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Heterogeneous catalytic redox reactions in the chemistry and technology of the nuclear fuel cycle

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Abstract. The published data on heterogeneous catalytic redox reactions involving uranium, neptunium, plutonium and americium ions in acidic and alkaline media as well as on catalytic decomposition of some organic and nitrogen-containing inorganic components of liquid inorganic wastes are generalised. The results of kinetic studies of these reactions are analysed and possible mechanisms are considered. The bibliography includes 93 references.

I. Introduction

The perfection of technological processes aimed at increasing the productivity and reducing production costs is of particular interest in the realisation of any industrial chain. The overgrowing environmental demands call for minimisation of industrial wastes, development of non-waste technologies and a switch, in a more remote perspective, to completely closed operation cycles.

In the chemical industry, these problems have long and successfully been solved by resort to technologies based on the use of catalytic reactions. To date, it is next to impossible to find an area of 'great' chemistry, be it sulfuric acid production, ammonia synthesis, petroleum cracking, fundamental organic synthesis or any other field, where catalysts are not employed. It is not incidental therefore that the branch of chemistry concerned with the study of catalytic reactions and properties of catalytic materials long ago became an independent science.

Radiochemical technology, which is an integral part of the nuclear fuel cycle, includes the fabrication of nuclear fuel compositions, reprocessing of the used nuclear fuel aimed at isolation of a fissile material for its reuse and separation of nuclear wastes for storage and safe disposal. The majority of existing technologies of hydrometallurgy of nuclear fuel and aqueous methods for reprocessing of the used heat-releasing elements are based on redox reactions intended for the stabilisation of components of the dissolved fuel in predetermined oxidation states suitable for their separation, isolation and purification.

Manufacture of uranium, neptunium and americium in predetermined oxidation states is sometimes complicated by low rates of redox reactions, especially if non-salt-forming molecular reducing agents are used. Heterogeneous catalysts are used to increase the rates of these reactions.

In practical terms, final reprocessing of radioactive wastes, which includes fractionation and vitrification in glass or ceramic matrices as the back end of the fuel cycle, cannot successfully be implemented without preliminary removal of organic and nitrogen-containing inorganic impurities (*e.g.*, oxalic acid, complexons, urea, hydrazine, ammonium nitrate, excess nitric acid, *etc.*) from the so-called 'water-tail' fractions. The problem of their removal can also be solved using heterogeneous catalysis as a means to increase the rates of oxidative decomposition of hazardous impurities as components of liquid radioactive wastes.

To date, a large body of experimental results has been accumulated concerned with the studies of heterogeneous catalytic redox reactions of actinide ions and the use of catalysts for the decomposition of some organic and nitrogen-containing inorganic compounds in aqueous media. However, the literature data are often fragmentary and incomplete. Therefore, the present review is an attempt at systematic generalisation of the published data on heterogeneous catalytic redox reactions already applied, or potentially applicable, for radiochemical technological wet processes.

II. Heterogeneous catalytic redox reactions of actinide ions in aqueous solutions

Heterogeneous catalytic processes can successfully be used for the stabilisation of predetermined valent forms of actinides in technological solutions at radiochemical plants. Activated charcoal or finely dispersed platinum on an inert support with a well-developed surface are commonly employed as heterogeneous catalysts. The role of a support is played by activated charcoal, alumina, silica gel or ion-exchange resins. Catalytic systems based on nickel, PdS, Re_2S_7, *etc.*, have also been investigated.

1. Uranium

The reduction of U(VI) to U(IV) is the most important process in the hydrometallurgy of the nuclear fuel cycle. Several methods for the conversion of U(VI) into U(IV) in a solution exist, *viz.*, electrochemical, photochemical and heterogeneous catalytic. The latter makes use of molecular hydrogen, hydrazine, formic acid and other compounds as reducing agents.

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The reduction of U(VI) with hydrogen was carried out in carbonate solutions at 100–150 °C in the presence of a nickel catalyst (3–10 g litre^{-1}).[1–3] The U(IV) formed precipitated as $UO_2 \cdot x\,H_2O$. It was found that the reduction rate was proportional to $p_{H_2}^{0.5}$ (p_{H_2} is partial hydrogen pressure). Thus, one can suggest the following scheme of the process. Hydrogen is dissolved and adsorbed on the nickel surface:

$$H_2(\text{gas}) \rightleftharpoons H_2(\text{solution}), \quad (1)$$

$$H_2(\text{solution}) \rightleftharpoons H_2(\text{ads}). \quad (2)$$

The adsorbed hydrogen undergoes dissociation:

$$H_2(\text{ads}) \rightleftharpoons 2\,H(\text{ads}). \quad (3)$$

The hydrogen atoms react with U(VI) adsorbed on the adjacent sites on the surface of the nickel catalyst:

$$U(\text{VI}) + H \longrightarrow U(\text{V}) + H^+.$$

The pentavalent uranium disproportionates both on the nickel surface and in the solution:

$$2\,U(\text{V}) \longrightarrow U(\text{VI}) + U(\text{IV}). \quad (4)$$

Considering that equilibria (1)–(3) are attained sufficiently fast, the kinetic equation for this process appears as:

$$\frac{d[U(\text{IV})]}{d\tau} = K[H_2]_{gas}^{0.5}[U(\text{VI})] = Kp_{H_2}^{0.5}[U(\text{VI})].$$

Large-scale production of U(IV) in acid solutions by reduction with hydrogen under pressure with Pt/SiO_2 as a catalyst was realised at the La Hague nuclear installation (France).[4]

The hydrogen technology was recommended for the production of UO_2 sols.[3] Treatment of a solution of uranyl nitrate (pH ~ 1) with hydrogen was carried out at 7–35 atm and 30–80 °C in the presence of platinum on charcoal.

The reduction of U(VI) with hydrazine was the subject of several investigations.[5–8] Thus U(VI) was reduced with $N_2H_4 \cdot HNO_3$ in nitric acid solution in the presence of 0.5% Pt/Al_2O_3 [5] both in a static and a flow regime (on a column) at constant temperature. Analysis of gaseous reaction products revealed that no hydrogen was formed.

With regard to the reaction stoichiometry

$$UO_2^{2+} + 0.5\,N_2H_5^+ + 1.5\,H^+ = U^{4+} + 0.5\,N_2 + 2\,H_2O, \quad (5)$$

it was noted [5] that one mole of U(VI) consumed ~1.5 moles of H^+, but the consumption of hydrazine exceeded 0.5 moles. In the author's opinion, decomposition of hydrazine on the catalyst yields H_2, and it is hydrogen that reduces U(VI) to U(IV) and hydrazine to ammonium ion. This conclusion seems to be erroneous, since in more recent studies [9] no hydrogen formation was observed upon catalytic decomposition of hydrazine on platinised catalysts in nitric acid solutions.

The kinetics of reaction (5) was studied predominantly in 1.2 M HNO_3 containing 1.5 and 0.5 mol litre^{-1} of U(VI) at 52 °C. The increase in the hydrazine concentration from 0.3 to 0.9 mol litre^{-1} caused a pronounced increase in the reaction rate. A decrease in the HNO_3 concentration from 1.2 to 0.5 mol litre^{-1} also increased the accumulation of U(IV). In the temperature range 46–65 °C, the activation energy of this reaction for the solution under study [1.8 mol litre^{-1} U(VI) + 1.4 mol litre^{-1} HNO_3 + 1.1 mol litre^{-1} $N_2H_5^+$] was estimated to be equal to 58 kJ mol^{-1}. At 65 °C, the formation rate of U(IV) decreased as its concentration exceeded 0.3 mol litre^{-1}. Presumably,[5] these conditions favour the oxidation of U(IV) by nitric acid.

Under conditions of column chromatography, the rate of accumulation of U(IV) diminished nearly twofold on going from 0.6 to 1.2 M HNO_3. A twofold reduction in the reaction rate was also observed upon a twofold decrease in the hydrazine concentration.

It was shown that technological solutions of U(VI) poison the catalyst. The search for impurities responsible for the decrease in the catalytic activity did not give any positive result despite the thorough analysis of cations and compounds present in the uranium(VI) solutions prior to their purification for catalytic experiments.

The stability of the catalyst with respect to prolonged exposure to U(VI) solutions (2 mol litre^{-1}) in 1.6 M HNO_3 at 50 °C has been studied. It was found that the catalytic activity decreased as a result of platinum entrainment. The result obtained can be attributed to the improper choice of the substrate (Al_2O_3), which possesses limited resistance to nitric acid-containing media. Platinised SiO_2 was used as a catalyst for the preparation of U(IV) solutions in nitric acid.[6,7] Solutions of 0.42 mol litre^{-1} U(VI) and hydrazine in 1.5–4 M HNO_3 were made to react with 1% Pt/SiO_2 (C : R was 1 : 10† at 55–70 °C). The reaction mixture was stirred by passing nitrogen at a controlled rate. The kinetic curves for the accumulation of U(IV) in the coordinates $\ln[c_0/(c_0-c)]$ *vs.* time [where c_0 is the initial concentration of U(VI) and c is the running concentration of U(IV)] are nearly straight lines, which can formally be interpreted as the first reaction order with respect to uranium(VI). Therefore, the kinetic regularities of this reaction were described by the equation:

$$-\frac{d[U(\text{VI})]}{d\tau} = k'[U(\text{VI})].$$

Here, k' (in min^{-1}) is the frequency factor or the apparent rate constant; its value is proportional to the initial reaction rate. Obviously, k' is not a true first-order rate constant, since the initial concentrations of uranium and hydrazine in this reaction mixture are commensurable and the decrease in the concentration of the reducing reagent during the reaction cannot be insignificant. The dependence of k' on the concentration of nitric acid is well approximated by a straight line in the logarithmic coordinates with an angular coefficient of about −0.6, which can be attributed to the apparent reaction order with respect to nitric acid. However, this value does not provide an unambiguous conclusion on the involvement of hydrogen ions in the rate-determining step of the reduction, since the experiments were carried out at various ionic strengths. At the same time, it is expected that higher concentrations of HNO_3 will increase the yields of nitrate complexes of uranium(VI), which manifest different (in comparison with free uranyl ions) reactivities with respect to hydrazine. Based on the general considerations, it may be assumed that the true order of this reaction with respect to H^+ will be equal to −1. This conclusion is based on an assumption that only neutral N_2H_4 molecules preactivated by adsorption on the surface of platinum are involved in the reaction with uranium(VI). The yield of the molecular form of hydrazine is inversely proportional to $[H^+]$, which should result in the −1 order of this reaction with respect to hydrogen ions. However, the catalytic activation of $N_2H_5^+$ ions and, as a consequence, the zero order of the reaction with respect to H^+ cannot be ruled out either.

Changes in the concentration of the reducing agent in the range 0.5–2 mol litre^{-1} do not influence the reaction rate, *i.e.*, the reaction is of the zero order with respect to hydrazine. The activation energy of the reduction was estimated in the temperature range 55–70 °C and was equal to 85.4 ± 3.0 kJ mol^{-1}.

The increase in the platinum content on silica gel from 0.25% to 2% resulted in a monotonic increase in the reaction rate. Increases in the catalyst concentration in the reaction mixture (the C : R ratio) accelerated the reduction.

The reduction of U(VI) (0.75 mol litre^{-1}) with hydrazine in HNO_3 has been studied by Shilov *et al.*[7] The catalyst was prepared by impregnation of silica gel (grain size 0.5–1 mm) with H_2PtCl_6 followed by drying and treatment with a hot solution of hydrazine hydrate (2–4 mol litre^{-1}). The experiments

† C : R is the ratio of the amount of the catalyst (in g) to the volume of the reaction mixture (in ml).

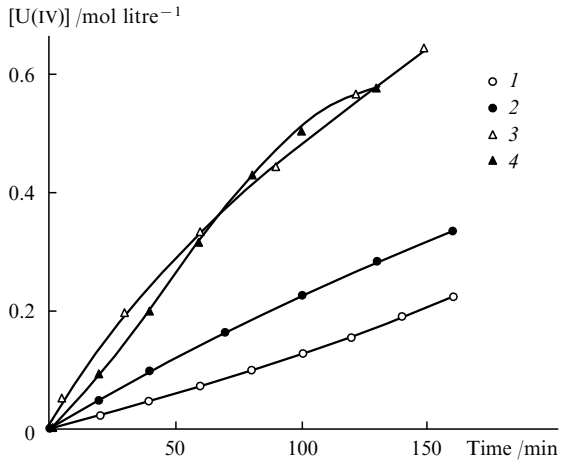


Figure 1. Kinetic curves of the reduction of U(VI) with hydrazine in the presence of Pt/SiO_2 containing different concentrations of Pt.[7] $[U(VI)]_0 = 0.75$ mol litre^{-1}, $[HNO_3]_0 = 2.0$ mol litre^{-1}, $[N_2H_5^+]_0 = 1.0$ mol litre^{-1} at 58.5 °C, C : R = 1 : 10; Pt content (%): (*1*) 0.76, (*2*) 0.83, (*3*) 1.0, (*4*) 1.0 (another sample).

were carried out in a thermostated cell mounted onto a shaker. The kinetic curves for U(IV) accumulation represent virtually straight lines up to the concentration of 0.5 mol litre^{-1}, which testified to a zero order of the reaction with respect to the metal (Fig. 1). For certain catalyst samples, the kinetic curves occupied an intermediate position between those for the zero and first order. In solutions of U(VI) (0.75 mol litre^{-1}) containing 2 mol litre^{-1} HNO_3 and 1–1.5 mol litre^{-1} $N_2H_5^+$, about 0.55 mol litre^{-1} of U(IV) was usually formed when the reaction was carried out for 2 h at 58 °C in the presence of 1% Pt/SiO_2 as a catalyst (C : R = 1 : 10). The reproducibility of the results with the same catalyst sample was satisfactory. The rate of formation of U(IV) decreased with a decrease in the platinum concentration on the support. A decrease in the $N_2H_5^+$ concentration to 0.75 mol litre^{-1} or an increase in the HNO_3 concentration to 3–4 mol litre^{-1} decelerated this process. Altogether, 1.2 mol of U(IV) was formed per mol of hydrazine. Thus, the reaction (5) paralleled catalytic decomposition of hydrazine or its reaction with HNO_3 in this system. It is known that the latter process yields N_2, N_2O, NH_4^+ and HN_3 (see Ref. 10). However, it was shown in special experiments that the gas evolved contained no HN_3. The activation energy of this reaction was measured in the temperature range 23–66 °C and was equal to 84 kJ mol^{-1}.

It may be assumed that this reaction proceeds through preliminary sorption of the reactants on the catalyst and is followed by their reaction

$$UO_2^{2+} + N_2H_5^+ \longrightarrow UO_2^+ + N_2H_3 + 2H^+.$$

In this case, metallic platinum plays the role of a bridge in the electron transfer from hydrazine to uranyl. U(V) disproportionates into U(IV) and U(VI) [reaction (4)], the radicals react with U(VI), NO_3^- and one another:

$$2N_2H_3 \longrightarrow N_4H_6,$$

$$N_4H_6 + 2H^+ \longrightarrow N_2 + 2NH_4^+.$$

In a series of experiments, leaching of silicon from the catalysts was studied. The concentration of silicon in a solution of U(VI) and hydrazine in 1 M HNO_3 in the presence of 1% Pt/SiO_2 (C : R = 1 : 10; 58 °C) amounted to 13, 36 and 58 mg litre^{-1} after 1, 2 and 3 h, respectively. An increase in HNO_3 concentration diminished leaching.

The catalyst 1% Pt/SiO_2 was used for the reduction of U(VI) with hydrazine in H_2SO_4 solutions.[8] The kinetic curves are well described by the first-order equation with respect to U(VI) over the whole range of experimental conditions. The reaction rate decreased slightly on going from 0.1 to 1.0 M H_2SO_4. The increase in the hydrazine content from 0.1 to 0.4 mol litre^{-1} only slightly increased the rate constant. The activation energy in the temperature range 30–60 °C was equal to 69.0 ± 4.0 kJ mol^{-1}. The reduction of uranium(VI) in H_2SO_4 solutions was not complicated by reverse oxidation of uranium(IV) and catalytic decomposition of hydrazine, which became apparent only at the temperatures above 60 °C, whereas the reduction of U(VI) occurred at a much higher rate even at 30 °C. The method described can be used for the preparation of H_2SO_4 solutions of uranium(IV) with concentrations of up to 0.25 mol litre^{-1} with respect to the metal. Further increase in uranium concentration is impossible due to the limited solubility of $U(SO_4)_2$.

The mechanism of U(VI) reduction by hydrazine in H_2SO_4 solutions is similar to that in HNO_3 solutions in general features.

The applicability of formic acid for the reduction of uranium(VI) in the presence of various catalysts was studied. Thus, 2%–5% Pt on Al_2O_3 was used as a catalyst in the preparation of U(IV) in HNO_3 solutions containing HCO_2H and $(NH_2)_2CO$.[11]

The catalyst Pt/Al_2O_3 was used for the reduction of U(VI) (0.1 mol litre^{-1}) in 0.4 M HCO_2H at 46–59 °C. $(NH_2)_2CO$ was added to the solution to remove traces of HNO_2.[12] The reduction rate was found to be proportional to [U(VI)] and did not depend on $[HCO_2H]$.

The method for the reduction of U(VI) by formic acid in HNO_3 solutions (0.5 mol litre^{-1}) in the presence of a platinum catalyst has been patented in Germany.[13] Virtually complete conversion of $UO_2(NO_3)_2$ (100 g litre^{-1} of uranium) into $U(NO_3)_4$ served as an example; the residual content of U(VI) was less than 10 mg litre^{-1}.

Platinum-group catalysts were used for the preparation of U(IV) in HNO_3 solutions.[7, 14, 15] It was found that formic acid containing no hydrazine failed to reduce U(VI) in 2 M HNO_3 in the presence of 1% Pt/SiO_2 (58 °C).[7] The addition of $N_2H_5^+$ resulted in the formation of U(IV), the threshold concentration of hydrazine being ~ 0.02 mol litre^{-1}. The increase in $[N_2H_5^+]$ up to 0.05 mol litre^{-1} favoured accelerated accumulation of U(IV). Further increase in the hydrazine concentration up to 0.1 mol litre^{-1} had little effect on the reaction rate. The reaction was decelerated with an increase in HNO_3 concentration; higher concentrations of HCO_2H increased the reduction rate. In the temperature range 17–65 °C, the activation energy was 48 kJ mol^{-1}.

