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# Kinetic analysis of sodium nitrate(III) inversion with nitric acid(V)

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## Abstract

Kinetic measurements of the sodium nitrate(III) inversion with the nitric acid(V) process, carried out in the range of $c_{0\mathrm{NaNO_2}}$: 0.25–0.5 mol/dm$^3$, $c_{0\mathrm{HNO_3}}$: 1.5–3.0 mol/dm$^3$, $T = 303$–$353$ K, $Re_\mathrm{m} = 8500$, were presented. A reaction rate equation and Arrhenius equation parameters were determined on the basis of the results obtained. It was found that in the examined parameter ranges the overall process rate could be described by a second-order kinetic equation.

*Keywords:* Sodium nitrate(III); Nitric acid(V); Inversion process; Kinetic equation

## 1. Introduction

Inversion (oxidation of $NaNO_2$ to $NaNO_3$ with the $HNO_3$) is an important element of handling solutions acquired in the process of nitrogen oxides removal from waste gases by means of the alkali absorption in $Na_2CO_3$ solution [1]. The obtained $NaNO_2$ and $NaNO_3$ solution is then exposed to sodium nitrate(III) fractional crystallisation, so its remaining part is oxidised to sodium nitrate(V) by means of nitric acid(V).

Inversion is a consecutive-parallel complex process carried out in the two-phase system and consists of the following stages [1–5]:

(a) decomposition of $NaNO_2$:

$$NaNO_2 + HNO_3 \rightarrow NaNO_3 + HNO_2 \tag{1}$$

(b) decomposition of $HNO_2$ (it may run by one of the three ways):

$$3HNO_2 = HNO_3 + 2NO + H_2O \tag{2}$$

$$2HNO_2 = NO_2 + NO + H_2O \tag{3}$$

$$HNO_2 + HNO_3 = 2NO_2 + H_2O \tag{4}$$

(c) desorption of nitrogen oxides from the solution.

Special physical and chemical properties of the discussed process strongly limit a possibility of creating its both stoichiometric and kinetic model.

Difficulty in balance calculations of the reacting system arises from the fact, that depending on $HNO_2$ decomposition process course (reactions (2)–(4)), it is possible to describe the overall inversion process by three different equations, which substantially differ from one another in the nitric acid balance:

$$3NaNO_2 + 2HNO_3 = 3NaNO_3 + 2NO + H_2O \tag{5}$$

$$2NaNO_2 + 2HNO_3 = 2NaNO_3 + NO + NO_2 + H_2O \tag{6}$$

$$NaNO_2 + 2HNO_3 = NaNO_3 + 2NO_2 + H_2O \tag{7}$$

The characteristic feature of the inversion process is that hydrodynamic conditions in the reacting system substantially influence the overall process rate. It results in essential difference in the literature kinetic data regarding the inversion process [4–11]. On the basis of the own kinetic measurements, carried out in a semi-batch reactor [12], it was found, that mixing exerts substantial effect on the inversion process rate and, thus, determines its limiting stage. Increase in mixing rate up to 1000 rpm (which corresponds to the mixing Reynolds number, $Re_\mathrm{m} = 8500$) causes in essential increasing in the inversion process overall rate (Fig. 1). In the $Re_\mathrm{m} \geq 8500$ range, increase in mixing intensity not effects the inversion process overall rate.

Another problem, making the inversion process kinetics measurements difficult, is a necessity of analytical determination of the reacting system composition. While the process is running, the system is in an unsteady state, thus the concentrations of all reagents present in the system ($NO_2{}^-$, $NO_3{}^-$ and $H_3O^+$ ions and nitrogen oxides dissolved in

