# MATHEMATICAL MODEL OF KINETICS OF THE TECHNETIUM-CATALYSED OXIDATION OF HYDRAZINE REACTION

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The technetium-catalysed destruction of hydrazine in nitric acid solutions proceeds through three stages: an induction period, a fast reaction period and a termination reaction period. The induction period is conditioned by the accumulation of Tc(IV). During the fast reaction period Tc(IV) is oxidized to Tc(VI) by nitrate and Tc(VI) is reduced to Tc(IV) again by hydrazine. In the terminal reaction stage technetium is slowly oxidized to Tc(VII). The oxidation of hydrazine does not proceed completely and there is some its terminal concentration in the termination of the reaction. The further oxidation of hydrazine does not occur, though there are all necessary conditions in the system for the reaction to continue.

The hydrazine oxidation in the presence of technetium in nitric acid proceeds through the forming of the intermediate product – hydrazoic acid, which is oxidized further to terminal reaction gaseous products. The oxidation of $HN_3$ is not complete, too. The maximum yield of it corresponds approximately to that time when a half of the initial amount of hydrazine is destroyed.

On the basis of experimental data on the hydrazine oxidation the empirical mathematical model of the reaction of the technetium-catalysed oxidation of hydrazine and hydrazoic acid has been made. It allows to calculate the hydrazine concentration ($C_H$) and the hydrazoic acid one ($C_{HA}$) in any moment of time. This model can be represented by the following equations:

$$C_H(t) = C_{H_t} + (C_{H_0} - C_{H_t})e^{-at^b};$$

$$a = (9{,}4 \pm 0{,}2)e^{T-328{,}41} + (2{,}2 \pm 0{,}3)e^{C_a - 6{,}91} + (0{,}12 \pm 0{,}04); \qquad b = 3 \pm 1;$$

$$C_{H_t} = (5{,}5 \pm 0{,}4) \cdot 10^{-3} e^{\frac{1}{C_{Tc}^2} - 6{,}908} + (2{,}3 \pm 0{,}1)e^{C_a - 9{,}210};$$

$$C_{HA}(t) = \frac{C_{HA_t}}{C_{H_t}} \cdot \frac{C_H(t)e^{1-C_r} - 1}{e - 1}; \qquad C_r = \frac{C_H - C_{H_t}}{C_{H_0} - C_{H_t}},$$

where $C_{H_0}, C_{H_t}$ – correspondingly an initial and a terminal $N_2H_4$ concentration, *mol/l*;

$C_{HA}, C_{HA_t}$ – correspondingly a current and a terminal $HN_3$ concentration, *mol/l*;

$C_a$ – $HNO_3$ concentration, mol/l;

$C_{Tc}$ – technetium concentration, *mol/l*;

$T$ – temperature, *K*.

The terminal hydrazine concentration $C_{H_t}$ in the system without plutonium does not depend on temperature $T$ reaction and initial hydrazine concentration $C_{H_0}$. The first fact shows that temperature influences the hydrazine oxidation rate only but does not on a completeness of this process. Independence $C_{H_t}$ on $C_{H_0}$ proves the fact that after the termination reaction a quite definite quantity of $N_2H_4$ remains in the system. It can be explained by bonding of hydrazine with some components of the studying system. One of them is hydrazoic acid. As a result relatively stable, undissociated and chemically inert compounds of $N_2H_4$ and $HN_3$ are formed. The simpliest of them is hydrazinazide. It can be assumed that Tc(IV) forms complex compounds with terminal products of hydrazine oxidation with a very branching space structure. These compounds bond hydrazine and hydrazoic acid in some associates. In a view of their large ion radiuses the hydratated ions of oxidizers have serious sterical difficulties to penetrate to molecules of $N_2H_4$ and $HN_3$.

In the system with plutonium the destruction of hydrazine and hydrazoic acid proceeds completely and there are not their remaining amounts in the termination reaction. In the system with plutonium the maximum yield of $HN_3$ is approximately twice lower than without plutonium. Equations of mathematical model for the plutonium system are as following:

$$C_H(t) = C_{H0} e^{-a' t^{b'}}; \quad a' = a - (0{,}003 \pm 0{,}001) C_{Pu}; \quad b' = 1{,}6 \pm 0{,}3;$$

$$\frac{C_{HA_{max}}}{dC_{H_0}} = q \cdot \frac{e^{\frac{1-d}{1-b}} - 1}{e - 1}; \quad q = \frac{C_{HA_{max}}}{\delta C_{H0}} \cdot \frac{e - 1}{e^{1-\delta} - 1}; \quad b = \frac{C_{Ht}}{C_{H0}},$$

where $C_{Pu}$ – plutonium concentration, *g/l*;

$\delta$ – amount of $N_2H_4$ remaining at the moment of time when the maximum yield of $HN_3$ is observed.

In the system with plutonium all conditions for the associates forming remains. An absence of remaining amounts of hydrazine and hydrazoic acid can be explained by the fact that tetravalent plutonium having a small ion radius is able to penetrate to fixed compounds of hydrazine and hydrazoic acid.

The obtained mathematical model corresponds to experimental data about the oxidation of hydrazine and hydrazoic acid well (correlation factor $R$ ~0,9).