The consumption of 1 mole of HCO_2H (with consideration of hydrazine consumed) was accompanied by formation of 0.83 mole of U(IV), *i.e.*, the catalytic reduction occurred mainly according to the reaction:

$$UO_2(NO_3)_2 + HCO_2H + 2HNO_3 = U(NO_3)_4 + CO_2 + 2H_2O.$$

This mechanism includes sorption of UO_2^{2+} and HCO_2H on the active sites of the catalyst with subsequent formation of UO_2^+ and the radical $^{\bullet}CO_2H$. This radical reduces UO_2^{2+} and UO_2^+. In addition, disproportionation of UO_2^+ occurs [reaction (4)]. In this reaction, the role of hydrazine is confined to stabilisation of U(IV) and prevention of the reaction of HCO_2H with HNO_2 by fast reduction of trace amounts of the latter and nitrogen oxides. Primary and secondary amines and $(NH_2)_2CO$ also serve as HNO_2 acceptors, however, control experiments have shown that urea does not replace hydrazine in the catalytic reaction of U(VI) with HCO_2H due to the low binding rate of HNO_2. The reduction of U(VI) by formic acid in the presence of 1% Pt/VP-1AP anion-exchange resin as a catalyst was studied. Its efficiency was found to be similar to that of 1% Pt/SiO_2.[7]

In addition to platinum-group catalysts, Re_2S_7 (see Refs 16 and 17) and PdS were used for the reduction of U(VI).[18] Dirhenium heptasulfide proved to be an efficient catalyst in the reactions of U(VI) with formaldehyde, formic acid and ethanol. These studies were carried out in acidic solutions at temperatures of 20–100 °C with stirring. It was found that U(VI) was com-

pletely reduced by formaldehyde at temperatures above 80 °C. The reduction was complete in 20–30 min in the presence of Re_2S_7 (0.2–0.3 g per g of uranium) and a threefold excess of HCHO. Cl^- ions decelerated, while F^- ions accelerated this reaction. The concentration of H^+ had little effect on the reaction rate. Ethanol and formic acid reacted with U(VI) at a slower rate than formaldehyde.

The kinetics of the reaction of U(VI) with C_2H_5OH in H_2SO_4 solutions in the presence of Re_2S_7 was studied at 50.6–90 °C.[17] The content of Re_2S_7 was ~0.8 g per g of uranium. Under these conditions, the reaction was of the first order with respect to U(VI). The increase in $[C_2H_5OH]$ from 0.17 to 2.52 mol litre^{-1} favoured a nearly proportional increase in the reaction rate. The increase in $[H_2SO_4]$ from 0.81 to 1.53 mol litre^{-1} had no effect on the reaction rate. The activation energy of this reaction was 69.4 kJ mol^{-1}.

Palladium sulfide was used as a catalyst in the reduction of U(VI) by formaldehyde in solutions of sulfuric, nitric or hydrochloric acids.[18] The concentration of uranium in the starting solutions was 50 g litre^{-1} (0.2 mol litre^{-1}). As the specific surface of powdered PdS was ~3.5 m^2 g^{-1}, more than 0.8 g PdS per g of uranium was required for efficient reduction. The efficiency of uranyl reduction depended on the anion present in the solution and increased in the series chloride < nitrate < sulfate. Fluoride ions increased the reduction rate. At a concentration of HF up to 1.5 mole per mole of uranium, all the U(IV) was present in the solution. Further increase in the HF concentration resulted in partial precipitation of U(IV) in the form of $UF_4 \cdot x\,H_2O$.

The catalytic reduction of uranyl by formaldehyde occurred at temperatures above 50 °C. In H_2SO_4 solutions, the concentration of formaldehyde should be in the range from 2 to 3 moles per mole of uranium. The change in H_2SO_4 concentration from 0.3 to 1 mol litre^{-1} had virtually no effect on the yield of U(IV).

The oxidation of formaldehyde by uranyl ions in solutions yields formic acid. Under similar conditions, HCO_2H competed favourably as a reducing agent with formaldehyde. Uranyl is not reduced by methanol. Repeated use of the catalyst demonstrated that PdS was not poisoned in the aqueous solutions under study and it could be employed many times without recourse to regeneration.

2. Neptunium

The known heterogeneous catalytic reactions of neptunium occur in acidic and alkaline media. Nitric acid plays the role of an oxidant, while hydrogen, hydrazine, hydroxylamine, formic acid and formaldehyde are reducing agents. Platinum-on-platinum, platinum-on-silica gel, platinum black and support-free palladium are used as catalysts.

Nitric and nitrous acids oxidise neptunium(IV) to a hexavalent state according to the reactions:[19]

$$3\,Np^{4+} + 2\,HNO_3 + 2\,H_2O = 3\,NpO_2^{2+} + 2\,NO + 6\,H^+,$$

$$Np^{4+} + 2\,HNO_2 = NpO_2^{2+} + 2\,NO + 2\,H^+.$$

However, these thermodynamically allowed reactions are extremely slow for kinetic reasons and the fact that the accumulation of Np(V,VI) over tens of hours in HNO_3 solutions is insignificant can be associated with radiolytic rather than chemical processes.[20,21] Being quite stable in 0.5–3 M HNO_3, neptunium(IV) undergoes fast oxidation in the presence of 1% Pt/SiO_2 as a solid-phase catalyst.[22] The catalytic oxidation of neptunium(IV) in HNO_3 solutions takes place even in the presence of antinitrite reagents, such as NH_2SO_3H, although in this case the reaction rate is somewhat smaller. The kinetics of heterogeneous catalytic oxidation of Np(IV) in HNO_3 solutions has been studied.[22] This reaction yields Np(V) with admixture of Np(VI) (up to 5%); the content of the latter depends on the concentrations of nitric and nitrous acids. The oxidation of neptunium(IV) by nitric acid follows first-order kinetics with respect to Np(IV) over the whole range of experimental conditions. An increase in the catalyst concentration results in a monotonic increase in the reduction rate. The linear dependence k' *vs.* (C : R) in logarithmic coordinates allows the estimation of the apparent reaction order with respect to the active sites of the catalyst. For the reaction under consideration, it is equal to 0.97 ± 0.07 in the C : R range under study (0.025–0.1). The oxidation rate of Np(IV) by nitric acid decreases with an increase in the solution acidity from 0.5 to 4.0 mol litre^{-1} $[H^+]$ at a constant concentration of nitrate ions ($[NO_3^-] = 0.5$ mol litre^{-1}). The linear dependence of the rate constants on the H^+ concentration in the logarithmic coordinates has an angular coefficient corresponding to the apparent reaction order of 0.7 ± 0.1 with respect to H^+. The increase in the total concentration of nitrate ions in the concentration range 0.5–4.0 mol litre^{-1} at constant acidity ($[H^+] = 0.5$ mol litre^{-1}) causes a slight increase in the reaction rate which corresponds to the apparent reaction order of 0.25 ± 0.07 for NO_3^-. The increment in $[HNO_3]$ in the range 0.5–4.0 mol litre^{-1} slows down the reaction up to its complete cessation, which occurs at $[HNO_3] > 4.0$ mol litre^{-1}. The apparent reaction order for nitric acid varies from −0.3 at low $[HNO_3]$ to −3.3 at a concentration of $HNO_3 > 3$ mol litre^{-1}, which suggests a complex type of heterogeneous catalytic interaction in the Np(IV)–HNO_3–Pt/SiO_2 system. The deceleration of the catalytic oxidation of Np(IV) in the presence of sulfamic acid can be attributed to the effect of nitrous acid formed in one of the reaction steps, which increases the rate of the catalytic oxidation of neptunium(IV).

The dependence of the apparent activation energy (E^*) on the concentration of nitric acid has a complex form.

$[HNO_3]$ /mol litre^{-1}	E^* /kJ mol^{-1}	$[HNO_3]$ /mol litre^{-1}	E^* /kJ mol^{-1}
0.5	60.1	2.0	83.3
1.0	61.0	3.0	85.1

These data show that an abrupt increase in E^* (by more than 20 kJ mol^{-1}) occurs in the concentration range of HNO_3 of 1.0–2.0 mol litre^{-1} where the change in the reaction mechanism apparently occurs.

The oxidative properties of nitric acid are usually considered in relation to the oxidising effect of nitroyl cations (NO_2^+) present in nitric acid solutions in a certain equilibrium concentration.[10,23,24] The NO_2^+ species are formed in the solution as a result of a fast equilibrium reaction:

$$NO_3^- + 2\,H^+ \rightleftharpoons NO_2^+ + H_2O. \quad (6)$$

One should not rule out the possibility of the formation of nitroyl ions in the system under consideration as a result of fast heterogeneous reactions.

$$HNO_3(ads) + H^+(ads) \rightleftharpoons NO_2^+(ads) + H_2O,$$

$$NO_2^+(ads) \rightleftharpoons NO_2^+(solution).$$

The fact that the catalytic oxidation of Np(IV) is decelerated in the presence of antinitrite reagents suggests that HNO_2 or one of its transformation products is involved in the formation of an activated complex on the surface of the catalyst. Taking into account the disproportionation equilibrium of HNO_2 and NO_2,

$$2\,HNO_2 \rightleftharpoons NO + NO_2 + H_2O, \quad (7)$$

$$2\,NO_2 + H_2O \rightleftharpoons HNO_2 + HNO_3,$$

the following scheme for heterogeneous catalytic conversions in the Np(IV)–HNO_3–Pt/SiO_2 system can be proposed:

$$Z + NO \rightleftharpoons ZNO, \quad (8)$$

Here, Z is the active site of the catalyst;

$$ZNO + NO_2^+ \rightleftharpoons ZA, \quad (9)$$

ZA is the intermediate oxidising species (quite probably, the oxidising species are formed from NO_3^- and HNO_2 and are then adsorbed on the active catalytic sites).

In dilute solutions ($[HNO_3] < 1$ mol litre^{-1}), the catalytic oxidation of neptunium(IV) can result from the following rate-limiting step:

$$ZA + Np^{4+} \cdot n\,H_2O \longrightarrow$$
$$\longrightarrow NpO_2^+ \cdot (n-2)\,H_2O + 4\,H^+ + NO_2 + NO,$$

Nitrous acid is formed in the reaction:

$$NO_2 + NO + H_2O \rightleftharpoons 2\,HNO_2\,.$$

In the presence of antinitrite reagents, HNO_2 and nitrogen oxides that are in equilibrium with it are absent from the solution. Such conditions apparently favour the direct oxidation of Np(IV) by NO_2^+(ads) species, although the rate of this is much lower.

As mentioned above, the mechanism of this reaction markedly changes in the $[HNO_3]$ range 1–2 mol litre^{-1}. Here, the concentration of $Np^{4+} \cdot n\,H_2O$ becomes negligibly small as a result of complexation with nitrate ions.[25,26] Under these conditions, it is nitrate complexes of neptunium(IV) that are the only oxidisable species. The formation of neptunium(V) dioxo cation from the aqua-ions $Np^{4+} \cdot n\,H_2O$ should occur more easily than from the nitrate Np(IV) complex where the H_2O molecules are partly displaced from the coordination sphere of Np by nitrate ions. Therefore, the increase in $[HNO_3]$ above 1 mol litre^{-1} is accompanied by a significant decrease in the oxidation rate and an increase in the activation energy.

The effect of neptunium(IV) concentrations on the yield of neptunium(III) in $HClO_4$ solutions under the action of hydrogen in the presence of a platinum-on-platinum catalyst using ^{237}Np and ^{239}Np was studied [27]. The degree of neptunium oxidation was established using extraction with tenoyltrifluoroacetone (TTA) in xylene: Np(IV) was extracted into the organic phase and Np(III) remained in the aqueous solution. The concentration of neptunium was determined from α- (^{237}Np) and γ- (^{239}Np) activities. It was shown that at neptunium concentrations above 10^{-3} mol litre^{-1} in 1 M $HClO_4$ its reduction to Np(III) was virtually complete. The contribution of Np(III) diminished with a decrease in the total neptunium concentration; no reduction of Np(IV) took place when its concentration dropped below 10^{-8} mol litre^{-1}. Neither purification of hydrogen by activated copper and pyrogallol, nor the prolongation of the reaction time with hydrogen to 3 h favoured this process. It was first suggested that if reoxidation of Np(III) that had been generated on the catalyst surface occurred in the bulk of the solution, the proportion of reduced neptunium depended on the surface area of the catalyst. However, even a 10-fold increase in the surface area of the catalyst did not affect the proportion of reduced neptunium. It was therefore suggested that the solution contained oxidising admixtures. Their effect could be neutralised where the oxidised forms of cations with redox potentials below the Np^{4+}/Np^{3+} pair [0.155 V relative to the normal hydrogen electrode (NHE)] were added to a support-free solution of ^{239}Np. The following pairs, Zn^{2+}/Zn (−0.763 V), U^{4+}/U^{3+} (−0.631 V), Cr^{3+}/Cr^{2+} (−0.41 V), Cd^{2+}/Cd (−0.403 V) and Ti^{4+}/Ti^{3+} (−0.055 V), with potentials lower than the hydrogen potential could not enhance ^{239}Np(IV) reduction. However support-free ^{239}Np(IV) was quantitatively reduced to a trivalent state when H_2 was passed for 2 h in the presence of Sn(IV) (10^{-2} mol litre^{-1}). At a concentration of tin(IV) of 10^{-3} mol litre^{-1}, its effect began to fade away and at concentrations $< 10^{-4}$ mol litre^{-1} no Np(III) could be detected. It should be noted that the results of these experiments are rather obscure, since oxidised forms of the added cations reacted with neither Np(III) nor hydrogen. In our opinion, it is adsorption of H_2 and its dissociation into hydrogen atoms that occur on the platinum surface [reactions (1)–(3)] and part of the H atoms are desorbed and pass into the solution. Pulse radiolysis of Np(III) in 1 M $HClO_4$ revealed [28] that Np(III) is oxidised by hydrogen atoms at a rate of 6×10^7 litre mol^{-1} s^{-1}. Thus, the hydrogen atoms leaving the platinum surface convert Np(III) into Np(IV). The oxidation of Np(III) by perchloric acid should not be ruled out either.

The effect of $[HClO_4]$ on the reduction of Np(IV) has been studied.[27] It was found that the fraction of Np(III) decreased with a decrease in $[HClO_4]$ and no reduction of 5×10^{-7} or 4×10^{-3} mol litre^{-1} solutions of ^{237}Np(IV) occurred in 2×10^{-3} M $HClO_4$. The absorption spectrum of the latter solution was similar to that of Np(IV) hydroxide. A decrease in yields of Np(III) seems to be due to hydrolysis of Np(IV), which brings about a shift of the potential of Np(IV)/Np(III) to a more negative region. This argument seems tenable. Thus calculations performed with consideration of Np(IV) hydrolysis constants (see Ref. 29) gave a more negative potential of the Np(IV)/Np(III) pair at $[H^+] = 2 \times 10^{-3}$ mol litre^{-1} than that of the H_2/H^+ pair.

Hydrazine in the presence of Pt/SiO_2 was also used for the reduction of Np(VI) and Np(V) in nitric acid.[30] Upon exposure to a catalyst (0.25% Pt/SiO_2 or 2% Pt/SiO_2) (C : R = 1 : 40 at 15 °C), the rate of reduction of Np(VI) (2.5×10^{-4} mol litre^{-1}) in 2 M HNO_3 containing $N_2H_5NO_3$ (1×10^{-3} mol litre^{-1}) depended on the intensity of stirring, and the reaction occurred under diffusion control. An increase in the rate of mechanical stirring in order to attain the kinetic regime failed because of attrition wear of the catalyst. The kinetic curves were rectified in semilogarithmic coordinates. The values of the first-order rate constants calculated from the slopes of the straight lines prompted the following conclusions. The increase in the platinum content on silica gel from 0.25 to 1% caused an increase in the reduction rate, while further increases in the platinum concentration had virtually no effect on the reaction rate. The rate constant changed in a virtually linear manner with a change in the C : R ratio as could be expected for the reaction occurring on a surface. The increase in $[HNO_3]$ from 1 to 2 mol litre^{-1} slightly inhibited this process, while the increase in hydrazine concentration in the range $(0.1-100) \times 10^{-3}$ mol litre^{-1} accelerated it. At 15–40 °C, the activation energy was about 19 kJ mol^{-1}, *i.e.,* typical of reactions whose rates are diffusion-controlled.[31]

Upon addition of a catalyst (Pt/SiO_2) to solutions of Np(V) and hydrazine in HNO_3 at 30–40 °C, the formation of Np(IV) occurred. The rate of the reduction was virtually independent of the intensity of stirring of the solution with the catalyst, therefore it was easy to select the stirring regime allowing the experiments to be carried out under kinetic control. The reaction rate is described by a first-order equation with respect to Np(V). The first-order rate constants obtained under different conditions characterised the reduction process and made it possible to estimate the contribution of each factor. First, the rate constant increased linearly with the platinum concentration on the support and the C : R ratio. Second, the rate constant increased with the acid concentration (from 0.2 to 7 mol litre^{-1}). Third, in the range 30–60 °C the activation energy is nearly 32 kJ mol^{-1}, which is much smaller than in the homogeneous catalytic reduction of Np(V) by hydrazine in the presence of Mo(VI) [100 kJ mol^{-1} at 60–88 °C (see Ref. 32)].

If the concentration of HNO_3 in solution is lower than 2 mol litre^{-1}, the reduction of Np(V) is incomplete with 2% to 4% of Np(V) remaining. Complete conversion of Np(V) into Np(IV) occurred in 4 M HNO_3 where the catalytic reduction of Np(V) is accompanied by simultaneous oxidation of Np(IV). The higher extent of reduction in 4–6 M HNO_3 is due to complexation with nitrate ions and the resistance of the complexes to oxidation. The rates of oxidation and reduction increase with temperature, but the degree of passage of neptunium into a hexavalent state at 30–60 °C changes only insignificantly. However, at temperatures above 70 °C the yields of Np(IV) decrease as a result of rapid decomposition of hydrazine in the presence of a catalyst, especially in 0.5–2 M HNO_3. The mechanism of this process is similar to that of U(VI) reduction.

In alkaline hydrazine solutions, the concentration of Np(V) did not change in the temperature range from 40 to 80 °C. Finely dispersed metallic palladium formed from palladium salts under these conditions plays the role of a catalyst in the reduction of Np(V). The Np(IV) formed precipitates as the hydroxide.[33] The amount of Np(V) reduced is proportional to the concentration of Pd(II). The increase in the alkali (LiOH) concentration inhibits this process. The increase in the hydrazine concentration from 0.02 to 0.2 mol litre^{-1} in 2 M NaOH slightly increases the reduction rate. The activation energy was estimated to be equal to $\sim$88 kJ mol^{-1} (40–80 °C).