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**Nomenclature**

| | |
|---|---|
| $\lambda$ | wavelength (nm) |
| $c$ | concentration (mol/dm$^3$) |
| $E$ | activation energy in Arrhenius equation (J/mol) |
| $k$ | reaction rate constant (dm$^3$/(mol s)) |
| $k_0$ | constant in Arrhenius equation (dm$^3$/(mol s)) |
| $n$ | number of experimental points |
| $R$ | gas constant (J/(mol K)) |
| Reg | regression coefficient |
| $r$ | reaction rate (mol/(dm$^3$ s)) |
| $Re_m$ | mixing Reynolds number |
| $S_c^2$ | concentration measurement variance ((mol/dm$^3$)$^2$) |
| $t$ | time (s) |
| $T$ | temperature (K) |

*Indexes*

| | |
|---|---|
| 0 | initial |
| calc | calculated |
| exp | experimental |

solution) are varying in time. Part of nitrogen oxides is desorbed from the system, the rest can again react with the water forming $HNO_3$ and $HNO_2$. Nitric acid(III) can desorb into gaseous phase directly from liquid phase as well, what was reported by Crowford and Counce [7].

In order to determine the actual liquid phase composition, it is necessary to stop chemical reactions and phase changes running in the system. For those purpose, a liquid sample from the reacting system is introduced to excess strong alkali solution (e.g. NaOH) [4–6]. The following neutralisation reactions proceed:

$$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O \tag{8}$$

$$HNO_2 + NaOH \rightarrow NaNO_2 + H_2O \tag{9}$$

and reactions of alkali with nitrogen oxides dissolved in the solution:

$$NO + NO_2 + 2NaOH \rightarrow 2NaNO_2 + H_2O \tag{10}$$

$$2NO_2 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O \tag{11}$$

$$N_2O_3 + 2NaOH \rightarrow 2NaNO_2 + H_2O \tag{12}$$

$$N_2O_4 + 2NaOH \rightarrow NaNO_2 + NaNO_3 + H_2O \tag{13}$$

On analytical way, it is possible to determine only an overall concentration of $NO_2^-$ ions ($c_{NO_2^-}$) corresponded to total concentration of both $NaNO_2$, $HNO_2$ in reacting solution and $NaNO_2$ being an effect of undesorbed nitrogen oxides presence (reactions (10)–(13)).

As an effect of outlined limitations there is a discrepancy in experimental data published. The differences in opinion appear both in assumed limiting stage (according to Krichewski and Kantorovich [5] an inversion process overall rate is limited by nitric acid(III) decomposition process rate, whereas according to Popovich [4]—a reaction (1) rate) and in the form of the inversion process kinetic equation [3,4,8–11].

The inversion kinetics in conditions corresponded to industrial reactor ($c_{0NaNO_2} = 4.06\,mol/dm^3$) and desorber ($c_{0NaNO_2} = 0.145\,mol/dm^3$) was described earlier [13–15]. However, the kinetic data were not described by appropriate kinetic equation. The aim of presented work was to investigate experimentally the inversion process course in the following parameters ranges: $c_{0NaNO_2} = 0.25–0.5\,mol/dm^3$, $c_{0HNO_3} = 1.5–3.0\,mol/dm^3$, $T = 303–353\,K$ and determined on the basis of the obtained data the inversion process kinetic equation.

## 2. Experiments

The kinetic measurements were carried out under isothermal conditions in a semi-batch reactor with a mixer. The specified amount of $NaNO_2$ solution was introduced to the reactor. Then, it was heated to the process temperature and, after that, the relevant amount of $HNO_3$ solution, heated to the same temperature, was dozed. The reactor content was mixed and a small vacuum (about 2 kPa) removed the produced nitrogen oxides. At certain time intervals samples of liquid phase were taken from the solution and their compositions were determined. The concentrations of $NO_2^-$ and $NO_3^-$ ions were determined by means of a direct spectrophotometric method [16]. The concentration of $NO_2^-$ ions was determined at the wavelength, $\lambda = 355\,nm$; whereas the concentration of the sum of $NO_2^-$ and $NO_3^-$ ions was determined at the wavelength, $\lambda = 301.5\,nm$. The

