/(\text{mol}\cdot\text{min})$.

At the second stage, the initial approximation for the rate constant of stage (6) was estimated. Therefore, the dependence of dithionite concentration on time was obtained by subtracting, for each time point; the concentration of dithionite consumed in stages (2) and (5). This dependence was processed assuming a third-order reaction, as follows from equation (6), considering that the hydrogen ion concentration was constant. The initial approximation was $kk_3 = 3.36 \cdot 10^{-2} \text{ } \pi^2/(\text{mol}^2\cdot\text{min})$.

The search for optimal values of the rate constants after solving the entire system of equations (8) – (13) using the obtained initial approximations led to the following results: $k_1 = 1.00 \text{ L}/(\text{mol}\cdot\text{min})$; $k_2 = 0.61 \text{ L}/(\text{mol}\cdot\text{min})$; $k_3 = 0.05 \text{ L}^2/(\text{mol}^2\cdot\text{min})$.

Figure 1 shows the calculated kinetic dependencies (curves 2, 4, 6) for the found optimal values of the rate constants of stages (2), (5), and (6) in comparison with experimental data. Figure 2 shows the calculated dependencies for dithionite decomposition products: sulfite (curve 1) and thiosulfate (curve 2). Additionally, Figure 2 shows kinetic dependencies for nickel, calculated from the modelling results (curve 3) based on experimental material balance data (curve 4).

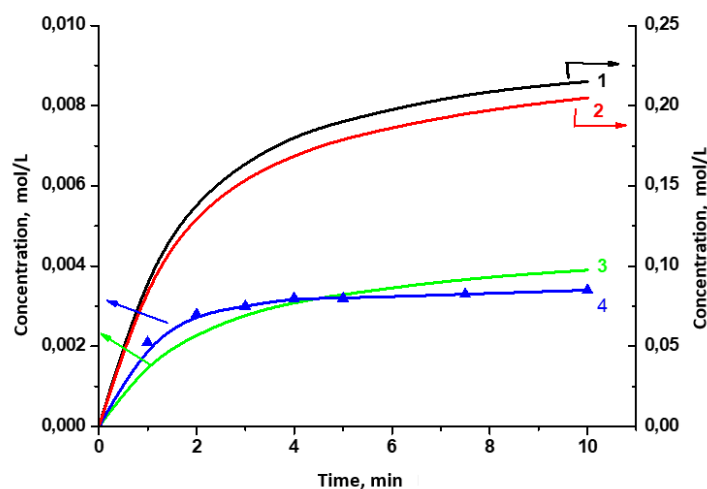


Fig. 2. Changes in the concentrations of sulfite (1), thiosulfate (2), and nickel (3,4). Dependencies 1, 2, 3 are calculated from the mathematical model (8)-(13); 4 is calculated from experimental data.

In general, the proposed stoichiometric mechanism of the studied complex reaction and the kinetic model describe the experimental data. The slight discrepancy between the calculated kinetic curve for NiS and the experimental data can be explained by the earlier assumption on stage (6) is autocatalytic and should be preceded by stage (5). Moreover, the induction period should be observed on the curve of nickel sulfide concentration versus time. However, as it can



be estimated from the slope of kinetic curve 5 (Fig. 1), it had not been observed due to the sufficiently high initial rates of both stages. The initial rate of NiS formation is lower than that of the calculated curve 6 (Fig. 1), possibly due to autocatalysis.

According to data in Fig. 2, the majority of the reducing agent - sodium dithionite - decomposes in the reaction to form sulfite and thiosulfate. The formation of metallic nickel consumed only a small reducing agent portion. For example, by the 10th minute, only 0.7% of the dithionite was used for nickel formation relative to its total consumption.

Table 1 shows the values of the degree of nickel chloride conversion to metallic nickel at different time points during the reaction. They were calculated from experimental α_{exp} and simulated α_{calc} data. These values were computed as the ratio of metallic nickel to initial nickel chloride formed by that time point.

Table 1. Degrees of nickel chloride conversion to metallic nickel at different time points. α_{exp} is calculated from experimental data; α_{calc} is calculated from the simulated kinetic curves.

	Time, min						
	1	2	3	4	5	7.5	10
α_{exp}	0.50	0.48	0.45	0.42	0.42	0.43	0.43
$\alpha_{\text{calcul.}}$	0.41	0.43	0.43	0.44	0.44	0.45	0.45

According to Table 1, on average 44% of nickel chloride is consumed for the formation of metallic nickel; 56% is used for the formation of nickel sulfide. Generally, the calculated and experimental data are in approximate agreement, except for the initial period of the reaction. It is associated with the previously noted discrepancy in the kinetic curves for nickel sulfide.

Conclusions

As a result of studying the reaction of nickel chloride with sodium dithionite, its stoichiometric mechanism has been established. Those includes the stages of metallic nickel and nickel sulfide formation, the decomposition of dithionite anions yielding sulfite, sulfide, and thiosulfate. Experimental kinetic dependencies for the initial reagents and one of the reaction products - nickel sulfide – allow us to perform mathematical modelling of the reaction kinetics and calculate the rate constants of its individual stages. The obtained results can be applied in the practical use of sodium dithionite in other reactions occurring in aqueous solutions.

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