The kinetics and mechanism of the Np(V) to Np(IV) reduction by hydroxylamine in nitric acid solutions in the presence of platinum black have been studied,[34] although no information on the procedure of the preparation of platinum black and the grain size and the catalyst surface was provided. No reaction occurred at room temperature in the absence of the catalyst. The solutions were magnetically stirred at 22.4 °C. The reaction rate did not depend on [NH_3OH^+] in the range 0.25–1.87 mol litre^{-1} and was described by the kinetic equation:

$$-\frac{d[Np(V)]}{d\tau} = k_0[Np(V)]^{0.54}[H^+]^{1.52}[Pt_{black}]^{1.01}$$

at [Np(V)] = $(0.83-5.82)\times10^{-3}$ mol litre^{-1}; [H^+] = 0.5–3.0 mol litre^{-1}; [Pt_{black}] = 2.04–10.16 g litre^{-1}. Based on the data obtained, the following mechanism was proposed:

$$NH_3OH^+ \longrightarrow NHOH + e^- + 2H^+$$

(this reaction is probably preceded by sorption of NH_3OH^+ on the surface of platinum black):

$$H^+ + e^- \longrightarrow H(ads),$$

$$2\,NHOH \longrightarrow (NHOH)_2 \longrightarrow N_2 + 2H_2O,$$

$$NpO_2^+ + H(ads) \longrightarrow NpO_2H^+,$$

$$NpO_2H^+ + 3H^+ \longrightarrow Np^{4+} + 2H_2O.$$

Formic acid plays the role of a reducing agent; the redox potential of the pair $CO_2,H^+/HCO_2H$ is equal to 0.199 V (NHE).[35] The redox potentials of the pairs Np(VI)/Np(V) and Pu(VI)/Pu(V) (1.24 and 1.02 V, respectively[36]) are much larger than that of formic acid. However, Np(VI) and Pu(VI) are not reduced in formate solutions.[37] A possible reason for the kinetic stability of hexavalent neptunium and plutonium ions in formate solutions is that formic acid, being a two-electron reducing agent, reacts with one-electron oxidants *via* formation of a radical.[38]

$$HCO_2H \longrightarrow {}^{\bullet}CO_2H + H^+ + e^-,$$

$$^{\bullet}CO_2H \longrightarrow CO_2 + H^+ + e^-.$$

For the first step, ΔG° = 157.2 kJ mol^{-1} (see Ref. 39), which is equivalent to the potential of 1.63 V, thus preventing the reduction of Np(VI) and Pu(VI). The above-said holds for Np(V), Pu(IV) and U(VI), since the redox potentials of the Np(V)/Np(IV), Pu(IV)/Pu(III) and U(VI)/U(IV) pairs are below 1 V.[36] It might be expected that the catalytic reduction of Np(VI) occurs at noticeable rates. This was demonstrated[40] in a study of kinetic regularities of the reaction of Np(VI,V) with HCO_2H in $HClO_4$ solutions in the presence of 1% Pt/SiO_2, the reaction mixture being stirred by a flow of argon.

The analysis of the kinetic curves revealed that the catalytic reduction of Np(VI) to Np(V) is a first-order reaction with respect to Np(VI) over the whole range of experimental conditions. The contributions of different factors to Np(VI) reduction were estimated based on the analysis of apparent rate constants k_1. The increase in k_1 with an increase in the stirring intensity points to the diffusion-controlled mechanism of this reaction.

An increase in the catalyst content in the reaction mixture results in a monotonic increase in k_1. The reaction rate increases with the concentration of formic acid in the range from 0.2 to 1.5 mol litre^{-1}. The apparent order of the reaction with respect to HCO_2H is 0.43 ± 0.01. The increase in the concentration of perchloric acid in the range from 0.2 to 4.0 mol litre^{-1} results in a slight decrease in the reaction rate. The apparent order of this reaction with respect to $HClO_4$ is -0.26 ± 0.02. The activation energy in the temperature interval from 30 to 60 °C is 18.3 ± 0.9 kJ mol^{-1}, which is consistent with the corresponding values for the diffusion-controlled processes.

The catalytic reduction of Np(VI) with formic acid is not stopped at the formation of Np(V), the concomitant accumulation of Np(IV) occurs in parallel (Fig. 2). The reduction rate of Np(V) does not depend on the stirring intensity, hence the reaction is kinetically controlled.

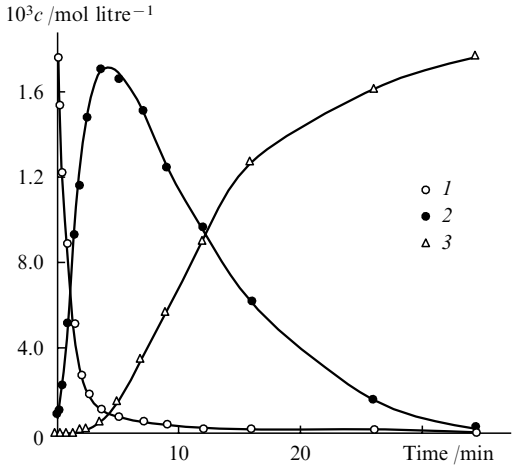


Figure 2. Time-dependent changes in the concentrations of valence forms of neptunium in the presence of 0.1 g ml^{-1} 1% Pt/SiO_2 at 60 °C (see Ref. 40). [$HClO_4$] = 1.0 mol litre^{-1}, [HCO_2H] = 0.1 mol litre^{-1}. (*1*) Np(VI), (*2*) Np(V), (*3*) Np(IV).

The stoichiometry of the catalytic reduction of Np(V) with formic acid was studied in solutions with [Np] = 6.20×10^{-3} mol litre^{-1} and [HCO_2H] = 1.01×10^{-3} mol litre^{-1}. The stoichiometric coefficient, *i.e.*, Δ[Np(V)]/Δ[HCO_2H], was equal to 2.15 ± 0.08.

The S-shaped curves of the Np(V) reduction, *i.e.*, the presence of an induction period is characteristic of reactions in solutions with [$HClO_4$] = 2 mol litre^{-1}. At [$HClO_4$] > 2 mol litre^{-1}, the reaction rate obeys the first-order law. The appearance of the induction period depends also on the concentration of HCO_2H. If the concentration of HCO_2H in 1 M $HClO_4$ is < 0.05 mol litre^{-1}, the induction period is absent and the reaction kinetics follows the first order with respect to Np(V). Using different initial concentrations of Np(V), it was possible to determine the orders of reactions described by kinetic curves with induction periods. The reaction rates were determined by the slopes of the tangents in the points corresponding to 50% conversion. The dependence of the reaction rate on $[Np(V)]_0$ was a straight line with the angular coefficient 1.05 in logarithmic coordinates. This suggests that the catalytic reduction of neptunium(V) with formic acid is a first-order reaction with respect to Np(V) for any composition of the reaction mixture. The duration of the induction period depends on the order of the addition of the reactants. If Np(V) is added last, the induction period is much longer than if it was formic acid or the catalyst (Fig. 3).

In solutions of $HClO_4$ with the concentration $\geqslant$2 mol litre^{-1}, the reaction rate was characterised by an apparent first-order rate constant k'. If [$HClO_4$] was smaller than 2 mol litre^{-1}, induction periods were observed in the kinetic curves and the reaction rates were measured in the points corresponding to the 50% conversion of Np(V).

An increase in the catalyst concentration in the reaction mixture resulted in a monotonic increase in the reduction rate.

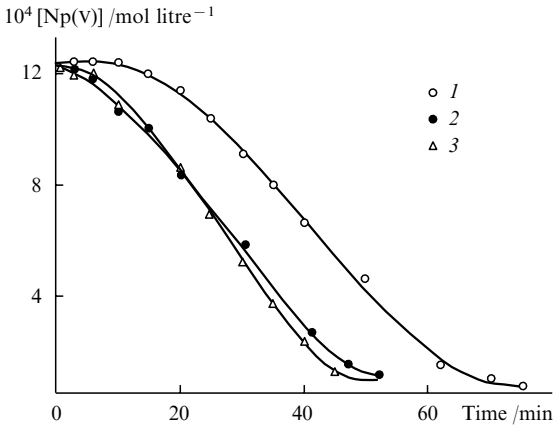


Figure 3. Effect of the mode of initiation of the reaction on the shapes of the kinetic curves in the catalytic reduction of neptunium(V) with formic acid in the presence of 0.1 g ml^{-1} of 1% Pt/SiO_2.[40]
$[HClO_4]$ = 1.0 mol litre^{-1}; $[HCO_2H]$ = 0.5 mol litre^{-1}; 59 °C. The reaction was initiated by the addition of Np(V) (*1*), the catalyst (*2*) and HCO_2H (*3*).

The linear type of the logarithmic dependence k' *vs.* (C : R) allowed the estimation of the apparent reaction order with respect to the active sites of the catalyst. For the reaction under consideration, it is equal to 1.11 ± 0.04 in the C : R range from 1 : 100 to 1 : 10.

The rate of the catalytic reduction of neptunium(V) increases with the increase in acid concentration in the solution. At low concentrations of $HClO_4$ (0.1–1.5 mol litre^{-1}) where the reaction occurs with an induction period, the apparent reaction order with respect to perchloric acid changes from 0 to ~0.25, while at 2–4 M $HClO_4$ it is constant and is equal to 1.38 ± 0.06. Taking into account the changes in the activity coefficients γ (1.055 and 2.08 for 2 M and 4 M $HClO_4$, respectively[41]) the reaction order with respect to hydrogen ions is less than unity.

The rate of the catalytic reduction of Np(V) is independent of $[HCO_2H]$ in the concentration range 0.04–1.0 mol litre^{-1}, but a certain statistically significant increase in the reaction rate with a decrease in $[HCO_2H]$ from 0.04 to 0.002 mol litre^{-1} is observed.

From the temperature dependences of the rate constants measured for 0.1 and 0.005 mol litre^{-1} HCO_2H in 2 M $HClO_4$, the apparent activation energy values of 60 ± 2 and 28.4 ± 0.8 kJ mol^{-1}, respectively, were determined.

Considering that in 2–4 M $HClO_4$ the reduction rate is proportional to the activities of the hydrogen ions, the reaction begins with the adsorption of protonated Np(V) ions and HCO_2H molecules in the active sites Z:

$$NpO_2^+ + H^+ \rightleftharpoons NpO_2H^{2+}, \quad (10)$$

$$Z + NpO_2H^{2+} \rightleftharpoons ZNpO_2H^{2+}, \quad (11)$$

$$Z + HCO_2H \rightleftharpoons ZHCO_2H. \quad (12)$$

The adsorbed reactants form an activated complex (AC) which is then slowly decomposed:

$$ZNpO_2H^{2+} + ZHCO_2H \rightleftharpoons AC, \quad (13)$$

$$AC \longrightarrow NpO_2H_2^{2+} + {}^{\bullet}CO_2H, \quad (14)$$

$$NpO_2H_2^{2+} + 2H^+ \longrightarrow Np^{4+} + 2H_2O, \quad (15)$$

$$NpO_2^+ + {}^{\bullet}CO_2H + 3H^+ \longrightarrow Np^{4+} + CO_2 + 2H_2O. \quad (16)$$

The independence of k' of $[HCO_2H]$ concentration above 0.04 mol litre^{-1} is characteristic of catalytic reactions where the surface of the catalyst is saturated with one of the reactants. A decrease in $[HCO_2H]$ below the adsorption threshold level favours the adsorption of Np(V) ions, which increases the reaction rate with a decrease in the concentration of the reducing agent. Significant difference in the activation energies obtained at the reducing agent concentrations of 0.1 and 0.005 mol litre^{-1} seems to be due to the same reasons. The change in E^* reflects the fact that the experimental values of the activation energy of a heterogeneous catalytic reaction are in fact apparent, they are related to the true activation energy of a heterogeneous process by an equation:

$$E^* = E_{true} - \lambda,$$

where λ is the integral heat of adsorption. In the general case, λ depends on the heats of adsorption of the reactants and their molar ratios. The heat of adsorption is the function of the degree of occupation of the active sites, which in turn is determined by the energetic nonuniformity of the catalyst surface. An increase in the concentration of formic acid favours its adsorption on the surface of a platinum catalyst. Since formic acid is used in a large excess, its molecules occupy the most energetically favourable active sites, thus diminishing the heat of adsorption of neptunoyl ions and, as a consequence, increasing the apparent activation energies.

The presence of an induction period in solutions with $[HClO_4] < 2$ mol litre^{-1} suggests the acceleration of the reaction by one of the reaction products. The fast disappearance of the radical ${}^{\bullet}CO_2H$ is accompanied by accumulation of Np(IV) (which is probably responsible for the catalytic effect). This ion takes part in several reactions:

$$Np^{4+} + H_2O \rightleftharpoons NpOH^{3+} + H^+, \; K_{hydr} = 2.4 \text{ (see Ref. 29)},$$

$$Np^{4+} + HCO_2H \rightleftharpoons NpHCO_2^{3+} + H^+, \; \log\beta_1 = 2.88 \text{ (see Ref. 42)},$$

$$Np^{4+} + NpO_2^+ \rightleftharpoons NpONpO^{5+}.$$

The formation of the $Np^{4+} \cdot NpO_2^+$ complex is very likely, since the formation of the $Th^{4+} \cdot NpO_2^+$ complex is now well established (see Ref. 43). The cation–cation complex is adsorbed on the active site. A decrease in the HCO_2H concentration results in a decrease in the concentration of the formate complex of Np(IV) and in an increase in the yield of the cation–cation complex Np(IV) · Np(V).

After introduction of a catalyst into a solution of Np(V) and HCO_2H in 1 M $HClO_4$, Np(V) ions and HCO_2H molecules simultaneously attack the surface, which is occupied in proportion to their concentrations and free energies of adsorption. Neptunium(V) occupies only a very small part of the active sites. As the reaction proceeds, Np(IV) is accumulated, the cation–cation complex occupies more active sites than NpO_2^+, the reaction is accelerated and the induction period is over.

If HCO_2H is added last to the reaction mixture, its molecules occupy free active sites and partly displace NpO_2^+ ions from the occupied positions. Then the reaction follows the scenario described above.

If Np(V) ions are added last, they have to displace HCO_2H molecules from the occupied active site. As this step is usually very slow, the induction period becomes longer (see Fig. 3).

The catalytic reduction of neptunium(VI) to neptunium(V) with formic acid on Pt/SiO_2 in HNO_3 solutions does not go to completion.[44] Neptunium(VI) remains in the solution at a certain steady-state concentration determined by the fast equilibrium reaction:[19]

$$2NpO_2^+ + 3H^+ + NO_3^- \rightleftharpoons 2NpO_2^{2+} + HNO_2 + H_2O.$$

In the presence of antinitrite reagents (urea, 0.05–0.5 mol litre^{-1}), the reduction of neptunium(VI) to neptunium(IV) proceeds *via* neptunium(V). In this case, the reduction of Np(VI) to Np(V) follows the same kinetic regularities as in $HClO_4$. At the same time, the reduction of Np(V) to Np(IV) in HNO_3 in the presence of urea has a number of features that make it different from the reduction in $HClO_4$. Thus the absence of an induction period in the catalytic curves of neptunium(V) reduction may be due to complexation, since in HNO_3 the cation–cation interaction $Np^{4+} - NpO_2^+$ is impossible because of the substitution of nitrate ions for water molecules in the hydrate shell of Np^{4+}.

Processing of the kinetic curves has shown that the best fit of the experimental results is achieved with the kinetic equation:

$$-\frac{d[Np(V)]}{d\tau} = k_{0.5}[Np(V)]^{0.5}.$$

In other words, in this case the order of the reaction is 0.5 with respect to neptunium(V). This is not changed with the increase in neptunium concentration from 10^{-3} to 10^{-2} mol litre^{-1}, which allows one to consider it as a true order [with respect to Np(V)] of the reaction occurring according to a redox mechanism rather than an apparent order of a heterogeneous process. Kinetic measurements performed at different concentrations of formic acid showed that the decrease in [HCO_2H] from 1.0 to 0.01 mol litre^{-1} caused a significant increase in the rate of neptunium(V) reduction. It is of note that in the HCO_2H concentration range from $\sim$0.1 to 0.05 mol litre^{-1} the reaction order changes from 0.5 to 1 with respect to Np(V). The rate of the catalytic reduction of neptunium(V) with formic acid increased with the concentration of nitric acid. The reaction orders with respect to HNO_3 are the same and constitute 0.71 ± 0.02 and 0.71 ± 0.01 for the reaction orders 0.5 and 1, respectively. The temperature dependences $k_{0.5}$ and k_1 in the range from 40 to 70 °C correspond to the values of apparent activation energies (43.6 ± 1.5 and 30 ± 2 kJ mol^{-1}, respectively).

It was suggested[44] that the mechanism of the catalytic reduction of Np(V) with formic acid in HNO_3 in the presence of urea is generally similar to that in $HClO_4$ and can be described by reactions (10)–(16). However, this reaction scheme cannot be regarded as a comprehensive presentation of events that take place in the catalytic reduction of Np(V) with formic acid in HNO_3. This covers a relatively narrow range of experimental conditions ([HCO_2H] < 0.1 mol litre^{-1}) where the reaction follows the first order with respect to neptunium(V). The reason for the order of 0.5 with respect to Np(V) at [HCO_2H] < 0.1 mol litre^{-1} is still obscure. In the general case, the reaction order 0.5 with respect to a reagent in heterogeneous catalytic processes is associated with its chemisorption on two adjacent sites of the catalyst, as follows from the Langmuir equation of the chemisorption isotherm.[45] Thus, it may be assumed that at a high degree of occupation of the catalyst with formic acid, secondary adsorption of NpO_2^+ ions occurs on two adjacent catalytic sites formed by the adsorbed HCO_2H molecules. The composition of the activated complex formed is conventionally described by the formula $\{_{ads}HO_2C-H\cdots O=Np^+=O\cdots H-CO_2H_{ads}\}^*$, while decomposition of this charge-transfer complex is accompanied by the generation of the species ($O=Np^+-OH$, $^{\bullet}CO_2H$) and a molecule of formic acid followed by the fast reactions (15) and (16).

The catalytic reduction of neptunium with formic acid using 1% Pt/γ-Al_2O_3 (grain size = 3–5 mm) as a catalyst for the preparation of neptunium(IV) sols has been studied.[46] The most complete reduction of Np(V) occurred where the initial concentrations of Np(V) and HCO_2H were 0.5 mol litre^{-1}. Higher concentrations of HCO_2H resulted in a higher percentage of Np(V) in the sols. At a concentration of Np(V) $\leqslant$0.1 mol litre^{-1}, the reduction was incomplete.

The concentration of Np(V) did not change over 5 h at 50–60 °C in 1–5 M NaOH solutions containing formate. The addition of $PdCl_2$ (2×10^{-3} mol litre^{-1}) resulted in formation of metallic palladium where Np(IV) hydroxide sedimented.[47] This process includes the reaction of hydrolysed Pd(II) ions with formate ions and formation of Pd(0). Palladium ions aggregate to form particles with a well-developed surface. Adsorption of formate and Np(V) ions on the active sites of the catalyst results in the reduction of Np(V). Platinum derivatives appeared to be less efficient in the reduction of Np(V) with formate.