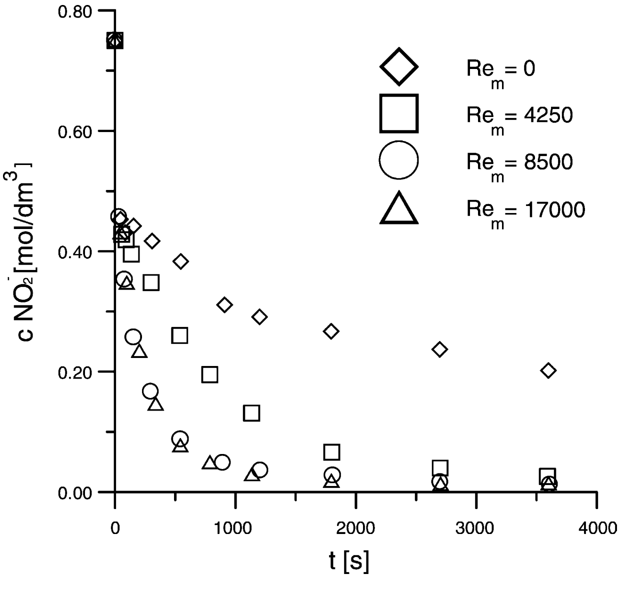

Fig. 1. The kinetic curves of $NaNO_2$ inversion process. $c_{0NaNO_2} = 0.75$ mol/dm$^3$, $c_{0HNO_3} = 3\,mol/dm^3$, $T = 303\,K$.

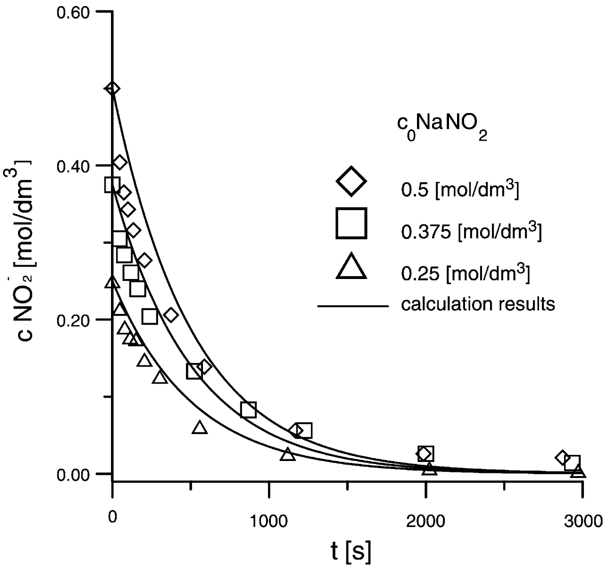

Fig. 2. Kinetic curves of the $NaNO_2$ inversion process—series I. $c_{0HNO_3} = 3\,mol/dm^3$, $T = 303\,K$.

current concentration of $H_3O^+$ ions was determined titrimetrically. The relative error of determination of $NO_2^-$ ions was 1.3%, $NO_3^-$ ions: 4.9% and $H_3O^+$ ions: 0.4%. The analytical method accuracy (expressed by a single result variance, $S_c^2$) was $S^2_{NO_2^-} = 5.86 \times 10^{-6}\,(mol/dm^3)^2$, $S^2_{NO_3^-} = 0.81 \times 10^{-3}\,(mol/dm^3)^2$ and $S^2_{H_3O^+} = 0.31 \times 10^{-6}\,(mol/dm^3)^2$, respectively. The total experimental method accuracy was determined for three parallel (i.e. carried out in the same conditions) introductory measurements. It was $S^2_{NO_2^-} = 7.87 \times 10^{-4}\,(mol/dm^3)^2$, $S^2_{NO_3^-} = 4.45 \times 10^{-4}\,(mol/dm^3)^2$ and $S^2_{H_3O^+} = 3.90 \times 10^{-3}\,(mol/dm^3)^2$, respectively.