The reduction of Np(V) with formate in alkaline solutions was studied in the presence of palladium or platinum on anion-exchange resins.[47]

3. Plutonium

The heterogeneous catalytic reactions of plutonium ions reported so far include reduction with hydrogen, hydrazine and formic acid in acidic media and reduction of plutonium(VII) with water in alkaline media.

In the presence of platinised platinum, Pu(VI) was reduced to Pu(V) with gaseous hydrogen. Hydrogen was passed through a solution of Pu(VI) (3.1×10^{-3} mol litre^{-1}) in 0.5 M HCl for 15 min at room temperature. Forty minutes later, the composition of the solution was as follows: 10% Pu(VI), 14% Pu(V), 6% Pu(IV) and 70% Pu(III). In 0.5–4 M HCl, the reduction of Pu(IV) (0.02 mol litre^{-1}) with hydrogen (40 min, room temperature) reaches 99% provided that 2 cm^2 of platinised platinum per ml of the solution was used and hydrogen was passed at a rate of 5 ml min^{-1} per ml of the solution.[48]

A mixture of H_2 (4%) and Ar (96%) was used for the reduction of Pu(IV) to Pu(III) in tributyl phosphate (TBP) with simultaneous reextraction of Pu(III) into the aqueous phase.[49] This was carried out on a column. Equal volumes of 0.5 M HNO_3 and 30% TBP containing U(VI) (95 g litre^{-1}), Pu(IV) (1 g litre^{-1}) and HNO_3 (0.1 mol litre^{-1}) were passed through a column filled with Al_2O_3 beads coated with 0.5% Pt; the elution time was $\sim$10 min. The extent of the Pu reduction was 99% and that of U, 1%. The reduction of U reached $\sim$3% if pure hydrogen was used.

A 0.5% Pt/Al_2O_3 catalyst was used[5] to increase the reaction rate of Pu(IV) with hydrazine in argon at 25 °C. The results obtained in the presence and in the absence of U(VI) are summarised in Table 1.

Table 1. Catalytic reduction of plutonium(IV) in 2 M HNO_3 containing 0.1 mol litre^{-1} of $N_2H_5NO_3$ at 25 °C.[5]

[Pu(IV)] × 10^3 /mol litre^{-1}	Exposure time /min	[Pu(III)] × 10^3 /mol litre^{-1}	
		in the presence of 0.12 mol litre^{-1} U(VI)	in the absence of U(VI)
1.9	1	0.7	0.5
	3	1.7	1.2
	5	–	1.6
4.7	1	1.6	1.4
	3	3.3	2.8
	5	4.3	3.8
	7	–	4.4

These data suggest that the reduction of Pu(IV) occurs according to two routes, *viz*., as the catalytic reduction of Pu(IV) itself with hydrazine and as the catalytic reduction of U(VI) to U(IV), which then quickly reduces Pu(IV). The kinetic dependences for U(IV)-free Pu(IV) solutions appear as straight lines, *i.e*., the reaction rate does not depend on the concentration of Pu(IV).

The catalytic reduction of Pu(IV) with hydrazine on platinum-on-silica gel (grain size = 0.5–1 mm) as a catalyst was studied in more detail.[50] The reaction rates of Pu(IV) [$(0.7-1) \times 10^{-2}$ mol litre^{-1}] with hydrazine (0.025–0.2 mol litre^{-1}) in 1.5–4 M HNO_3 (C : R = 1 : 100) depended only slightly on the stirring intensity.

The kinetic curves for the loss of [Pu(IV)] were rectified in the semilogarithmic coordinates, *i.e*., the reduction virtually followed the first-order law. The rate constant of the first-order reaction k' increased linearly with the catalyst concentration. An increase in the platinum content on the support resulted in a linear increase in the rate constant. The reaction order with respect to hydrazine was 0.5. In 1.5–4 M HNO_3, hydrogen ions had no effect on the reaction rate. The activation energy in the temperature range 30–60 °C was equal to 23 kJ mol^{-1}. This is somewhat higher than the corresponding values for the mass transfer-controlled

reactions. It may thus be concluded that the catalytic reaction occurred in a virtually kinetic regime.

The reduction process can schematically be presented as follows. Its first step includes adsorption of $N_2H_5^+$ and Pu(IV) ions [Pu^{4+} forms nitrate complexes $PuNO_3^{3+}$, $Pu(NO_3)_2^{2+}$, *etc.*]. Adsorbed hydrazine reacts with Pu(IV) either in an electron-transfer mode (from hydrazine to plutonium) through Pt–Pt bridges or by preliminary formation of an activated complex, which is further decomposed to Pu(III), N_2H_3 and H^+. Part of the radicals reduce NO_3^- and Pu(IV), while the other part undergoes dimerisation to give NH_4^+ and N_2.

Catalysts based on ruthenium,[51] activated charcoal[52] and heteropoly compounds were also used for the reduction of Pu(IV) with hydrazine.[53] The ruthenium catalysts were prepared by treatment of silica gel (grain size = 0.5–1 mm) with ruthenium nitrosonitrate with subsequent drying and reduction with hydrogen at 350–500 °C. Studies of the catalytic reduction of Pu(IV) solutions (1×10^{-2} mol litre^{-1}) with hydrazine revealed that the reaction rate depended on the stirring intensity. Therefore, the rate of stirring was selected so as to ensure the kinetic regime. The concentration of Pu(IV) decreased with time according to the first-order reaction, and the reaction rate increased linearly with the amount of the catalyst (the C : R ratio varied from 1 : 100 to 1 : 10) and the Ru content (the latter varied from 0.5% to 5%). The orders of the reactions with respect to hydrazine (0.1–0.5 mol litre^{-1}) and hydrogen ions (0.5–4.8 mol litre^{-1} of HNO_3) were ~1 and −1, respectively. The activation energy was 78 kJ mol^{-1} at 30–60 °C.

It was suggested that $N_2H_5^+$ and Pu(IV) ions adsorbed on the catalyst formed an activated complex with simultaneous elimination of a hydrogen ion:

$$N_2H_5^+ + Pu(IV) \rightleftharpoons Pu(IV)\cdot N_2H_4 + H^+.$$

The activated complex was slowly converted into Pu(III), N_2H_3 and H^+.

Ruthenium catalysts are less effective than their platinum analogues, but their advantage over the latter is very slow decomposition of hydrazine.

It was recommended to use activated charcoal for the reduction of Pu(IV) (1–20 g litre^{-1}) in HNO_3 solutions (0.1–1 mol litre^{-1}) containing >0.2 mol litre^{-1} $N_2H_5NO_3$.[52] Activated charcoal (50–100 g litre^{-1}) effected 99.5% reduction of Pu(IV) (1.2 g litre^{-1}) in 30 min.

It was found[53] that support of $Cs_5PV_2Mo_{10}O_{40}$ onto silica gel increased the rate of Pu(IV) reduction with hydrazine in HNO_3. The catalyst was prepared by impregnating silica gel (grain size = 0.5–1 mm) with a solution of a heteropolyacid or its sodium salt and subsequent treatment with a solution of a caesium salt. This resulted in formation of a poorly soluble heteropoly compound (HPC) on the surface of SiO_2. The concentration of HPC on SiO_2 was 1 mol.%–10 mol.%. The reduction of Pu(IV) depended only slightly on the stirring intensity, *i.e.*, it occurred in a nearly kinetically-controlled mode. The reaction rate was described by a first-order equation with respect to Pu(IV). In the presence of 10% HPC/SiO_2, the first-order rate constant increased linearly with a change in C : R from 1 : 100 to 1 : 20, while the decrease in the HPC content on the support decreased the rate constant. The calculated value of the activation energy was 80 kJ mol^{-1} at 25–80 °C.

In contrast to platinum catalysts, HPC/SiO_2 did not increase the rate of U(VI) reduction with hydrazine in HNO_3 solutions. It was suggested[53] that hydrazine caused the reduction of the heteropolyanion (HPA) $PV_2Mo_{10}O_{40}^{5-}$ to the so-called 'heteropolyblue' which had a heteropolyanionic structure. For $PV_2Mo_{10}O_{40}^{5-}$, the first half-wave of reduction $E_{1/2}$ was about 0.65 V;[54] therefore, the 'heteropolyblue' was able to convert Pu(IV) into Pu(III) through oxidation to the original HPC.

As mentioned above, finely dispersed platinum accelerates the reduction of Np(VI), Np(V) and Pu(IV) with hydrazine in HNO_3 solutions to give Np(IV) and Pu(III). In 6–8 M HNO_3, the former yields anionic complexes with the composition $Np(NO_3)_n^{4-n}$, which can be adsorbed on anion-exchange resins. This is not inherent in Pu(III) nitrate complexes. Therefore, 1% Pt/VP-1Ap was used as a catalyst for the reduction and separation of neptunium and plutonium.[55] Passage of a solution of a neptunium–plutonium mixture of any valence state in 6–7 M HNO_3 containing hydrazine through a layer of the anion-exchange resin with supported platinum resulted in sorption of Np(IV), while Pu(III) remained in the eluate. The effects of various factors (*e.g.*, the mode of preparation of the catalyst, temperature variation from 30 to 50 °C, hydrazine concentration [0.1–0.2 mol litre^{-1}]) on the separation of the neptunium–plutonium mixture have been studied.[55] Under optimum conditions, neptunium contained no more than 2×10^{-3}% of plutonium. In addition to platinum-based catalysts, the separation of neptunium and plutonium was carried out on anion-exchange resins with a supported heteropolyanion in HNO_3 containing hydrazine.[56] The catalysts were prepared by sorption of $PV_2Mo_{10}O_{40}^{5-}$ on various anion-exchange resins (VP-1Ap, VPBs, PX-1, AV-17), the former being catalysts of choice (the grain size was 0.18–0.63 mm). The effects of the catalyst preparation procedure, the content of HPA on the resin, the concentration of hydrazine in the solution as well as of temperature on the degree of separation of neptunium and plutonium were investigated.

The catalytic reduction of Pu(IV) in the process of denitration with excess of formic acid in highly radioactive solutions containing palladium and ruthenium was studied.[57] Partial reduction of Pu to the trivalent state was also observed[58] in the final step of the catalytic denitration of plutonium-containing solutions in the presence of 1% Pt/SiO_2. It was suggested[57] that Pu(IV) was reduced with atomic hydrogen formed upon catalytic decomposition of HCO_2H on the surface of reduced blacks of noble metals. No hydrogen formation was observed upon catalytic denitration on Pt/SiO_2,[58] therefore, it was concluded that the reduction of Pu(IV) under these conditions results from direct catalytic reaction of Pu(IV) with HCO_2H. More recent investigations (including kinetic studies)[59] have shown that Pu(IV) was completely and irreversibly reduced to the trivalent state in 0.27–2.0 M HNO_3 containing formic acid and urea in the presence of 1% Pt/SiO_2. In the presence of urea, the catalytic reduction of Pu(IV) with formic acid proceeded at a noticeable rate even at room temperature. If the reaction was carried out at 60 °C, the reduction of Pu(IV) (0.01 mol litre^{-1}) with formic acid (0.5 mol litre^{-1}) in 1 M HNO_3 was complete within less than 10 min. The rate of catalytic reduction of plutonium(IV) did not depend on the intensity of stirring of the reaction mixture with nitrogen, *i.e.,* in this case we deal with a kinetically controlled first-order reaction with respect to Pu(IV). The fact that the reaction rate did not depend on the urea concentration in the range 0.05–1.0 mol litre^{-1} places additional emphasis on the role of $(NH_2)_2CO$ as an antinitrite agent. Virtually no effect of the concentration of formic acid (from 0.2 to 1.0 mol litre^{-1}) on the rate constant k' was observed. The rate of plutonium(IV) reduction depended only slightly on the concentration of HNO_3 in the range from 0.3 to 2.0 mol litre^{-1}. Further increase in nitric acid concentration resulted in rapid decomposition of urea accompanied by abundant gas evolution and denitration of the solution. Under these conditions, plutonium(IV) was first partly reduced to the trivalent state and then oxidised as urea decomposed. The activation energy of this process at 30–60 °C was 29.6 ± 1.8 kJ mol^{-1}.

In the authors' opinion, the reduction of Pu(IV) on the catalyst surface proceeds *via* an activated complex:

$$Pu^{4+} + (HCO_2H)^*_{ads} \rightleftharpoons \{Pu\cdot HO_2CH\}^{4+}_{ads};$$

its slow decomposition yields Pu(III) and the radical $^\bullet CO_2H$

$$\{Pu\cdot HO_2CH\}^{4+}_{ads} \longrightarrow Pu^{3+} + {}^\bullet CO_2H + H^+.$$

The radical $^\bullet CO_2H$ formed reacts with Pu(IV) ions:

$$Pu^{4+} + {}^{\bullet}CO_2H \longrightarrow Pu^{3+} + CO_2 + H^+.$$

The overall stoichiometry of this reaction appears as:

$$2\,Pu(IV) + HCO_2H = 2\,Pu(III) + CO_2 + 2\,H^+.$$

A possibility of adsorption of Pu(IV) ions on the active sites vicinal to $(HCO_2H)^*_{ads}$ with subsequent charge transfer through the catalytic bridge Pt–Pt and decay of the radical $({}^{\bullet}HCO_2H)^*_{ads}$ into ${}^{\bullet}CO_2H$ and the hydrogen ion was also considered. However, these two processes were found to be kinetically indistinguishable.

It was also found [58] that formic acid derivatives, *viz.*, formaldehyde and formamide, also efficiently reduce plutonium(IV) in the presence of a catalyst (1% Pt/SiO_2).

The effect of immersion of platinum, graphite and lead dioxide electrochemically deposited on a platinum support on the stability of Pu(VII) solutions in 0.5 M NaOH was studied.[60] It was found that these conductive non-reducing materials decreased markedly the stability of Pu(VII) as could be judged from the formation of oxygen bubbles on the surface of the submerged materials. However, no visible changes occurred with the materials themselves. Thus, they exerted a purely catalytic effect on the Pu(VII) reduction. The reduction of Pu(VII) with water in the presence of the assayed electrode materials proceeded as a first-order reaction with respect to Pu(VII). The rate constants k' increased linearly with the increase in the visible surface area of the electrode materials, which is in good accord with the concepts of heterogeneous kinetics. Under comparable conditions, the rates of catalytic reduction of Pu(VII) being in contact with these electrode materials decreased in the following order: Pt > PbO_2/Pt > graphite. In the authors' opinion, the catalytic effect of the conductive materials on the Pu(VII) reduction with water is electrochemical in its character. Plutonium(VII) created a high potential on the surface (0.98 V), which exceeded the sum of the equilibrium potential for H_2O oxidation in alkaline solutions and the overvoltage of liberation of oxygen on this material. Hence, the electrode material becomes an anode where oxygen evolves owing to the catalytic reduction of Pu(VII).

Presumably, the molecular mechanism of the catalytic reduction of Pu(VII) with water in the presence of platinum, graphite and PbO_2 on platinum consists merely of electron transfer from hydroxyl ions and water molecules adsorbed on the surface to Pu(VII) ions.

4. Americium

Americium(V) is rather stable in weakly acidic aqueous solutions. Many reducing agents including multielectron agents, *e.g.,* hydrazine, hydroxylamine, formic acid and other organic acids, virtually do not react with Am(V). The chemical stability of Am(V) is determined by kinetic rather than thermodynamic factors [the potential of the Am(V)/Am(III) pair is 1.72 V (see Ref. 36)]. However, the low potential of the Am(V)/Am(IV) pair and high first potentials of the reducing agents should be taken into consideration. Therefore, catalysts should accelerate the reduction.

Some reduction reactions of americium(V) in the presence of 1% Pt/SiO_2 as a catalyst have been studied.[61] The reduction pattern depended on the intensity of an air flow through the reaction mixture. However, in the majority of cases where the air passed through a 20 ml solution at 5 litre h^{-1} and higher rates, the reaction rate only slightly depended on the stirring efficiency. Thus, these reactions are predominantly kinetically controlled. The results of the experiments carried out at 25 °C (C : R = 1 : 20) and an air flow of 6 litre h^{-1} are summarised in Table 2. It can be seen that finely dispersed platinum increased the reaction rate not only in the presence of conventional reducing agents ($N_2H_5^+$, H_2O_2), but also in the presence of nitrilotriacetic acid (NTA), EDTA and even ethylene glycol.

The change in pH from 1 to 4 had little effect on the reduction. This was accelerated with an increase in temperature and decreased almost linearly with a drop of C : R ratio from 1 : 5 to 1 : 50. The reduction rate increased with the increase in the Pt content on the silica gel surface from 0.1% to 4%, however, to a lesser degree than the increase in the platinum content.

Table 2. Reduction of Am(V) [$(0.6-1.5)\times10^{-3}$ mol litre^{-1}] in the presence of 1% Pt/SiO_2 (0.05 g litre^{-1}) at 25 °C.[61]

Reducing agent (X)	[X] /mol litre^{-1}	pH	Reduction time (50%) /min
$N_2H_5^+$	0.05	1	6.5
H_2O_2	0.0075	1	120
	0.18	1	50
HCO_2H	0.5	1	6
Tartaric acid	0.5	4	< 5
Nitrilotriacetic acid (NTA)	0.4	3	~ 50
EDTA	0.01	1	150
Acetoxime	0.25	2.3	~ 50
Formaldehyde	0.5	1	~ 60
Ethylene glycol	0.5	1	50

These data prompt several conclusions about the mechanisms of this reduction. Presumably, transfer of an electron or a hydrogen atom from the adsorbed reducing agent to the Am(V) ion also adsorbed on the platinum surface is the limiting step. The Am(IV) ions formed either undergo disproportionation or react with the reducing agent. Higher local concentration of Am(IV) favours disproportionation due to adsorption on the catalyst. Moreover, by virtue of its high oxidation potential Am(IV) is highly reactive with respect to the reducing agents mentioned above.

It was found [62] that trace amounts of metallic platinum accelerated dramatically the reduction of Am(VI) with formic acid, especially at pH > 4.

III. Catalytic decomposition of organic and inorganic components of liquid radioactive wastes

The reprocessing of radioactive wastes (including those of the nuclear fuel cycle) is often complicated without preliminary removal of certain organic and inorganic impurities, such as complexones, oxalic acid, hydrazine, hydrazoic acid, urea, excess nitric acid, nitrates, *etc*. This problem is successfully overcome by heterogeneous catalytic decomposition of these compounds in HNO_3 solutions or the use of strong oxidants, *e.g.,* ozone, bichromate, permanganate.[63,64] Catalytic reactions are preferable, since no additional reactants are needed.

1. Decomposition of complexones

It was found [65] that polyaminopolycarboxylic complexones are decomposed at moderate rates upon heating of their solutions in HNO_3 in the presence of heterogeneous catalysts, such as Pt/SiO_2, Pt/anion-exchange resin AV-17, activated charcoals AG-3, BAU, SKT, *etc*.

The decomposition of diethylenetriaminopentaacetic acid (DTPA) (0.05 mol litre^{-1}) in HNO_3 in the presence of 1% Pt/SiO_2 (C : R = 1 : 10) at 40–80 °C proceeded as a first-order reaction with respect to DTPA. The quantitative characteristics of this reaction were calculated from the half-time $\tau_{1/2}$, *i.e.,* the time required for a twofold decrease in the complexone concentration.

The decomposition rate of DTPA increased with the increase in the HNO_3 concentration from 0.5 to 2.0 mol litre^{-1}. Further increase in [HNO_3] inhibited the reaction. The reaction rate increased as the content of Pt on SiO_2 changed from 0.5% to 2%. The activation energy was 67 kJ mol^{-1}. The use of the anion-exchange resin AV-17 instead of silica gel as a support for platinum decreased the decomposition rate of DTPA 20-fold. This suggests direct involvement of the support in the formation of active sites of the catalyst.

Organic and inorganic impurities can be removed from all known brands of activated charcoals by washing. Their concen-

tration was the lowest in BAU, therefore, this was selected for kinetic studies. The rate of DTPA decomposition in the presence of BAU charcoal (C : R = 1 : 10) increased with the HNO_3 concentration, although to a far lesser degree than in the presence of Pt/SiO_2. The activation energy at 50–80 °C was equal to ~61 kJ mol^{-1}.

In contrast to DTPA, the decomposition of EDTA (0.05 mol $litre^{-1}$) in 0.3–0.5 M HNO_3 in the presence of BAU charcoal (C : R = 1 : 10) was described by a zero- or a close to zero-order rate constant with respect to the complexone. In 1–2 M HNO_3 solutions, the decomposition rate increased nearly twofold.

A series of experiments were devoted to the elucidation of the role of the anion in the decomposition of DTPA and EDTA in the presence of BAU (C : R = 1 : 10, 80 °C). Hydrochloric, perchloric and sulfuric acids (0.5–2.0 M) had similar effects on the catalytic decomposition of complexones and were nearly 100 times less efficient than HNO_3. Similar results were obtained in the presence of Pt/SiO_2.

The following scheme for the process was suggested. The first step included sorption of the complexone molecule on the active site of the catalyst. The adsorbed molecule underwent thermal decomposition in HCl, $HClO_4$ and H_2SO_4. In HNO_3 solutions, the adsorbed species were subject to an attack by NO_3^- (or NO_2^+) ions and were oxidised. No complexone decomposition products were identified, therefore, it is difficult to specify the details of the reaction mechanism.

2. Decomposition of oxalic acid

Decomposition on solid-phase catalysts is the most convenient and reliable method for removal of $H_2C_2O_4$ from nitric acid solutions.[66] Different brands of activated charcoals, platinum on silica gel and on anion-exchange resins AV-17 and VP-3Ap were assayed as such catalysts.

In semilogarithmic coordinates, the kinetic curves for $H_2C_2O_4$ decomposition in the presence of 1% Pt/SiO_2 appeared as straight lines up to the degree of conversion of 85%–90%. Then the reaction rate showed a further increase. In the authors' opinion, the gaseous products generated in the first steps of the reaction prevent penetration of the solution into the pores. Gas evolution slowed down to the end of the process, which results in an increase in the effective surface area of the catalyst and a parallel increase in the reaction rate. The decomposition of $H_2C_2O_4$ to the degree of conversion of 90% is characterised by a first-order equation with respect to $H_2C_2O_4$ and a first-order rate constant.

An increase in the rate of air flow through the solution (10 ml) from 50 to 400 ml min^{-1} caused only a small (1.4-fold) increase in k. This suggests that the decomposition of $H_2C_2O_4$ is predominantly under kinetic control.

The rate of the catalytic decomposition increased threefold with an increase in the HNO_3 concentration from 1 to 3 mol $litre^{-1}$. No catalytic decomposition of oxalic acid took place in HCl, $HClO_4$ and H_2SO_4. An increase in the amount of the catalyst resulted in an increase in the reaction rate. The activation energy of decomposition of $H_2C_2O_4$ (0.3 mol $litre^{-1}$) in 2.5 M HNO_3 in the presence of 1% Pt/SiO_2 (C : R = 1 : 10) was 54.8 kJ mol^{-1} at 40–70 °C. The decomposition rate of $H_2C_2O_4$ increased ~ fourfold with an increase in the Pt content on silica gel from 0.25% to 4%.

The catalysts prepared by reduction of H_2PtCl_6 with hydrogen or boiling hydrazine hydrate possessed similar efficiencies.

The effect of impurities on the catalytic decomposition of $H_2C_2O_4$ in 2.5 M HNO_3 at 60 °C in the presence of 1% Pt/SiO_2 (C : R = 1 : 10) has also been studied. The presence of Ni(II) (0.1 g $litre^{-1}$) and U(VI) (5 g $litre^{-1}$) had little effect on the reaction rate. At the same time, the decomposition rate decreased in the presence of Cr(III) (2 g $litre^{-1}$), Fe(III) (5 g $litre^{-1}$) and Pu(IV) (0.3 g $litre^{-1}$), apparently as a result of formation of oxalate complexes.

Stirring of solutions with catalysts results in attrition wear and crushing of silica gel. The concentration of silicon during $H_2C_2O_4$ decomposition at 60 °C reached 20–30 mg $litre^{-1}$. This drawback is absent from the catalysts prepared by absorption of $PtCl_6^{2-}$ on the anion-exchange resins AV-17 and VP-3Ap and subsequent reduction of platinum with hydrazine. The catalysts thus prepared were activated by refluxing in 2–4 M HCO_2H for 15–30 min and were only slightly inferior to catalysts based on silica gel in the ability to decompose $H_2C_2O_4$.

The decomposition of $H_2C_2O_4$ in HNO_3 solutions in the presence of seven different brands of activated charcoals without additional stirring has been studied. Stirring was effected by the gas evolved during the reaction. Upon heating to 80–100 °C, the decomposition of $H_2C_2O_4$ in the presence of activated charcoals proceeded at moderate rates. The reaction rate increased with the increase in the C : R ratio. With BAU charcoal, the maximum value of C : R did not exceed 1 : 3.5.

In addition to static experiments, the decomposition of $H_2C_2O_4$ was studied upon continuous passage of the solution through a column filled with the catalyst. The solution was fed into the thermostated column from the bottom. The degree of $H_2C_2O_4$ decomposition depended on the flow rate of the solution.

In the presence of hydrazine, the mode of decomposition of $H_2C_2O_4$ changed considerably.[67] The concentration of $H_2C_2O_4$ remained constant until the decomposition of $N_2H_5^+$ was nearly complete and diminished only thereafter. This suggests that hydrazine inhibits the catalytic decomposition of $H_2C_2O_4$ in HNO_3 solutions and that its effect is related to removal of HNO_2 from the solution.

The stoichiometry and the mechanism of heterogeneous catalytic decomposition of $H_2C_2O_4$ in nitric acid solutions have been studied.[68] Under the conditions specified (1% Pt/SiO_2, 80 °C, $[H_2C_2O_4]$ = 0.3 mol $litre^{-1}$, exposure time 30 min), the ratio $n = \Delta[HNO_3]/\Delta[H_2C_2O_4]$ was 0.4–0.5; it changed only slightly in 0.2–0.5 M HNO_3 and increased to 1.01 and 1.74 in 5 and 7 M HNO_3, respectively. In 7 M HNO_3, the value of n dropped to 1.1 with an increase in the exposure time. A decrease in temperature had no effect on this parameter (at 50 °C in 7 M HNO_3, n was equal to 0.9). In an argon atmosphere, the value of n exceeded those in aerated solutions.

In the presence of Pt/anion-exchange resins, the decomposition of $H_2C_2O_4$ proceeded with virtually the same stoichiometry as with 1% Pt/SiO_2.

Nitric acid at a concentration $\geqslant$ 7 mol $litre^{-1}$ behaves as a one- or two-electron oxidant of $H_2C_2O_4$.

$$H_2C_2O_4 + 2\,HNO_3 = 2\,CO_2 + 2\,NO_2 + 2\,H_2O,$$

$$H_2C_2O_4 + HNO_3 = 2\,CO_2 + HNO_2 + H_2O.$$

This was concomitant with more profound partial reduction of nitric acid.

In dilute solutions, the reaction of HNO_3 with $H_2C_2O_4$ is described by the equation:

$$5\,H_2C_2O_4 + 2\,HNO_3 = 10\,CO_2 + N_2 + 6\,H_2O.$$

The reaction:

$$H_2C_2O_4 + O_2 = 4\,CO_2 + 2\,H_2O$$

also takes place.

Thus, the increase in HNO_3 concentration prevents its more complete reduction with oxalic acid.

The IR spectra of gaseous products obtained under different conditions of catalytic oxidation of $H_2C_2O_4$ contained the bands corresponding to NO_2, N_2O_4, CO_2 and H_2O. No bands corresponding to NO or N_2O were detected.

The decomposition of $H_2C_2O_4$ in solutions containing HNO_3 (0.2 mol $litre^{-1}$) and variable amounts of $HClO_4$ in the presence of 1% Pt/SiO_2 (C : R = 1 : 2, 60 °C) reached 6%, 31% and 68% after 60 min, $[H^+]$ being 0.2, 1.2 and 2.2 mol $litre^{-1}$, respectively.

This suggests that H^+ ions are involved in the rate-determining step or in a preceding step.

The dependence of the decomposition rate of $H_2C_2O_4$ (0.33 mol litre^{-1}) on the reaction conditions (1% Pt/SiO_2, C : R = 1 : 2, 60 °C, 90 min) in the presence of HNO_2 (0.17 mol litre^{-1}) can be seen from the following data (no decomposition occurred in the absence of $HClO_4$ and HNO_3):

$[HClO_4]$ /mol litre^{-1}	$[HNO_3]$ /mol litre^{-1}	Degree of decomposition (%)
2	–	5
–	0.2	80

The decomposition of $H_2C_2O_4$ depends on $[HNO_2]$: the loss of $H_2C_2O_4$ in a solution containing 0.2 mol litre^{-1} HNO_3 and 0.17 mol litre^{-1} HNO_2 was 80% (*cf.* 6% in 0.2 M HNO_3 containing minor amounts of HNO_2). The reaction does not go further after removal of trace amounts of HNO_2 with hydrazine. In the absence of HNO_3 no reaction occurred either. It is the simultaneous presence of nitric and nitrous acids that brings about the catalytic decomposition of $H_2C_2O_4$.

The catalytic reaction occurs through sorption of the reducing agent ($H_2C_2O_4$) and the oxidant. In the authors' opinion,[68] the role of the oxidant is played by NO_2^+ ions and NO molecules formed in the equilibrium reactions (6) and (7). The formation of the intermediate oxidising species ZA in the active catalytic site Z proceeds in conformity with reactions (8) and (9). Subsequent conversions include the following reactions:

$$Z + H_2C_2O_4 \longrightarrow ZH_2C_2O_4,$$

$$ZA + ZH_2C_2O_4 \longrightarrow ZNOH + 2CO_2 + NO_2 + xH^+.$$

If the concentration of HNO_3 (and, correspondingly, of NO_2^+) is small, the reaction probably follows another pathway:

$$ZNOH + ZNOH \longrightarrow Z + ZH_2N_2O_2,$$

$$ZH_2N_2O_2 + H_2C_2O_4 \longrightarrow Z + N_2 + 2CO_2 + 2H_2O.$$

High concentrations of NO_3^- ions trigger the reaction:

$$ZNOH + NO_3^- \longrightarrow Z + NO_2^- + HNO_2.$$

In addition, molecular oxygen oxidises intermediate reducing species.

3. Decomposition of hydrazine

The kinetics and mechanisms of catalytic decomposition of hydrazine in the presence of various catalysts were studied in detail. The results of these investigations are generalised in a monograph.[69] The studies cited therein are devoted to the catalytic decomposition of anhydrous N_2H_4 or the hydrate $N_2H_4 \cdot H_2O$ in the gaseous or liquid state. Therefore, the available data do not provide an adequate explanation for the behaviour of hydrazine in the presence of heterogeneous catalysts in acidic solutions where it exists in the form of the hydrazinium ion, $N_2H_5^+$.

The stoichiometry, kinetics and mechanism of the catalytic decomposition of hydrazine were studied in solutions of perchloric and sulfuric acids in the presence of 1% Pt/SiO_2 as a catalyst.[70] It was found that the catalytic decomposition of hydrazine was accompanied by the formation of ammonium ions and nitrogen. It is noteworthy that the stoichiometric ratio $[N_2H_5^+] : [NH_4^+]$ was 0.746 ± 0.08 and did not depend on the nature of the acid ($HClO_4$ or H_2SO_4) or the concentration of hydrogen ions in the range from 0.3 to 3 mol litre^{-1}, *i.e.*, the decomposition of hydrazine occurred according to the equation:

$$3N_2H_5^+ + H^+ = 4NH_4^+ + N_2.$$

Kinetic studies revealed that the reaction order with respect to hydrazine was variable and changed from 0.2 to 1 with the decrease in $[N_2H_5^+]_0$ from 0.2 to 0.01 mol litre^{-1}. The fractional order of the reaction with respect to hydrazine was probably apparent and reflected the adsorption-type character of heterogeneous catalytic decomposition of hydrazine. Actually, this reaction was of zero and first orders with respect to $N_2H_5^+$ and the contribution of each of them to the overall process depended on the concentrations of hydrazine and the amount of the catalyst in the reaction system. At low initial hydrazine concentrations (0.01 mol litre^{-1}) where the catalytic decomposition strictly followed first-order kinetics with respect to $N_2H_5^+$, the reaction rate decreased monotonically with an increase in the concentration of hydrogen ions. The reaction order with respect to H^+ was -0.24 ± 0.1. The negative fractional order of the reaction with respect to H^+ suggests that hydrogen ions are not directly involved in the chemical reaction leading to the decomposition of hydrazine. Apparently, the inhibitory effect is due to competitive adsorption on the active sites of the catalyst.

The experimental values of the activation energies for the catalytic decomposition of hydrazine increased monotonically with the acid concentration.

$[H^+]$ /mol litre^{-1}	E^* /kJ mol^{-1}	$[H^+]$ /mol litre^{-1}	E^* /kJ mol^{-1}
$\sim 10^{-5}$	31.6 ± 1.6	1.2	59.2 ± 2.2
0.1	36.1 ± 2.4	3.4	79.9 ± 1.4
0.2	36.4 ± 2.1		

The monotonic increase in E^* with an increase in the acid concentration reflects the fact that the experimental values of activation energies of the heterogeneous catalytic reactions are apparent. The true activation energy of any chemical conversion always exceeds that determined experimentally by a value of the heat of adsorption. The latter depends on the degree of occupation of the active sites of the catalyst, which in turn reflects the nonuniformity of the catalyst surface with respect to energy. Adsorption of hydrogen ions on the surface of a platinum catalyst increases with the increase in acid concentration in the solution. Being present in large excess, H^+ ions occupy the most energetically favourable active sites, which results in a decrease in the heats of adsorption of interacting species and hence in an increase in apparent activation energy of a heterogeneous catalytic reaction.

The mechanism of catalytic decomposition of hydrazine in $HClO_4$ and H_2SO_4 postulated on the basis of stoichiometric and kinetic data can be described by the following scheme:

$$H^+(\text{solution}) \rightleftharpoons H^+(\text{ads}),$$

$$N_2H_5^+(\text{solution}) \rightleftharpoons N_2H_4(\text{ads}) + H^+(\text{solution}), \quad (17)$$

$$N_2H_4(\text{ads}) \longrightarrow 2NH_2^{\bullet}(\text{ads}), \quad (18)$$

$$NH_2^{\bullet}(\text{ads}) + N_2H_5{+}(\text{solution}) \longrightarrow NH_5^+(\text{ads}) + N_2H_3^{\bullet}(\text{solution}),$$

$$NH_4^+(\text{ads}) \rightleftharpoons NH_4^+(\text{solution}),$$

$$2N_2H_3^{\bullet}(\text{solution}) + 2H^+(\text{solution}) \longrightarrow N_2 + 2NH_4^+(\text{solution}). \quad (19)$$

The dissociation of adsorbed hydrazine molecules seems to be the rate-limiting step of the overall process (reaction 18). The first order of the reaction with respect to hydrazine is determined by the adsorption equilibrium (17). The reaction of the adsorbed radical $NH_2^{\bullet}$(ads) with the hydrazinium ion must be fast, otherwise further dissociation of the amino radical would result in the production of hydrogen:

$$NH_2^{\bullet}(\text{ads}) \longrightarrow NH^{\bullet}(\text{ads}) + H^{\bullet}(\text{ads}),$$

$$2H^{\bullet}(\text{ads}) \longrightarrow H_2.$$

The disproportionation of $N_2H_3^{\bullet}$ radicals into nitrogen and ammonium ions [reaction (19)] is yet another example of a very fast reaction: ($k > 3\ 10^{12}$ litre mol^{-1} s^{-1}).[71]

The catalytic decomposition of hydrazine (0.20–0.23 mol litre^{-1}) in HNO_3 was studied in a thermostated cell mounted onto a shaker.[67] The loss of $[N_2H_5^+]$ in 1.25 M HNO_3 in

the presence of 0.7% Pt/SiO_2 (50–80 °C) was described by kinetic curves; their initial segments correspond to the first-order reaction, which changes to the zero order in the terminal steps of the process. The decomposition of $N_2H_5^+$ in the presence of activated charcoal occurred at a slower rate than on Pt/SiO_2 and strictly obeyed the zero-order kinetics. When BAU and Pt/SiO_2 containing up to 1% platinum were used as catalysts in 0.2–7 M HNO_3 at 50–80 °C, the reaction rate did not depend on the stirring intensity, *i.e.*, the reaction was kinetically controlled.

With an increase in $[HNO_3]$, the kinetic parameters of the $N_2H_5^+$ decomposition on Pt/SiO_2 changed: the zero-order rate constant, k_0, was invariable, whereas the first-order rate constant k_1 manifested a peak around 1–2 M HNO_3. The overall effect of $[HNO_3]$-dependent changes in $k_0 + k_1$ led to a situation where the maximum decomposition rate of hydrazine was observed in 1–2 M HNO_3. The activation energies of first- and zero-order reactions in the presence of Pt/SiO_2 (50–80 °C) were equal to 61 and 50.6 kJ mol^{-1}, respectively. For BAU, the activation energy was 68.6 kJ mol^{-1} at 70–95 °C. With an increase in the Pt content on SiO_2 from 0.5% to 4%, k_0 and k_1 showed a tendency to increase, this increase being more pronounced for k_1.