The experiments covered three measurement series. The measurements of the first one were carried out for following initial conditions: $c_{0NaNO_2} = 0.25$–$0.5\,mol/dm^3$, $c_{0HNO_3} = 3\,mol/dm^3$, $T = 303\,K$. The aim of the first series was to determine reaction order related to $NaNO_2$. The aim of the second series was to determine reaction order related to $HNO_3$. The measurements were carried out for the following initial conditions: $c_{0NaNO_2} = 0.25\,mol/dm^3$, $c_{0HNO_3} = 1.5$–$3\,mol/dm^3$, $T = 303\,K$.

To investigate a dependence of kinetic constant on temperature, the measurements of the third series were carried out for solution of initial concentration, $c_{0NaNO_2} = 0.375\,mol/dm^3$ and $c_{0HNO_3} = 3\,mol/dm^3$, respectively, in the temperature range $T = 303$–$353\,K$. During the process course the reaction mixture was mixed mechanically at the mixing rate 1000 rpm (which corresponded to $Re_m = 8500$). The results are shown in Figs. 2–4.

## 3. Discussion of the results

Description of the experimental data obtained with the use of reaction rate kinetic equation was performed. As a basis of $NaNO_2$ inversion process kinetic analysis a rate of the $NO_2^-$ ions concentration ($c_{NO_2^-}$) change was taken into consideration. It could be treated as the overall process rate (being a result of rates of all the complex inversion process stages (a)–(c), thus reactions (1)–(4) and nitrogen oxides desorption).

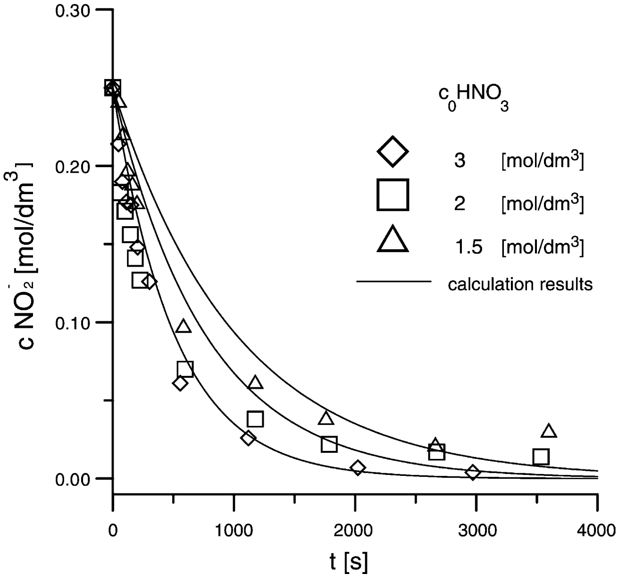

Fig. 3. Kinetic curves of the $NaNO_2$ inversion process—series II. $c_{0NaNO_2} = 0.25\,mol/dm^3$, $T = 303\,K$.

For the experimental data interpretation, an integral method was employed. It was assumed, that the inversion process is described by the following kinetic expression:

$$r = r_{NO_2^-} = -\frac{dc_{NO_2^-}}{dt} = k \times c_{NO_2^-} \times c_{HNO_3} \qquad (14)$$