The stoichiometry, kinetics and mechanism of the catalytic decomposition of hydrazine in HNO_3 in the presence of 1% Pt/SiO_2 were studied in detail.[9] The results obtained by chemical and mass spectrometric methods suggest that N_2, N_2O and ammonium nitrate are the main decomposition products of hydrazine in HNO_3. The formation of trace amounts of NO and NO_2 was also noted. The reaction products contained no hydrazoic acid (HN_3), which made this reaction totally different from homogeneous oxidation of hydrazine with nitric acid.[10] The stoichiometric ratios $[NH_4^+]_\infty : [N_2H_5^+]_0$ and $([NO_3^-]_0 - [NO_3^-]_\infty) : [N_2H_5^+]_0$ reflecting accumulation of ammonium ions and decrease in the total nitrate content vary depending on the concentration of nitric acid. Thus the increase in $[HNO_3]$ in the range 0.075–9.34 mol $litre^{-1}$ results in a decrease in $[NH_4^+]_\infty : [N_2H_5^+]_0$ from 0.65 ± 0.01 to 0.36 ± 0.03, whereas $([NO_3^-]_0 - [NO_3^-]_\infty) : [N_2H_5^+]_0$ increased from 0.40 ± 0.01 to 0.97 ± 0.04. These data suggest a complex mechanism of catalytic decomposition of hydrazine in nitric acid-containing media. Presumably, the overall process is a superposition of two or more reactions where the contribution of each component is determined by the concentration of nitric acid. In 0.5–5 M HNO_3, changes in these ratios are insignificant, which suggests that in the given range of $[HNO_3]$ the catalytic decomposition of hydrazinium nitrate occurs according to the stoichiometric equation:

$$36\,N_2H_5NO_3 + 2\,HNO_3 = \\ = 20\,NH_4NO_3 + 32\,N_2 + 3\,N_2O + 51\,H_2O.$$

The kinetics of the catalytic decomposition of hydrazine was studied in a thermostated glass reactor equipped with a reflux condenser. Stirring of the reaction mixture was carried out by a flow of argon at a controlled rate. Kinetic studies were performed at low initial concentrations of hydrazine (0.01 mol $litre^{-1}$) in order to avoid problems in determining the reaction order with respect to $N_2H_5^+$ due to adsorption saturation of active catalytic sites. The rate of catalytic decomposition of hydrazine increased with the intensity of the argon flow, which suggests that either this reaction proceeded in the diffusion regime or one of the volatile decomposition products decelerated the primary reaction by blocking the catalyst active sites.

The reaction order with respect to $N_2H_5^+$ is not a constant value and varies from 0 to 1 with a change in $[HNO_3]$. The dependence of the rate of the catalytic decomposition of hydrazine on the concentration of nitric acid is complex and has a minimum around $[HNO_3]$ 3.0–3.7 mol $litre^{-1}$. The kinetic curves for this reaction are well described by the equation

$$-\frac{dc}{d\tau} = k_1 c + k_0$$

over the whole range of experimental conditions.

The nature of the changes in the rate constants of the first- and zero-order reactions reflects the complex nature of heterogeneous catalytic reactions in the $N_2H_5^+ - HNO_3 - Pt$ system with an increase in $[HNO_3]$ (Fig. 4). At low concentrations of HNO_3 (0.25–2.0 mol $litre^{-1}$), the changes in the first-order rate constant correspond with the negative fractional order (-0.24 ± 0.01) with respect to nitric acid. At higher concentrations of HNO_3 (4.0–8.0 mol $litre^{-1}$), the value of the constant k_1 increases according to the apparent reaction order with respect to HNO_3 equal to 2.6 ± 0.2. The changes in the zero-order rate constants are consistent with the apparent reaction orders (1.96 ± 0.3 at 1.0–4.0 mol $litre^{-1}$ HNO_3 and -3.07 ± 0.3 at 4.0–7.0 mol $litre^{-1}$ HNO_3). It is noteworthy that in 3 M nitric acid the catalytic decomposition of hydrazine strictly follows zero-order kinetics with respect to $N_2H_5^+$.

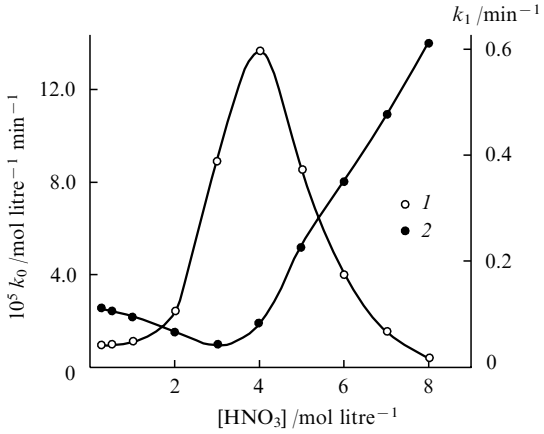


Figure 4. Changes in the zero- (*1*) and first- (*2*) order rate constants in the catalytic decomposition of hydrazine at 42 °C in the presence of 0.06 g ml^{-1} of 1% Pt/SiO_2 with an increase in the concentration of nitric acid.[6]

The temperature dependences of these rate constants were studied at three different concentrations of nitric acid (0.25, 3.1 and 6.2 mol $litre^{-1}$).

In 0.25 M HNO_3, the catalytic decomposition of hydrazine occurred predominantly as a first-order reaction with respect to $N_2H_5^+$. Therefore, only the k_1 values were used for the calculation of apparent activation energies. The value of $E^* = 34.2 \pm 0.5$ kJ mol^{-1} measured at 30.5–69 °C agreed, within the limits of experimental error, with that previously established for the catalytic decomposition of hydrazine in 0.2 M $HClO_4$ (36.4 ± 2.1 kJ mol^{-1}) (see Ref. 70).

In 3.1 M HNO_3, the values of apparent activation energies determined from the temperature dependences k_0 and k_1 were equal to 114.6 ± 4 kJ mol^{-1} (22–52 °C) and 33.7 ± 2 kJ mol^{-1} (22–41 °C) for zero- and first-order reactions with respect to $N_2H_5^+$, respectively. In 6.2 M HNO_3, the apparent activation energy of the first-order reaction with respect to $[N_2H_5^+]$ was 44.73 kJ mol^{-1} in the temperature range 28–50 °C. The zero-order component was not taken into consideration, since its contribution to the overall process was extremely small under the given conditions. It is of note that the increase in temperature increased the contribution of the zero-order (with respect to $N_2H_5^+$) reaction to the overall process in 3.1 M HNO_3, whereas in 6.2 M HNO_3 an opposite regularity was observed. The experimental apparent activation energies markedly exceeded those of diffusion-controlled processes [~ 19 kJ mol^{-1} (see Ref. 31)], thus suggesting that all reactions involved in the heterogeneous cata-

lytic decomposition of hydrazine in HNO_3 solutions are under kinetic control.

The analysis of kinetic curves revealed that the catalytic decomposition of hydrazine in nitric acid in the presence of Pt/SiO_2 is a superposition of three independent first- and zero-order processes with respect to $N_2H_5^+$. These reactions occur in parallel and their contributions to the overall process are determined by the concentration of nitric acid. At low concentrations of HNO_3 (0.25–2.0 mol litre^{-1}), the first-order reaction with respect to $N_2H_5^+$ and the negative fractional order with respect to the concentration of nitric acid are determined by heterogeneous decomposition of hydrazine on the platinum surface; the mechanism of this process was described previously for non-nitric acid solutions.[70] This conclusion is derived from the formal coincidence of reaction orders with respect to acid and apparent activation energies for solutions in perchloric and nitric acids. With an increase in the nitric acid concentration up to 1 mol litre^{-1}, the contribution of the zero-order reaction with respect to $N_2H_5^+$ becomes more apparent. In 3 M HNO_3, the reaction rate is of the zero order with respect to hydrazine. At low concentrations of hydrazine (0.01 mol litre^{-1}) in the C : R range from 1 : 100 to 1 : 10, no saturation of the catalyst surface with hydrazine occurs[70] and the appearance of a zero-order component with respect to $N_2H_5^+$ cannot be attributed to the adsorption nature of this process. Most probably, the zero order of the reaction with respect to hydrazine is determined by its fast reaction with hydrazoic acid or one of its derivatives generated on the catalyst surface upon contact with HNO_3. The rate of hydrazine loss depends on the rate of formation of HNO_2. The possibility of oxidation of the surface of the platinum catalyst with nitric acid was substantiated[9] by thermodynamic calculations of equilibrium electrochemical potentials of platinum and nitric acid. It was shown that the equilibrium potential of the HNO_3/HNO_2 pair in 3 M nitric acid at nitrous acid concentrations of 10^{-6}–10^{-4} mol litre^{-1} (where γ_{HNO_2} was taken equal to unity) varied from 1.14 to 1.08 V relative to NHE. At the same time, assuming arbitrarily that $[Pt^{2+}] = 10^{-6}$ mol litre^{-1} and $\gamma_{Pt^{2+}} = 1$, the equilibrium potential values for the Pt^{2+}/Pt and PtO_2/Pt^{2+} pairs in 3 M HNO_3 are 1.011 and 1.077 V (NHE), respectively. A comparison of experimental values of equilibrium oxidation potentials suggests that metallic platinum is oxidised in HNO_3 solutions to a tetravalent state (PtO_2). This process is accompanied by the reduction of nitric acid to HNO_2. The following reaction scheme can be proposed:

$$Pt + NO_2^+ \longrightarrow PtO + NO^+(ads)\ (slow), \tag{20}$$

$$PtO + NO_2^+ \longrightarrow PtO_2 + NO^+(ads)\ (slow). \tag{21}$$

The adsorbed nitrosyl cations derived from nitrous acid according to the equilibrium

$$NO^+ + H_2O \rightleftharpoons H_2NO_2^+ \rightleftharpoons HNO_2 + H^+, \tag{22}$$

react with hydrazine by a cascade of fast reactions on the catalyst surface, which determines the zero order of the overall process with respect to $N_2H_5^+$:

$$NO^+(ads) + N_2H_5^+ \longrightarrow N_2H_2(ads) + HNO(ads) + 2H^+, \tag{23}$$

$$2N_2H_2(ads) \longrightarrow HN=N-NH-NH_2(ads) \longrightarrow \longrightarrow HN_3(ads) + NH_3(ads), \tag{24}$$

$$2N_2H_2(ads) \longrightarrow H_2N-N=N-NH_2(ads) \longrightarrow \longrightarrow N_2(ads) + N_2H_4(ads), \tag{25}$$

$$2HNO(ads) \longrightarrow H_2N_2O_2(ads) \longrightarrow N_2O(ads) + H_2O, \tag{26}$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3. \tag{27}$$

The oxidised active sites of the catalyst are regenerated as a result of their reaction with hydrazine

$$PtO_2 + N_2H_4(ads) \longrightarrow Pt + N_2 + 2H_2O \tag{28}$$

and thus become accessible for the next catalytic act.

From the above scheme, it can be seen that HN_3 is a product of reaction (24). However, as mentioned above, no hydrazoic acid was detected either in the solution or in the effluent gases. Presumably, the HN_3 molecules adsorbed on the catalyst were not desorbed into the solution, but underwent catalytic decomposition directly on the platinum surface.

The rate of the catalytic decomposition of hydrazine increases with an increase in the concentration of nitric acid in the range 4–8 mol litre^{-1} simultaneously with a rapid change in the reaction order from zero to first with respect to $N_2H_5^+$. Presumably, in the region of high concentrations of HNO_3 the crucial role should be ascribed to the catalytic oxidation of hydrazine with nitric acid. The rate-determining step of this reaction is the reaction of hydrazine molecules adsorbed on the catalyst surface with nitroyl cations generated in the equilibrium reaction (6):

$$N_2H_4(ads) + NO_2^+ \longrightarrow NO^+ + N_2H_2 + H_2O. \tag{29}$$

The concentration of adsorbed hydrazine is directly proportional to its solution concentration, which determines the first order of the reaction with respect to $N_2H_5^+$. The diimide and the nitrosyl cation generated in the reaction (29) undergo a series of fast transformations (23)–(27) both on the catalyst and in the solution.

A comparative analysis of experimental results[9,67] of the catalytic decomposition of hydrazine in nitric acid suggests that the kinetic characteristics of this process depend critically on the mode of stirring of the reaction components. Thus the decomposition rate of hydrazine showed virtually no dependence on the shaking intensity[67] and passed through a maximum with an increase in $[HNO_3]$ from 0.2 to 7 mol litre^{-1}, whereas more intense stirring by a flow of argon caused a monotonic increase in the reaction rate. With an increase in the nitric acid concentration from 0.25 to 8 mol litre^{-1}, the decomposition rate first slowed down and then showed an increase passing through a minimum around 3.0–3.7 mol litre^{-1}. The reason for such a difference is that shaking of the reaction components in a closed volume results in accumulation of the gaseous decomposition products in the solution and on the catalyst surface, which inhibits the catalytic process by blocking the active sites. At the same time, passage of argon favours degassing of the solution and faster regeneration of the active surface of the catalyst.

4. Decomposition of hydrazoic acid

The use of hydrazine together with nitric acid in reprocessing of the used nuclear fuel results in the formation of hydrazoic acid as an undesirable intermediate. HN_3 is formed in the reaction of hydrazine with nitrous acid. The overall oxidation reaction

$$N_2H_5^+ + 2HNO_2 \longrightarrow N_2 + N_2O + 3H_2O + H^+$$

occurs in two steps:

$$N_2H_5^+ + HNO_2 \xrightarrow{k_1} HN_3 + 2H_2O + H^+,$$

$$HN_3 + HNO_2 \xrightarrow{k_2} N_2 + N_2O + H_2O.$$

In solutions of moderate acidity, $k_1 \approx 5k_2$ (see Ref. 72). From the above scheme it follows that the oxidation of excess hydrazine results in the accumulation of hydrazoic acid in the solution. At elevated temperatures, HN_3 is formed by direct oxidation of hydrazine with nitric acid.[31]

$$17N_2H_4 + 16HNO_3 \longrightarrow \longrightarrow 4NH_4NO_3 + 4HN_3 + 4N_2O + 11N_2 + 32H_2O.$$

The pertechnetate ions present in technological solutions catalyse hydrazine oxidation to give HN_3.[73]

Hydrazoic acid is related to the class of potentially hazardous chemical compounds due to its toxicity and explosive risk under certain conditions.[74] Therefore, its uncontrolled accumulation in technological solutions is inadmissible from the standpoint of

environmental and technological safety. The problem of elimination of hydrazoic acid from solutions can successfully be solved by using heterogeneous catalysis due to its ability to undergo catalytic decomposition in the presence of platinum black.[75] The kinetics and the decomposition mechanism of hydrazoic acid in solutions of nitric and perchloric acids in the presence of a catalyst (1% Pt/SiO_2) have been studied.[76] The rate of the catalytic decomposition of HN_3 did not depend on the intensity of stirring of the reaction mixture. The reaction rate followed first-order kinetics with respect to HN_3 over the whole range of experimental conditions. An increase in the amount of the catalyst resulted in a proportional increase in the rate constant. The catalytic decomposition of HN_3 in nitric acid solutions first slowed down with an increase in the nitric acid concentration followed by its acceleration after passage through a minimum at $[HNO_3]$ 6 mol litre^{-1}. In perchlorate solutions, the reaction rate decreased monotonically over the whole range of $HClO_4$ concentrations (0.5–8 mol litre^{-1}) (Fig. 5). The apparent reaction orders with respect to nitric acid determined in 0.5–6 M HNO_3 and in 0.5–8.0 M $HClO_4$ were equal to -0.37 and -0.47, respectively. The negative fractional order of the reaction with respect to the acid in the concentration range specified suggests that neither hydrogen ions nor HNO_3 molecules directly participate in the chemical reaction resulting in the catalytic decomposition of hydrazoic acid. The inhibitory effect of H^+ ions may be due to competitive adsorption on the active catalytic sites.

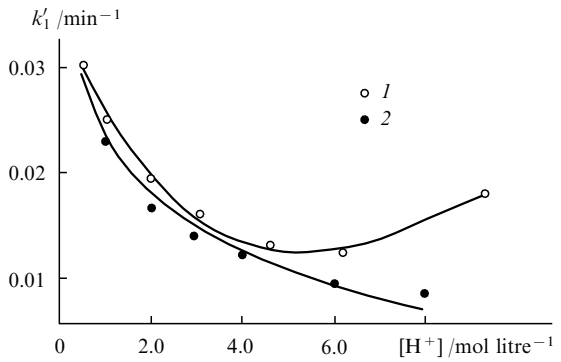


Figure 5. Effect of acid concentration on the decomposition rate of hydrazoic acid at $[HN_3]_0 = 0.025$ mol litre^{-1} and 64 °C in the presence of 0.1 g ml^{-1} of 1% Pt/SiO_2.[76]
(*1*) HNO_3, (*2*) $HClO_4$.

The effect of temperature on the decomposition rate of HN_3 was studied in solutions of various compositions. The values of apparent activation energies are listed in the table below:

Acid	E^* /kJ mol^{-1}	Acid	E^* /kJ mol^{-1}
1.0 M HNO_3	63.5 ± 1.8	6.2 M HNO_3	74.6 ± 2.3
3.1 M HNO_3	69.0 ± 2.0	3.0 M $HClO_4$	67.2 ± 1.6

The increase in E^* with an increase in the acid concentration is due to the same reasons as in the catalytic decomposition of hydrazine in non-nitric acid media.[70] The mechanisms of the catalytic decomposition of hydrazoic acid in 0.5–8 M $HClO_4$ and in 0.5–6 M HNO_3 are virtually identical and based on heterogeneous catalytic decomposition of HN_3 adsorbed on the active sites of the catalyst.

$$HN_3(\text{solution}) \rightleftharpoons HN_3(\text{ads}),$$

$$HN_3(\text{ads}) \longrightarrow NH^{\bullet} + N_2 \text{ (rate-determining step)},$$

$$NH^{\bullet} + HN_3 \longrightarrow N_2H_2 + N_2, \quad (30)$$

$$N_2H_2 + HN_3 \longrightarrow NH_3 + 2N_2. \quad (31)$$

The fast reactions (30) and (31) may occur both on the catalyst surface and in solution. The general stoichiometric equation for both reactions is as follows:

$$3HN_3 = NH_3 + 4N_2.$$

The rate of the catalytic decomposition of HN_3 in solutions with $[HNO_3] > 6$ mol litre^{-1} increases considerably due to an increase in the contribution of oxidation reactions involving nitric acid.[76] The catalytic oxidation of hydrazoic acid consists of heterogeneous reactions of adsorbed HN_3 molecules with nitroyl ions in nitric acid media according to the equilibrium (6) followed by a series of fast homogeneous transformations *via* intermediate radicals.

$$HN_3(\text{ads}) + NO_2^+ \rightleftharpoons N_3NO_2(\text{ads}) + H^+,$$

$$N_3NO_2(\text{ads}) \longrightarrow 2NO^{\bullet} + N_2 \text{ (rate-determining step)},$$

$$2NO^{\bullet} + NO_2^+ + 2H^+ \longrightarrow 3NO^+ + H_2O,$$

$$NO^+ + HN_3 \longrightarrow N_2O + N_2 + H^+.$$

In general, the oxidation process can be presented as follows:

$$4HN_3 + 2HNO_3 = 4N_2 + 3N_2O + 3H_2O.$$

It is noteworthy that the kinetic regularities and catalytic decomposition mechanisms of hydrazoic acid and hydrazine in nitric acid are roughly similar. In both cases, in solutions of low or medium acidities, the heterogeneous catalytic disproportionation of these compounds due to increase in $[HNO_3]$ is followed by heterogeneous catalytic oxidation, which involves nitroyl cations. It may thus be assumed that the catalytic decomposition of HN_3 in nitric acid, as of hydrazine, occurs through a catalytic redox cycle on the surface of platinum, which is similar to reactions (20), (21) and (28). However, in the case of HN_3 this process is kinetically indistinguishable, since its rate is considerably lower than the rates of catalytic disproportionation and oxidation of HN_3, which occur in parallel.

The catalytic decomposition of hydrazoic acid in nitric acid was studied in the dynamic regime[77] using 1% Pt/SiO_2 as a catalyst. It was shown that the main characteristics of the continuous process, *viz.*, the effects of nitric acid concentration and temperature on the decomposition rate of HN_3, were in good agreement with the kinetic data obtained in the static regime. The presence of sodium nitrate (20 g litre^{-1}) and uranium (0.1 g litre^{-1}) in the solution had no effect on the efficiency of the catalytic decomposition of hydrazoic acid. The decomposition rate of HN_3 decreased slightly when 0.5 M nitric acid saturated with spent TBP was used. However, such an effect was not related to the progressive poisoning of the catalyst, since the effects of TBP and its decomposition products on the reaction rate were of a steady and therefore reversible character. The decrease in the decomposition rate of HN_3 in the presence of TBP might be attributed to the equilibrium adsorption of organic molecules on the catalyst surface, as a result of which part of the active sites appeared to be occupied and did not take part in the catalytic process. The decrease in the reaction rate can be compensated for by mere elevation of temperature or by reduction of the flow rate of the working solution.

The catalytic decomposition of hydrazoic acid in the dynamic regime is a technologically efficient process and can be recommended for removal of HN_3 from radioactive wastes before their final processing.

5. Catalytic denitration of nitric acid solutions

Modern wet technologies for processing waste nuclear fuels starting from the dissolution of fuel elements and ending with separation and purification of isolated radioactive components are based on the use of nitric acid solutions. However, the problem of processing of water-tail fractions by their further vitrification cannot successfully be solved without removal of excess nitric acid and nitrates. This is usually accomplished by chemical denitration

of solutions with formic acid or formaldehyde.[78–82] The main problem in this procedure consists of the autocatalytic mode of the reaction of nitric acid with HCO_2H and HCHO. Such reactions are usually characterised by induction periods where accumulation of threshold concentrations of nitrous acid in the solution occurs and subsequent fast propagation of the process. Under certain conditions, the denitration assumes the form of an explosive process that is difficult to control. This circumstance makes chemical denitration a potentially dangerous process. Numerous cases of grave accidents upon denitration at pilot-plant and industrial installations for processing used materials are documented in the literature.[83,84]

It has been established[58] that the reaction of nitric acid with formic acids in the presence of a catalyst (Pt/SiO_2) begins without any induction period and proceeds without any pressure surge in the reaction system (Fig. 6). The kinetics and stoichiometry of the catalytic reaction of HNO_3 with HCO_2H were studied in a broad range of experimental conditions ($[HNO_3]_0 = 0.7–8.0$ mol litre^{-1}; $[HCO_2H]_0 = 0.5–4.3$ mol litre^{-1}; temperature 55–85 °C; C : R = 1 : 10–1 : 50, 1% Pt/SiO_2). In all cases, the reaction began without any induction period. If such a period did exist, its duration would be no longer than the time required for the mixing of the reactants. In dilute (2 mol litre^{-1}) HNO_3 solutions, the kinetic curves were described by a first-order equation with respect to HCO_2H. In more concentrated HNO_3 solutions, the reaction was of the first order with respect to formic acid until the extent of decomposition reached 40%–50%; at higher degrees of conversion, the reaction rate decreased. In these cases, the first-order equation was used for the estimation of the initial rate of the reaction. The increase in the stirring intensity on passing an inert gas through the reaction mixture resulted in deceleration of the reaction, which points to the involvement of intermediate gaseous products in the oxidation of HCO_2H. A similar phenomenon was observed where the reaction was carried out in the absence of the catalyst.[78] The rate of the reaction of HCO_2H with HNO_3 increased linearly with the increase in the C : R ratio, which points to the catalytic nature of the process. The reaction rate increased rapidly with the concentration of nitric acid. The dependence of the rate constant on $[HNO_3]$ had a complex form, which did not permit an unambiguous estimation of the reaction order with respect to nitric acid. It may be concluded, however, that the apparent order of the reaction with respect to nitric acid approximated 3 with an increase in $[HNO_3]$ above 2 mol litre^{-1}, which is characteristic of reactions occurring in the absence of a catalyst.[78,80] The apparent reaction order with respect to hydrogen ions at a constant concentration of nitrate ions changed monotonically from 0 to 4 with an increase in $[H^+]$ from 0.7 to 5 mol litre^{-1}. The activation energy of the reaction of HNO_3 with HCO_2H in the presence of a platinum catalyst was determined at different concentrations of nitric acid:

$[HNO_3]$ /mol litre^{-1}	E^* /kJ mol^{-1}
0.94	84.2 ± 2.2
3.14	105.0 ± 4.0
4.92	113.2 ± 3.1

It can be seen that the increase in the concentration of nitric acid results in a considerable increase in the apparent activation energy, which gradually approximates that for a denitration process occurring in the absence of a catalyst [126 kJ mol^{-1} (see Ref. 80)].

This fact and the effects of acidity and total concentration of nitric acid on the reaction rate suggest that two parallel processes, *viz.*, catalytic reaction of nitric acid with HCO_2H and homogeneous denitration, occur in the system under study, the contribution of the latter to the overall process being increased with $[HNO_3]$. Earlier studies[38] have demonstrated the absence of autocatalytic accumulation of nitrous acid at low (1 mol litre^{-1}) concentrations of HNO_3. If HNO_2 was present in the solution from the very first steps, its concentration diminished gradually during its reaction with HCO_2H. Here, the denitration occurred only in the presence of a catalyst according to a heterogeneous catalytic mechanism. Therefore, the value of $E^* = 84.2$ kJ mol^{-1} obtained at $[HNO_3] = 0.94$ mol litre^{-1} can be regarded as an apparent activation energy of the catalytic process. At higher concentrations of nitric acid that favour the accumulation of HNO_2, the contribution of the autocatalytic reaction increased and at $[HNO_3] > 4$ mol litre^{-1} the process occurred mainly according to the kinetic regularities of homogeneous denitration.

The catalytic denitration gaseous products are represented by CO_2, NO_2, NO and N_2O; the evolution of N_2O was suppressed upon increase in the concentration of nitric acid. The fact that no hydrogen was found in the gaseous reaction products suggests the absence of catalytic self-decomposition of formic acid under the given experimental conditions. Calculations of the gas balance of HCO_2H based on the results of gas analysis and kinetic measurements show the formation of 1 mole of CO_2 per mole of the consumed formic acid. Stoichiometric measurements demonstrated that the consumption of formic acid in the catalytic denitration was 1.1–1.5 moles of HCO_2H per mole of the consumed HNO_3 (Table 3), which is virtually the same as in a non-catalysed reaction, all other experimental conditions being the same.

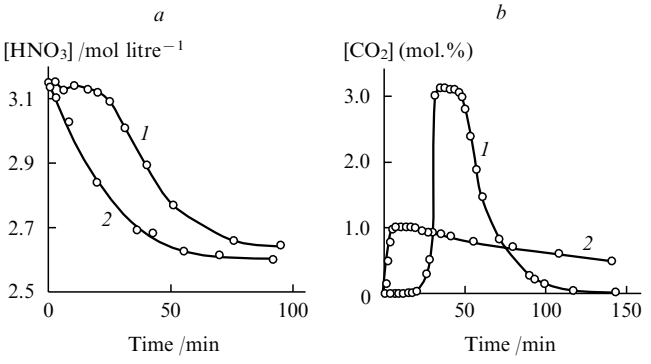


Figure 6. Effect of a platinum catalyst on the decomposition kinetics of nitric acid (*a*) and CO_2 formation (*b*) in the denitration.[58]
$[HNO_3]_0 = 3.14$ mol litre^{-1}; $[HCO_2H]_0 = 1.1$ mol litre^{-1} at 70 °C.
(*1*) without catalyst, (*2*) with catalyst (1% Pt/SiO_2); (*a*) 0.04 g ml^{-1}, (*b*) 0.1 g ml^{-1}.

Table 3. Stoichiometry of the denitration reaction in the presence of a catalyst (1% Pt/SiO_2) at 60 °C.[58]

$[HNO_3]_0$ /mol litre^{-1}	$[HCO_2H]_0$ /mol litre^{-1}	C : R /g ml^{-1}	Time /min	Degree of conversion of HCO_2H (%)	$\frac{\Delta[HCO_2H]}{\Delta[HNO_3]}$ (see [a])
4.72	1	0.04	30	50	1.19 ± 0.04
4.75	1	0.04	30	50	1.18 ± 0.03
4.75	1	0.04	60	80	1.25 ± 0.01
4.75	1	0.04	120	92	1.26 ± 0.02
4.08	4.3	0.03	70	82	1.49 ± 0.02
4.08	4.3	0.03	120	92	1.50 ± 0.01
4.08 [b]	4.3	0.07	120	96	1.49 ± 0.02
4.08	4.3	see [c]	70	85	1.44 ± 0.01
6.37	1	0.04	16	47	1.06 ± 0.01
6.37	1	0.04	25	73	1.09 ± 0.01
6.37	1	0.04	45	85	1.11 ± 0.01
6.37	1	0.04	60	90	1.2 ± 0.1
5.52	4.17	0.04	120	98	1.36 ± 0.01

[a] Average values from five measurements. [b] In this case, the temperature was 70 °C. [c] Without catalyst.

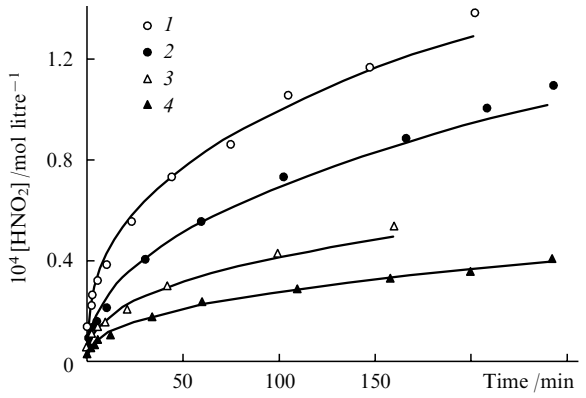


Figure 7. Effect of the catalyst (1% Pt/SiO_2) on the accumulation of nitrous acid in 1.1 M HNO_3 at 60 °C.[58]
C : R /g ml^{-1}: 0.20 (*1*), 0.15 (*2*), 0.10 (*3*), 0.05 (*4*).

The mechanism of catalytic denitration and the role of a platinum catalyst in the initiation of the reaction and suppression of the induction period have been reviewed.[58, 85] It was found[58] that the addition of a catalyst (Pt/SiO_2) to 0.5–4 M solutions of HNO_3 resulted in rapid accumulation of nitrous acid (Fig. 7), which reacts with HCO_2H to initiate the denitration.

$$HCO_2H + HNO_2 \longrightarrow {}^{\bullet}CO_2H + NO + H_2O, \quad (32)$$

$$^{\bullet}CO_2H + HNO_2 \longrightarrow CO_2 + NO + H_2O, \quad (33)$$

$$2\,NO + NO_3^- + H^+ + H_2O \rightleftharpoons 3\,HNO_2, \quad (34)$$

$$HNO_2 + HNO_3 \rightleftharpoons 2\,NO_2 + H_2O. \quad (35)$$

Accelerated formation of HNO_2 in nitric acid solutions upon a contact with a platinum catalyst results from oxidation of surface platinum atoms with nitroyl cations [see reactions (20)–(22)], as is the case with catalytic decomposition of hydrazine in HNO_3 solutions.[9] In the absence of a reducing agent, the catalyst surface is passivated and the formation of hydrazoic acid is discontinued.[85] After addition of formic acid to the reaction system, the oxidised platinum atoms react with HCO_2H molecules and thus become accessible to a new attack by nitric acid resulting in the formation of HNO_2. Thus, the surface catalytic redox cycle is implemented in the system, which favours fast initial accumulation of the threshold concentration of nitrous acid [$\sim 10^{-2}$ mol litre^{-1} (see Ref. 79)] required for triggering the denitration reaction. The mechanism of the catalytic denitration is schematically depicted in Fig. 8.

A significant advantage of catalytic denitration over the homogeneous process is that it occurs even in the presence of the antinitrite reagent (urea), although the reaction is slowed down.[58] However, the reaction rate increases after complete decomposition of $(NH_2)_2CO$. The same is true for hydrazine. Studies on catalytic decomposition of excess nitric acid in plutonium-containing solutions have shown that in the presence of Pt(IV) (2–25 g litre^{-1}) the denitration proceeds without any induction period and complications in a broad range of initial concentrations of nitric and formic acids. In the presence of excess of HCO_2H, partial (up to 30%) reduction of Pu(IV) to Pu(III) is observed at the end of the process.[58] The catalytic denitration in the presence of excess of HCO_2H enables virtually complete decomposition of nitric acid. Thus no nitric acid could be detected by potentiometry in a solution containing ~ 1 mol litre^{-1} of formate following denitration. Long-term use of catalysts for denitration does not result in their poisoning. After more than 100 cycles, not a single case of a decrease in the catalytic activity of the catalyst (1% Pt/SiO_2) taken from the same batch was noted.[58]

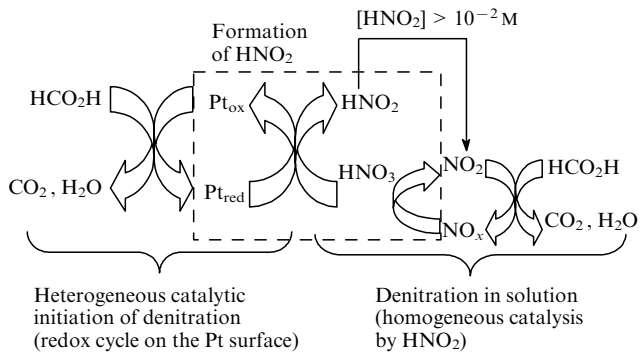


Figure 8. A schematic representation of a catalytic denitration mechanism.

6. Decomposition of urea and ammonium nitrate in the catalytic denitration

Urea (carbamide) is widely employed in radiochemical processes as an antinitrite reagent, *e.g.*, for electrochemical reduction of uranium(VI) in nitric acid solutions.[19] Like any other antinitrite reagent, urea is decomposed by an addition of sodium nitrite to nitric acid solutions[72] or by passage of gaseous nitrogen oxides NO and NO_2 (NO_x-gases) through a solution.[86] However, despite the obvious simplicity and efficiency of these procedures, the addition of $NaNO_2$ to the solution is not always desirable, since it is accompanied by an increase in the total salt content, whereas the latter method requires an additional source of NO_x gases.

As shown above, the platinum-catalysed reaction of nitric acid with formic acids (catalytic denitration) occurs successfully in the presence of urea and is accompanied by its efficient decomposition.[58] At the same time, this reaction is impossible in the absence of a catalyst and carbamide-containing HNO_3-HCO_2H mixtures remain stable over indefinitely long periods of time even at elevated temperatures. The specific behaviour of urea in the catalytic denitration in the presence of a catalyst (1% Pt/SiO_2) has been studied.[87, 88] It was shown that in the absence of formic acid carbamide was not subject to catalytic decomposition in 0–8 M HNO_3 even at temperatures close to the boiling point of the solution. However, the addition of 0.1–2 mol litre^{-1} of HCO_2H to 2 M HNO_3 containing 0.5 mol litre^{-1} of carbamide and 0.02–0.2 g ml^{-1} of 1% Pt/SiO_2 induced the decomposition of $(NH_2)_2CO$ at 60 °C resulting in the denitration of the solution. The catalytic decomposition of urea in the presence of 0.2–1.3 mol litre^{-1} of HCO_2H and at C : R = 1 : 50 began at 60 °C at a concentration of nitric acid equal or higher than 2 mol litre^{-1} (see Ref. 87). The kinetic curves of the consumption of $(NH_2)_2CO$ changed significantly with an increase in [HNO_3] (Fig. 9). In the HNO_3 range 2–2.5 M, the reaction occurred with an induction period followed by accelerated decomposition of urea. At higher concentrations of nitric acid, the decomposition of urea occurred without the induction period and is zero order with respect to $(NH_2)_2CO$. The rate of this zero-order process did not depend on the intensity of stirring of the solution, *i.e.*, the reaction proceeded under kinetic control. The increase in C : R in the range 1 : 50–1 : 10 resulted in a proportional increase in the reaction rate, which is characteristic of heterogeneous catalytic processes in solutions. The reaction rate increases with the concentration of formic acid; the reaction order with respect to HCO_2H was close to unity. With an increase in the initial concentration of nitric acid from 2.3 to 7.0 mol litre^{-1}, the decomposition rate of urea decreased considerably. The dependence of k_0 on [HNO_3] in logarithmic coordinates was not approximated by a straight line, which excluded the unambiguous interpretation of the reaction order with respect to nitric acid. The apparent activation energy of this reaction determined at $[HNO_3]_0 = 2.9$ mol litre^{-1}, $[HCO_2H]_0 = 1.0$ mol litre^{-1} and $[(NH_2)_2CO]_0 = 0.2$ mol litre^{-1} was 58.7 ± 1.6 kJ mol^{-1}.