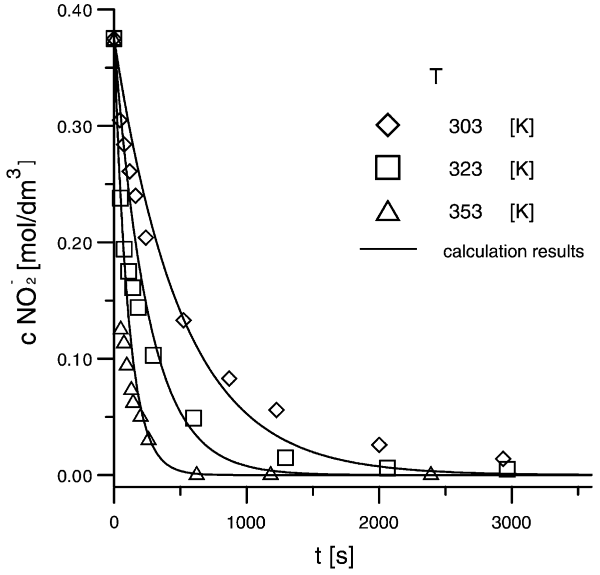

Fig. 4. Kinetic curves of the $NaNO_2$ inversion process—series III. $c_{0NaNO_2} = 0.375\,mol/dm^3$, $c_{0HNO_3} = 3\,mol/dm^3$.

Table 1
Kinetic calculation results

| No. | $c_{0NaNO_2}$ (mol/dm$^3$) | $c_{0HNO_3}$ (mol/dm$^3$) | $T$ (K) | $k'$ ($\times\ 10^3\ s^{-1}$) | $k$ ($\times\ 10^4$ dm$^3$/(mol s)) | Reg |
|---|---|---|---|---|---|---|
| 1 | 0.500 | 3 | 303 | 2.38 | 7.93 | 0.971 |
| 2 | 0.375 | 3 | 303 | 1.89 | 6.30 | 0.972 |
| 3 | 0.250 | 3 | 303 | 2.16 | 7.19 | 0.988 |
| 4 | 0.250 | 2 | 303 | 1.22 | 6.10 | 0.930 |
| 5 | 0.250 | 1.5 | 303 | 1.01 | 6.71 | 0.977 |
| 6 | 0.375 | 3 | 313 | 2.99 | 9.97 | 0.983 |
| 7 | 0.375 | 3 | 323 | 3.95 | 13.15 | 0.934 |
| 8 | 0.375 | 3 | 333 | 4.67 | 15.56 | 0.978 |
| 9 | 0.375 | 3 | 343 | 7.71 | 25.70 | 0.931 |
| 10 | 0.375 | 3 | 353 | 9.12 | 30.40 | 0.968 |

For a large HNO3 excess $c_{HNO_3} \approx$ const, thus:

$$r_{NO_2^-} = (k c_{HNO_3}) c_{NO_2^-} = k' c_{NO_2} \qquad (15)$$

After integration:

$$\ln \frac{c_{NO_2^-}}{c_{0NO_2^-}} = \ln \frac{c_{NO_2^-}}{c_{0NaNO_2}} = -k't = -(k c_{0HNO_3})t \qquad (16)$$

Both calculation results ($k'$, $k$ and regression coefficient 'Reg' of the Eq. (16) used) for individual measurements were collected in Table 1.

For Arrhenius equation parameter evaluation, the calculation results (series III—measurement 2, 6–10; Table 1) were presented in a following form (Fig. 5):

$$k = k_0 \exp\left(-\frac{E}{RT}\right) \qquad (17)$$

obtaining:

$$k\ (\mathrm{dm^3/(mol\ s)}) = 38.990 \exp\left(-\frac{3331.82}{T}\right),$$

$$\mathrm{Reg} = 0.983 \qquad (18)$$

Thus, the activation energy of the inversion process equals, $E = 27\,700$ J/mol.

Therefore, in the considered parameter ranges the inversion process is described by the following kinetic expression:

$$-\frac{dc_{NO_2^-}}{dt}\ (\mathrm{mol\ NO_2^-/(dm^3\ s)}) = 38.990 \exp\left(-\frac{3331.82}{T}\right) \times c_{NO_2^-} \times c_{HNO_3} \qquad (19)$$