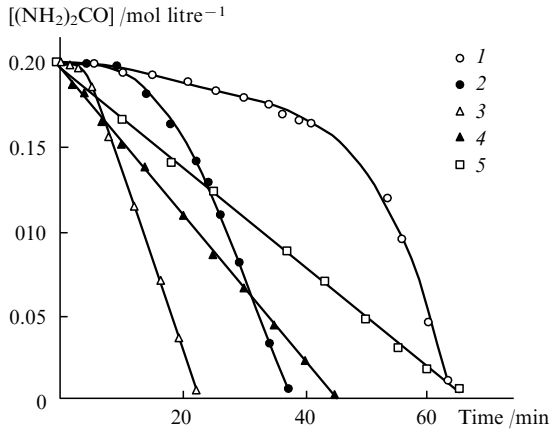


Figure 9. Kinetic curves for the decomposition of urea (0.2 mol litre^{-1}) in nitric acid solutions of variable concentrations in the presence of 0.1 g ml^{-1} of 1% Pt/SiO_2 at $[HCO_2H]_0$ = 1.0 mol litre^{-1} and at 60 °C.[87] $[HNO_3]$ /mol litre^{-1}: 2.0 (*1*), 2.1 (*2*), 2.3 (*3*), 2.6 (*4*), 5.6 (*5*).

The kinetic data altogether, namely, the threshold type of the reaction with respect to $[HNO_3]$, the induction period, the zero reaction order with respect to $(NH_2)_2CO$, the impossibility of performing the catalytic decomposition of carbamide in the absence of HCO_2H, prompt a conclusion that the decomposition of urea is a result of its reaction with nitrous acid generated in the reaction system upon catalytic denitration according to the equations (32)–(34). The rate of decomposition of carbamide is determined by the rate of formation of HNO_2 generated upon catalytic reaction of nitric acid with HCO_2H according to a mechanism presented in Fig. 8.

As mentioned above, the kinetics of decomposition of urea manifests a rather complex dependence on the concentration of nitric acid. The threshold type of this reaction with respect to $[HNO_3]$ and the induction period in the range 2.0–2.3 M HNO_3 are determined by the autocatalytic type of the reaction of nitric acid with formic acid. The concentration of nitrous acid in the HNO_3-HCO_2H mixture increases in an autocatalytic manner at $[HNO_3]$ = 1–3.8 mol litre^{-1} and decreases at $[HNO_3]$ < 1 mol litre^{-1}.[38] This is associated with a strong effect of $[HNO_3]$ on the rate and the equilibrium of the reaction (34).[89] In a system containing HCO_2H, HNO_3 and carbamide, a positive balance of HNO_2 generated by reaction (34) with respect to HNO_2 consumed in reactions (37) and (38) (see below) in the presence of Pt/SiO_2 is established at $[HNO_3]$ > 2 mol litre^{-1}. Reaction of excess nitrous acid with urea leads to the decomposition of the latter. At $[HNO_3]$ = 2–2.3 mol litre^{-1}, the formation of nitrous acid occurs with acceleration, which results in the appearance of an induction period. Urea is related to the class of 'mild antinitrite reagents'. The rate of its reaction with nitrous acid is relatively low, but shows a rapid increase with an increase in the solution acidity.[73] It is this fact that is responsible for the decrease in the rate of the catalytic decomposition of urea with an increase in the concentration of nitric acid. Indeed, the formation of nitrous acid in the solution (the reaction system) results from two different processes, *viz*., the catalytic redox cycle involving nitric acid and HCO_2H on the platinum surface and autocatalytic generation of HNO_2 in the solution [see reactions (32)–(34)]. The rapid acceleration of the rate of the reaction of nitrous acid with carbamide at increasing $[HNO_3]$ leads to the inhibition of autocatalytic formation of HNO_2. As a result, the rate of formation of nitrous acid in the solution decreases with a concomitant decrease in the decomposition rate of urea with an increase in $[HNO_3]$.

The composition of the reaction products and the stoichiometry of the catalytic decomposition of urea in the HNO_3-HCO_2H-Pt/SiO_2 system have been studied in detail.[88] Gaseous decomposition products of urea include CO_2, N_2O and N_2. A small amount of NO_2 and trace amounts of H_2 are also formed. Ammonium nitrate and formamide are formed in the solution. In general, the decomposition of urea under catalytic denitration conditions can be described in terms of the stoichiometric equation:

$$3(NH_2)_2CO + 3\,HCO_2H + 5\,HNO_3 = \quad (36)$$
$$= 2\,N_2 + N_2O + 2\,NH_4NO_3 + NH_2CHO + 5\,CO_2 + 6\,H_2O.$$

Although this process is based on the reaction of $(NH_2)_2CO$ with nitrous acid formed, the compositions of gaseous and soluble decomposition products of urea in the HNO_3-HCO_2H-Pt/SiO_2 system differ essentially from that expected for the generally accepted scheme of the reaction of carbamide with HNO_2.[72, 86, 90]

$$(NH_2)_2CO + 2\,HNO_2 \longrightarrow 2\,N_2 + CO_2 + 3\,H_2O. \quad (37)$$

The reason for this discrepancy is that carbamide, being in excess under catalytic denitration conditions, reacts with HNO_2 formed. In this case, the following reaction sequence leading to ammonium nitrate as a result of acid hydrolysis of the intermediate product, *viz*., cyanic acid, is implemented:[91]

$$(NH_2)_2CO + HNO_2 \longrightarrow N_2 + HCNO + 2\,H_2O, \quad (38)$$
$$HCNO + HNO_3 + H_2O \longrightarrow NH_4NO_3 + CO_2.$$

Formamide and nitrogen(I) oxide also seem to be partial oxidation products of urea with nitrous acid in the presence of excess of $(NH_2)_2CO$.

$$(NH_2)_2CO + HNO_2 \longrightarrow N_2O + NH_2CHO + H_2O.$$

Formamide is less subject to acid hydrolysis in comparison with cyanic acid[92] and is therefore accumulated in the solution until the decomposition of carbamide is complete.

The rate of catalytic denitration increases after urea decomposition is over. This is accompanied by a jump-like increase in $[HNO_2]$ in the solution with subsequent rapid return to the quasi-steady state; $[HNO_2]$ remains at this level up to the end of the denitration (Fig. 10). Under these conditions, soluble decomposition products of urea, *viz*., formamide and ammonium nitrate, are unstable and undergo further degradation.[88] Apparently, these reactions can be described by the following equations:

$$NH_2CHO + HNO_2 \longrightarrow N_2 + CO_2 + 2\,H_2O,$$
$$NH_4NO_3 + HNO_2 \longrightarrow N_2 + HNO_3 + 2\,H_2O. \quad (39)$$

It was suggested[88] that the decomposition of formamide and ammonium nitrate is accelerated in the presence of catalysts. The regularities of decomposition reactions of nitrogen-containing compounds present substantial scientific and practical interest.

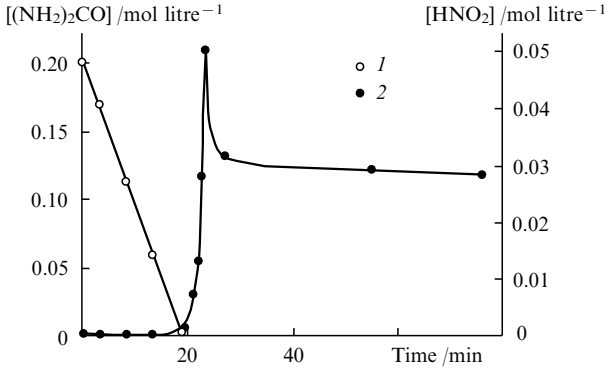


Figure 10. Dynamics of changes in the concentrations of urea (*1*) and nitrous acid (*2*) in the decomposition of urea in the presence of 0.1 g ml^{-1} of 1% Pt/SiO_2 at 70 °C.[87]
$[HNO_3]_0$ = 3.3 mol litre^{-1}, $[HCO_2H]_0$ = 1.0 mol litre^{-1}

In the first place, this concerns ammonium nitrate. The search for approaches to its removal from water-tail fractions of radiochemical plants presents a serious problem for the technology of the nuclear fuel cycle. The decomposition of ammonium nitrate under conditions of denitration was considered in detail.[93] A series of experiments on the denitration of nitric acid solutions containing ammonium nitrate under static conditions have been carried out recently in order to elucidate the role of platinum catalysts in the homogeneous and catalytic decomposition of ammonium nitrate formed in the reaction of HNO_3 with HCO_2H. As expected, in the absence of catalysts the denitration was preceded by an induction period of 3–60 min, which varied depending on the initial concentration of nitric acid, and followed by a fast reaction characteristic of homogeneous denitration. In all cases, in the presence of a platinum catalyst this reaction proceeded without an induction period. The results obtained suggest that the presence of Pt/SiO_2 in the reaction system has virtually no effect on the degree of decomposition of ammonium nitrate in the course of denitration. From the kinetic point of view, the role of the catalyst is only reduced to the elimination of the induction period, *i.e.*, to the initiation of the reaction of nitric acid with HCO_2H. As a consequence, the chemical reaction resulting in the oxidation of the ammonium ion takes place in the solution rather than on the catalyst surface, *i.e.*, is homogeneous. It was found that the degree of decomposition of ammonium nitrate increases with an increase in the initial concentration of nitric acid in the range 0.5–4 mol litre^{-1}. Further increase in $[HNO_3]$ slightly reduces the reaction yield. The increase in the concentration of formic acid in the presence of an excess of HNO_3 enhances the decomposition of NH_4NO_3. However, the efficiency of this reaction diminishes at the molar ratios $[HCO_2H]:[HNO_3] > 0.8-1.0$. The increase in temperature from 80 to 100 °C increases the reaction yields by 12%. These regularities were interpreted under the assumption that the disappearance of ammonium nitrate is due to the homogeneous oxidation of ammonium ions with nitrous acid [reaction (39)]. In this case, the role of a nitrous acid precursor is played by the HNO_3-HCO_2H system where HNO_2 is accumulated by an autocatalytic mechanism [reactions (32)–(34)] underlying chemical denitration of nitric acid solutions. Obviously, the oxidation rate of the ammonium ion with nitrous acid is lower than its formation rate, otherwise the presence of ammonium nitrate in the solution will prevent denitration in the absence of a platinum catalyst due to inhibition of the autocatalytic formation of HNO_2. The efficiency of ammonium nitrate decomposition should be determined by the steady-state concentration of nitrous acid rather than its formation rate. The equilibrium concentrations of HNO_2 in nitric acid solutions in the absence of other oxidants and reducing agents are largely determined by the interrelated reversible reactions (34) and (35). A comparison of these equilibria shows that an increase in the concentration of nitric acid in the reaction system results, on the one hand, in an increase in the yield of HNO_2 and, on the other hand, in its decomposition due to oxidation to nitrogen dioxide. If reactions are carried out in open systems, the yields of NH_4NO_3 decomposition products are lower as a result of removal of gaseous NO_2 from the reactor. It is this factor that accounts for the decrease in the reaction rate and prevents further increases in the yields of decomposition of ammonium nitrate at $[HNO_3] > 4$ mol litre^{-1}. The non-monotonic changes in the degree of decomposition of ammonium nitrate with an increase in the ratio $[HCO_2H]:[HNO_3]$ can be attributed to the changes in the stoiochiometry of the denitration reaction, which in turn is determined by the ratio of concentrations of nitric and formic acids.[57] The maximum yield of NO involved in the formation of nitrous acid is observed at the $[HCO_2H]:[HNO_3]$ molar ratio $\approx 0.8-1.0$, which accounts for the observed pattern of changes in the degree of decomposition of NH_4NO_3. The maximum (close to 100%) degree of decomposition of ammonium nitrate is reached upon continuous addition of formic acid to solutions of ammonium nitrate in nitric acid in the presence of a catalyst (Pt/SiO_2). This method can be used for the decomposition of ammonium nitrate in solutions with complex compositions. Thus it was shown[93] that the presence of caesium or uranyl nitrates (10 g litre^{-1} with respect to the metal) in the solution has no effect on the reaction efficiency. If compounds containing NH_2 groups (*e.g.*, hydrazine, urea or acetamide) are added, their catalytic degradation precedes the decomposition of ammonium nitrate. In this case, the process occurs only in the presence of a catalyst.

IV. Conclusion

Analysis of the literature data on the kinetics of heterogeneous catalytic redox reactions of actinide ions in aqueous media revealed that the majority of publications on the subject are devoted to studies of reduction of actinide ions with molecular reducing agents to the lowest oxidation states. The array of catalysts assayed is confined to activated charcoal and finely dispersed metals of the platinum group (as a rule, Pt) on inert supports. Despite the fact that catalytic properties of palladium and rhenium sulfides are now well established, these materials have not found wide application because of poorly developed surfaces. It seemed therefore tempting to prepare PdS or Re_2S_7 immobilised on supports with a more developed surface and to examine their activities in reactions with U(VI), Np(V) and Pu(IV). It would also be interesting to broaden the range of non-platinum catalysts and to study catalytic properties of Tc_2S_7 or a $Re_2S_7 + Tc_2S_7$ mixture.

The choice of a support for active catalytic components is a task of no less importance due to demands from radiochemical technology. Aggressive nitric acid media and high-intensity radiation pose serious restrictions on the choice of supports. They should possess high chemical stability and radiation resistance, high mechanical strength and ease of application of the active component. Catalysts with finely dispersed platinum supported on spherical silica gel beads (Pt/SiO_2) were chosen for the totality of properties. Silica gel is most often used as a support; it possesses high chemical stability in nitric acid media, however, it is not a support of choice due to low mechanical strength and low abrasion resistance, which inevitably leads to mechanical degradation of the catalyst grains upon long-term utilisation. Moreover, the use of SiO_2 is restricted to acidic media. The use of silica gel as a support in alkaline and carbonate solutions is impossible due to its low chemical stability in these media. Therefore, a search for novel supports is a topical task in heterogeneous catalysis in aqueous media. In this respect, composite materials based on titanium, zirconium and thorium dioxides are promising. By virtue of their high chemical stability in acidic and alkaline media, sintered porous microgranules prepared by the sol-gel procedure should manifest sufficiently high mechanical strengths and high durability. Of special interest are studies of the effect of the nature of the support on the catalytic properties of the active component.

As regards the mechanisms of heterogeneous catalytic reactions of actinide ions, many of their aspects remain obscure. The ionic–molecular schemes of heterogeneous catalytic processes are largely based on the formal kinetics and the generally accepted concepts on the existence of different actinide species in the media under study. As a rule, there are three possible mechanisms of adsorption-type reactions that are discussed. These include: (1) activated adsorption and dissociation (atomisation) of molecular reagents on the active sites of the catalyst followed by reactions of reactive radicals with metal ions in solution, as in the case of reduction of actinide molecules with molecular hydrogen and, probably, hydrazine; (2) complexation of reactants in solution and its activated adsorption on the catalyst surface followed by decomposition due to charge transfer within the complex; (3) adsorption of reactants on the adjacent catalytic sites and charge transfer through the Pt–Pt bridge with subsequent desorption of the reaction products. As a rule, these

mechanisms are kinetically indistinguishable and the choice of a reaction relies on indirect data and is purely arbitrary.

The role of active catalytic components in the initiation of heterogeneous redox reactions in aqueous solutions remains to be elucidated. All the substances previously described in the literature that manifest catalytic activities in redox reactions of actinide ions in aqueous media are conductive or electrode materials. In electrolyte solutions, to which category all the above-mentioned systems belong, these materials acquire a surface charge the magnitude of which is determined by the potential-forming components of the aqueous medium. Catalysts play the role of electrodes on which electrochemical processes occur at rates that obey the laws for the electrode kinetics. Such a mechanism is realised in the catalytic reduction of Pu(VII) with water [the potential-forming pair is Pu(VII)/Pu(VI)] and probably in the catalytic oxidation of Np(IV) with nitric acid (the potential-forming pair is HNO_3/HNO_2). Here, the platinum catalyst plays the role of an anode on which electrochemical decomposition of water or oxidation of Np(IV) takes place. A similar approach can be applied, in principle, to any other catalytic reaction of actinide ions. In the general case, the analysis of mechanisms of heterogeneous catalytic reactions in aqueous solutions should take into consideration both the adsorption-type and electrochemical constituents of the process.

Catalytic decomposition of organic compounds in nitric acid media largely occurs as redox reactions of organic molecules adsorbed on the surface of a catalyst with oxidising species generated in homogeneous equilibrium reactions (NO_2^+) or in a heterogeneous catalytic redox cycle involving nitric acid and reducing agents on the catalyst surface (HNO_2). In the latter case, the reaction occurs first as a heterogeneous process, but can further be extended to the bulk of the solution owing to the autocatalytic formation of nitrous acid (catalytic denitration with formic acid). Here, the platinum catalyst does not accelerate the process but only initiates it by 'triggering' the reaction of HCO_2H with HNO_3 . In acidic solutions devoid of nitrate ions, molecular inorganic nitrogen-containing compounds (hydrazine, hydrazoic acid, *etc*.) decompose in the presence of platinum catalysts through an adsorption–dissociation mechanism. This consists of cleavage of the N—N bond as a result of chemisorption. Taking into account the oxidation states of nitrogen in the starting compounds and reaction products, the overall process can be defined as heterogeneous catalytic disproportionation. In nitric acid media, the contribution of this reaction to the decomposition of nitrogen-containing compounds decreases with an increase in $[HNO_3]$. Under these conditions, the catalytic redox cycle involving surface platinum atoms and direct heterogeneous catalytic oxidation of adsorbed molecules with nitroyl cations are the main processes determining the decomposition.

The behaviour of catalysts themselves in the reaction systems under study is among the main problems of heterogeneous catalysis in aqueous media that still await solution. Indeed, the published data are devoted to chemical conversions of reaction components in aqueous media. At the same time, studies on hydrazine decomposition and catalytic denitration have shown that the catalytic redox reactions involve surface atoms of the active component of the catalyst, *i.e*., platinum (the surface catalytic redox cycle). Therefore, elucidation of the role of catalysts in the initiation of heterogeneous catalytic redox reactions in aqueous media demands a deeper insight into the mechanisms of their action and in-depth studies of the catalyst surface, determination of the forms of atoms of active components existing on the surface and studies of the effects of chemical environment on their changes.

Despite the obvious progress in the application of catalysts based on platinum-group metals in radiochemical practice, the use of heterogeneous catalytic processes in the technology of the nuclear fuel cycle opens up broad opportunities for their more extensive application. This is explained by obvious advantages and high competitivity of catalytic methods in comparison with electrochemical and chemical technologies.

The main disadvantage of the recently developed catalytic methods is the use of expensive and scarce platinum as an active component of catalysts, which are materials subject to strict control. At the same time, due to naturally occurring attrition wear and corrosion of the catalysts, it inevitably falls into the radioactive wastes and its recovery is impossible due to specific features of the radiochemical technology. It is this fact that often restricts the use of catalytic processes in large-scale technologies of the nuclear fuel cycle. From this standpoint, a search for novel catalysts able to initiate redox reactions in aqueous media and their in-depth studies still remain an important scientific and practical problem.

Once such problems have been solved, heterogeneous catalysis will occupy a worthy place in the chemistry and technology of wet processes relevant to the nuclear fuel cycle.

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