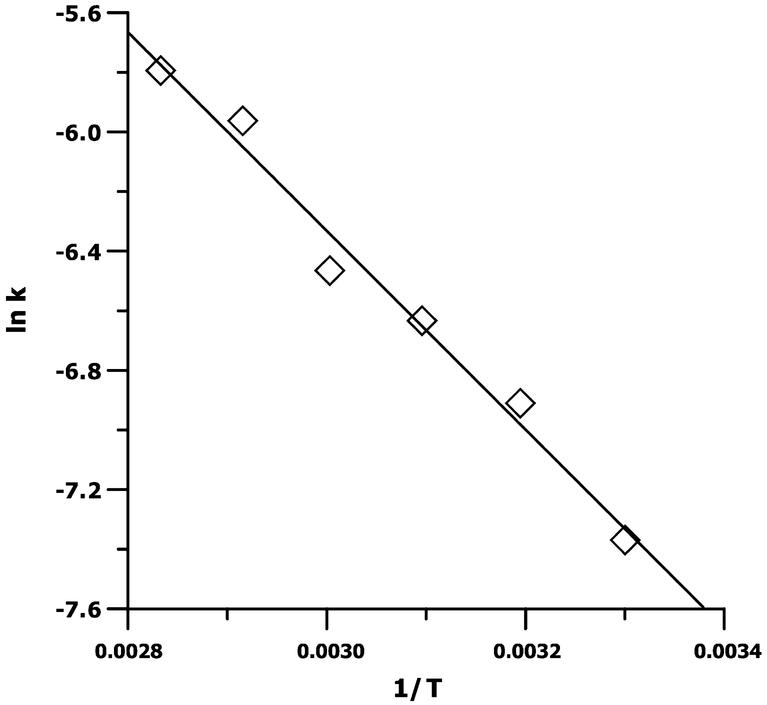

Fig. 5. Dependence of reaction rate constant $k$ on temperature.

A statistical analysis of agreement between calculation results ($c^{\text{calc}}_{\text{NO}_2^-}$), calculated by Eq. (19) and experimental data ($c^{\text{exp}}_{\text{NO}_2^-}$) was performed. The mean difference ($\text{MD}_c$) and root mean square difference ($\text{RMSD}_c$) were calculated:

$$\text{MD}_c\ (\text{mol/dm}^3) = \frac{\sum(c^{\text{calc}}_{\text{NO}_2^-} - c^{\text{exp}}_{\text{NO}_2^-})}{n} = \frac{2.104}{108} = 0.0195 \qquad (20)$$

$$\text{RMSD}_c\ (\text{mol/dm}^3) = \sqrt{\frac{\sum(c^{\text{calc}}_{\text{NO}_2^-} - c^{\text{exp}}_{\text{NO}_2^-})^2}{n-1}} = \sqrt{\frac{0.1397}{107}} = 0.0361 \qquad (21)$$

Comparison between experimental data and calculated (Eq. (19)) results was presented in Figs. 2–4 (solid lines).

## 4. Conclusions

On the basis of the kinetic experiment results it was found, that in the following parameter ranges:

- $c_{0\text{NaNO}_2} \leq 0.5\,\text{mol/dm}^3$,
- $c_{0\text{HNO}_3} \leq 3\,\text{mol/dm}^3$,
- $T = 303\text{–}353\,\text{K}$,
- $Re_{\text{m}} \geq 8500$.

the kinetics of an inversion of $\text{NaNO}_2$ with $\text{HNO}_3$ process is described by second-order kinetic equation of the form:

$$-\frac{\text{d}c_{\text{NO}_2^-}}{\text{d}t} = k \times c_{\text{NO}_2^-} \times c_{\text{HNO}_3}$$

and Arrhenius equation:

$$k\ (\text{dm}^3/(\text{mol s})) = k_0 \exp\left(-\frac{E}{RT}\right) = 38.990 \exp\left(-\frac{3331.82}{T}\right)$$

is satisfied. In the presented process conditions, its kinetics is consistent with $\text{NaNO}_2$ decomposition being the rate-limiting step:

$$\text{NaNO}_2 + \text{HNO}_3 \rightarrow \text{NaNO}_3 + \text{HNO}_2$$

The obtained kinetic expression describes the inversion process correctly and can find practical application in design calculations connected with the problems of $\text{NO}_x$ removal from waste gases by means of the alkali absorption method.

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